

# **Compilation of Rate Constants for the Reactions of Metal Ions in Unusual Valency States**

---

George V. Buxton and Robin M. Sellers

Cookridge Radiation Research Centre,  
Cookridge Hospital,  
Leeds LS16 6QB,  
Great Britain



---

U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, Secretary

Dr. Sidney Harman, Under Secretary

Jordan J. Baruch, Assistant Secretary for Science and Technology

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

Issued June 1978

**Library of Congress Cataloging in Publication Data**

Buxton, George V

Compilation of rate constants for the reactions of metal ions in unusual valency states.

(Nat. stand. ref. data ser., Nat. Bur. of Stand. ; NSRDS-NBS 62)

Supt. of Docs. no.: C 13.48:62

1. Chemical reaction, Rate of—Tables, etc. 2. Metal ions—Tables.

I. Sellers, Robin M., joint author. II. Title. III. Series: United States. National Bureau of Standards. National standard reference data series ; NSRDS-NBS 62.

QC100.U573 no. 62 [QD502] 602'.1s [546'.3]  
78-816

**NSRDS-NBS 62**

Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 62, 78 pages (June 1978)

CODEN: NSRDAP

© 1978 by the Secretary of Commerce on Behalf of the United States Government

U.S. GOVERNMENT PRINTING OFFICE  
WASHINGTON: 1978

---

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

Stock No. 003-003-01882-1 Price \$2.40

(Add 25 percent additional for other than U.S. mailing).

## Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

A handwritten signature in dark ink, reading "E. Ambler." The signature is fluid and cursive, with a large initial "E" and a trailing flourish.

ERNEST AMBLER, *Director*

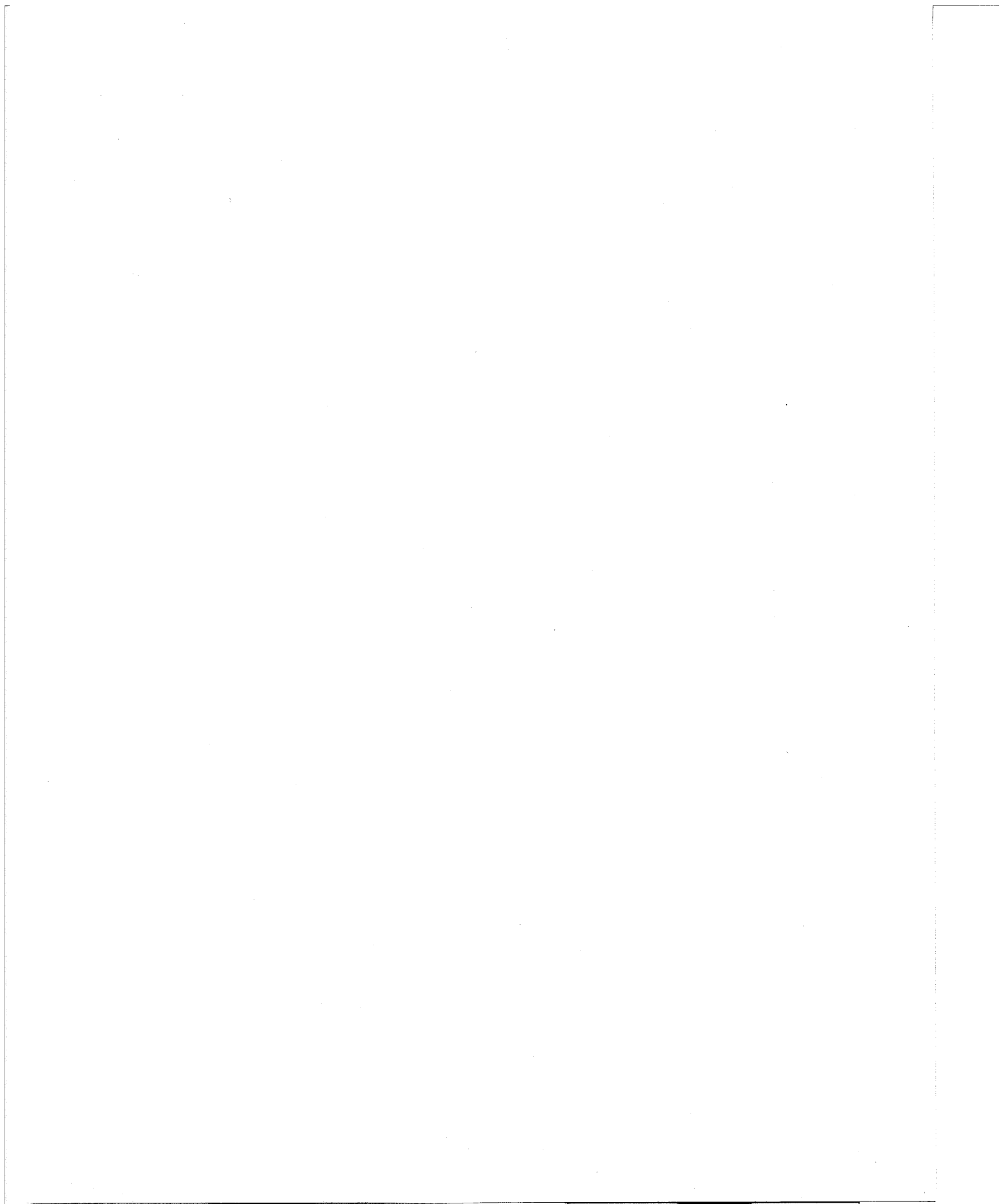
## Preface

This report is one of a series of data publications on radiation chemistry; the aim of the series is to compile, evaluate, and present the numerical results on processes occurring in systems which have been subjected to ionizing radiation. Various kinds of data are important in radiation chemistry. The quantities which were measured first were the observed radiation yields or  $G$  values (molecules formed or destroyed per 100 eV). Various indirect methods based on  $G$  values have been used to determine yields of transient species and relative rates of reactions. The spectral properties (optical, electron spin resonance) of transients have provided a direct method for their identification, and rates of the very fast reactions of transients which occur in irradiated systems have been measured directly by spectroscopic methods. Conductivity and luminescence methods have also provided a means of measuring properties of transients and their kinetics. Some reactions which occur in irradiated systems have also been studied by other methods, such as photochemistry, electric discharge, ultrasonics, chemical initiation, electron impact, etc. The emphasis in these publications is on the data of radiation chemistry, but where other pertinent data exist, they are included.

The data of radiation chemistry are voluminous; thousands of systems have been investigated. As a result there are certain collections, *e.g.* rate constants of particular types of reactions or certain properties of transients, for which tabulations of the data are considered essential, but for which critical assessment of each value is impossible. On the other hand, certain systems and properties have been studied so extensively that critical examination of these data is desirable and timely. Authors of this series of data publications have been asked to evaluate the extent to which the data can be critically assessed, to describe their criteria for evaluation, and to designate preferred values whenever possible.

## Contents

|                                                                                        | Page |
|----------------------------------------------------------------------------------------|------|
| Introduction.....                                                                      | 1    |
| Arrangement of the tables .....                                                        | 2    |
| List of abbreviations .....                                                            | 4    |
| Table 1. Silver(0) and (II) reactions .....                                            | 5    |
| Table 2. Gold(0) and (II) reactions.....                                               | 6    |
| Table 3. Cadmium(I) reactions.....                                                     | 7    |
| Table 4. Cobalt(I) reactions.....                                                      | 13   |
| Table 5. Chromium(I), (II) and (V) reactions .....                                     | 20   |
| Table 6. Copper(I) and (III) reactions .....                                           | 24   |
| Table 7. Europium(II) reactions.....                                                   | 29   |
| Table 8. Iron(II) reactions .....                                                      | 30   |
| Table 9. Mercury(0) and (I) reactions.....                                             | 31   |
| Table 10. Indium(II) reactions.....                                                    | 35   |
| Table 11. Iridium(II) reactions .....                                                  | 35   |
| Table 12. Manganese(I) reactions .....                                                 | 35   |
| Table 13. Molybdenum(II) reactions .....                                               | 36   |
| Table 14. Nickel(I) reactions .....                                                    | 37   |
| Table 15. Lead(I) reactions .....                                                      | 44   |
| Table 16. Praesodymium(IV) reactions .....                                             | 45   |
| Table 17. Platinum(I) and (III) reactions .....                                        | 46   |
| Table 18. Rhodium(II) reactions.....                                                   | 50   |
| Table 19. Ruthenium(I), (II), (III) and (IV) reactions .....                           | 51   |
| Table 20. Samarium(II) reactions .....                                                 | 53   |
| Table 21. Thallium(0) and (II) reactions .....                                         | 55   |
| Table 22. Thulium(II) reactions.....                                                   | 59   |
| Table 23. Ytterbium(II) reactions .....                                                | 60   |
| Table 24. Zinc(I) reactions.....                                                       | 62   |
| Table 25. Intramolecular electron transfer reactions for<br>some metal complexes ..... | 65   |
| References.....                                                                        | 66   |



# Compilation of Rate Constants for the Reactions of Metal Ions in Unusual Valency States\*

George V. Buxton and Robin M. Sellers\*\*

*Cookridge Radiation Research Centre, Cookridge Hospital,  
Leeds LS16 6QB, Great Britain.*

Kinetic data have been compiled for reactions of uncommon oxidation states of metals which are produced by radiolysis of aqueous solutions of metal ions. Most of the reaction rates are for transient species, and the rates were determined by pulse radiolysis; some data were obtained by flash photolysis and gamma radiolysis. Metal ions from Groups IB, IIB, IIIA, IVA, VIB, VIIB, VIIIB, and the lanthanides are included in the compilation.

Key words: Aqueous solution; chemical kinetics; complex ions; electron transfer; metal ions; radiation chemistry; rates; transients..

## Introduction

The discovery of the hydrated electron as a major product of the radiolysis of water and the development of pulse radiolysis have together resulted in the accumulation, during the last ten years, of a considerable amount of information on the chemistry of unusual valency states of metal ions in aqueous solution, which has been reviewed recently (G. V. Buxton and R. M. Sellers, 77-0121).<sup>1</sup> For the most part attention has been focussed on hyper-reduced states produced in reaction (1), which affords a simple, and often unique, method of their formation. Reactions of hydroxyl radicals and hydrogen atoms, and of simple radicals derived from them, with metal ions have been less commonly studied.



This compilation lists the rate constants for reactions of these metal ions in unusual valency states. In the majority of cases the species are unstable, generally decaying by dismutation (2), or reaction with the solvent or a solute (3). This instability has been the principal criterion on which the decision to include data in this tabulation has been based. However, because the bulk of information on these metal ions has been obtained by pulse radiolysis methods, we have also included some rate constants for the reactions of stable metal ions such as  $Cu^+$ ,  $Cr^{2+}$  and  $Eu^{2+}$  measured by these methods. In these examples, indicated in the tables, much other data not recorded here has been obtained by other techniques.

\*This is a data review prepared for, and in cooperation with, the Radiation Chemistry Data Center of the Radiation Laboratory, University of Notre Dame, Indiana 46556. The Laboratory is operated under contract with the Department of Energy. The work of the Center is supported in part by the National Bureau of Standards, Office of Standard Reference Data.

\*\*Present address: Central Electricity Generating Board, Berkeley Nuclear Laboratories, Berkeley, Gloucestershire GL13 9PB, Great Britain.

<sup>1</sup>Literature references are given at the end of this paper.

## Arrangement of the Tables

The tables are listed in alphabetical order of the chemical symbols of the metals involved. Within each table the arrangement is by oxidation state, starting with the lowest, and is further subdivided according to the complexing ligands in the order aquo ions (and hydrolysed forms), inorganic ligands in alphabetical order of the first letter of the chemical symbol of the principal element of that ligand (e.g. N for ammonia), and organic ligands in alphabetical order of their written names. For each individual transient species the reactants are in the order: inorganic species, organic radicals, both in alphabetical order of their chemical symbols, followed by organic compounds in alphabetical order of their written names.

Table 25 is somewhat different, and lists the rate constants for some intramolecular electron transfer reactions. The reactions are subdivided according to the method of production of the transient species. Note that all the rate constants in this table are first order, and have therefore units of  $s^{-1}$ . Reactions of metallo-proteins and related compounds are not dealt with in this compilation.

The data given for each reaction are the measured rate constant, and a brief description of the experimental conditions etc. as outlined below. Literature data published to approximately mid-1976 are covered.

*Reaction:* Three main methods have been used to measure the rate constants reported here:

- (i) by monitoring the rate of removal of the absorption of the metal species at some convenient wavelength
- (ii) by monitoring the rate of formation of some product
- (iii) by competition kinetics.

Methods (i) and (iii) have the disadvantage that they do not involve characterisation of the products of the reaction, and in many instances in the literature no additional experiments have been performed to overcome this. Often the reaction type has been assumed. Particular attention has been given to this problem in this compilation. Where there is no experimental information on the products given in the original work or elsewhere, only the left hand side of the equation is given, followed in brackets by the possible type of reaction as originally suggested, or as seems appropriate. If experimental evidence is given, the products are quoted, and the nature of the evidence indicated in the column headed 'Comments'.

In some cases the reactive intermediates themselves have not been fully characterised, and in such instances brief details of the method and conditions of formation are given.

*Rate Constants:* Most of the rate constants listed were measured under conditions where the reaction obeyed first order kinetics and no knowledge of absolute concentrations of the *transient* species is required. Error limits on the rate constants are those quoted in the original work. In the great majority of cases their magnitude is  $\pm 10 - 15\%$  of the rate constant value, which is typical of the precision of the mean of pseudo first order rate constants measured by pulse methods. If the data source gives no errors none are shown here, but they should be assumed to be at least  $\pm 25\%$  to allow for the possibility that the rate constant is derived from a single measurement.

Second order rate constants are prefaced by " $2k =$ " or " $2k/\epsilon_\lambda =$ " as appropriate. In cases where it is not clear whether the value refers to  $2k$  or  $k$  this is noted in the 'Comments' column. The measured quantity is  $2k/\epsilon_\lambda$  and is subject to the same limitations given above for pseudo first order rate constants. Calculation of  $2k$  requires a knowledge of  $\epsilon_\lambda$ , and where this quantity is quoted in the original work it is given under 'Comments'. In many instances, however, the values of  $\epsilon_\lambda$  used to calculate  $2k$  have not been clearly stated.

Evaluation of  $\epsilon_\lambda$  requires a knowledge of the concentration of transient species present which, in radiation chemical systems, means that the dose per pulse and the  $G$  value<sup>2</sup> of the species must be known. In our experience these quantities are each likely to be uncertain by  $\pm 10\%$ , so that the error in  $2k$  may be as much as three times as large as the error in  $2k/\epsilon_\lambda$ . Therefore, in the absence of any quoted errors, the error in  $2k$  should be assumed to be  $\pm 50\%$ .

<sup>2</sup> $G$  is the number of molecules of a species produced per 100 eV of absorbed energy.

Equilibrium constants are quoted under the 'Rate Constants' heading, and are prefixed by " $K =$ " followed by the appropriate units. If the individual rate constants for the forward and reverse processes are known these are shown as " $k_f$ " and " $k_r$ " respectively. Activation energies are prefaced by " $E_a =$ " and are given in units of  $\text{kJ mol}^{-1}$ .

*Ionic Strength (I):* Ionic strengths have either been taken directly from the original work, or calculated from the conditions given. In the few instances where the formation of ion pairs has been taken into account the values are followed by an asterisk. If insufficient information is given to enable the ionic strength to be calculated the column has been left blank. The ionic strength of rate constants extrapolated to zero ionic strength is given as " $\rightarrow 0$ ". Unfortunately in a number of studies little or no attempt has been made to maintain the ionic strength constant. The practice of many reaction kineticists of adding a high concentration of inert electrolyte, such as  $\text{NaClO}_4$ , has not been widely adopted by radiation chemists, no doubt because of possible complications due to direct radiolysis of the electrolyte (cf. J. Konstantatos and D. Katakis, 67-0019). There is no reason however why an ionic strength of say 0.1 or 0.5  $\text{mol dm}^{-3}$  should not become standard for pulse radiolytic measurements. It is to be hoped that more consideration will be given to this problem in future studies.

*Temperature:* Where temperatures are quoted in the original work these have been given. In the absence of any information temperatures are given as room temperature (RT). The temperature ranges over which activation parameters have been measured are given as appropriate. Since many of the rate constants quoted in these tables are near the diffusion controlled limit and have therefore small activation energies, little uncertainty is engendered by an imprecise knowledge of the temperature. For example a change in temperature of  $5^\circ$  from  $25^\circ$  changes  $k$  by 11% for an activation energy of  $16 \text{ kJ mol}^{-1}$ .

*Comments:* Information and comments relevant to the reactions and rate constants are given in this column as outlined above. No attempt has been made to give a complete description of the conditions employed in the measurement of the rate constants quoted, but where the concentration of one or more of the solutes exceeds 0.1  $\text{mol dm}^{-3}$  this has been noted.

*References:* The references are listed following the tables in order of the serial number of the paper in the files of the Radiation Chemistry Data Centre at the University of Notre Dame. The first two digits of this number represent the year in which the work was published. The references in the tables also give the first four letters of the first author's name and a dot for each additional author up to a maximum of four dots.

## List of Abbreviations

|                            |                    |                                                           |
|----------------------------|--------------------|-----------------------------------------------------------|
| Reaction:                  | af                 | adduct formation                                          |
|                            | dis                | dismutation (disproportionation)                          |
|                            | et                 | electron transfer                                         |
|                            | int et             | intramolecular electron transfer                          |
|                            | O at               | oxygen atom transfer                                      |
|                            | pt                 | proton transfer                                           |
|                            | et – is            | inner sphere electron transfer                            |
| Rate Constant:             | ?                  | uncertain                                                 |
|                            | $2k$               | rate constant for second order reaction                   |
|                            | $\epsilon_\lambda$ | extinction coefficient at wavelength $\lambda$            |
|                            | $E_a$              | activation energy (units $\text{kJ mol}^{-1}$ )           |
|                            | $K$                | equilibrium constant                                      |
|                            | $\text{p}K$        | acid dissociation constant ( $= -\log_{10}K$ )            |
|                            | $k_f$              | rate constant for forward reaction of equilibrium         |
|                            | $k_r$              | rate constant for reverse reaction of equilibrium         |
|                            | ?                  | value uncertain                                           |
|                            | $\rightarrow 0$    | extrapolated to zero ionic strength                       |
| Ionic Strength:<br>( $I$ ) | *                  | calculated taking into account the formation of ion pairs |
|                            | var                | various                                                   |
| Temperature:               | RT                 | room temperature                                          |
| pH:                        | nat                | natural pH of the solution                                |
| Method:                    | comp.              | competition kinetics                                      |
|                            | f.ph.              | flash photolysis                                          |
|                            | $\gamma$           | $\gamma$ -radiolysis                                      |
| Chemical Symbols:          | pr                 | pulse radiolysis                                          |
|                            | bpy                | bipyridyl                                                 |
|                            | en                 | ethylenediamine                                           |
|                            | gly                | glycine                                                   |
|                            | $\text{EDTA}^{4-}$ | ethylenediamine tetraacetate                              |
|                            | $\text{NAD}^+$     | nicotinamide adenine dinucleotide                         |
|                            | $\text{NTA}^{3-}$  | nitrilotriacetate                                         |
|                            | PNDA               | <i>p</i> -nitroso- <i>N,N</i> -dimethylaniline            |
|                            | L                  | ligand (specified in table).                              |

TABLE 1. Silver(0) and Silver(II) reactions

| No.                                    | Reaction                                                                                                    | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$             | $t/^\circ\text{C}$ | pH     | Method | Comments                                                                                                                                                                         | Ref.           |
|----------------------------------------|-------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-----------------|--------------------|--------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| <i>Ag(0) - aquo ions and complexes</i> |                                                                                                             |                                                              |                 |                    |        |        |                                                                                                                                                                                  |                |
| 1.1                                    | $\text{Ag}^0 + \text{Ag}^+ \rightarrow \text{Ag}_2^+$                                                       | $5.9 \times 10^9$                                            | —               | RT                 | —      | pr     | Product characterised by absorption spectrum and charge.                                                                                                                         | Puki.68-0431   |
|                                        |                                                                                                             | $(6.5 \pm 0.3) \times 10^9$                                  | —               | 29                 | 1.0    | pr     | —                                                                                                                                                                                | Farh...73-1053 |
|                                        |                                                                                                             | $(5.2 \pm 0.3) \times 10^9$                                  | —               | 29                 | 1.0    | pr     | Measured at pressure of 6.72 kbar.                                                                                                                                               | Farh...73-1053 |
| 1.2                                    | $\text{Ag}_2^+ + \text{Ag}^+ \rightarrow \text{Ag}_3^{2+} + \text{Ag}^0$                                    | $3.8 \times 10^9$                                            | $\rightarrow 0$ | RT                 | —      | pr     | Products characterised by absorption spectrum.                                                                                                                                   | Puki.68-0431   |
| 1.3                                    | $\text{Ag}_2^0 + \text{Ag}^+ \rightarrow \text{Ag}_3^+$                                                     | $ca.10^9$                                                    | —               | RT                 | —      | pr     | Product characterised by absorption spectrum.                                                                                                                                    | Puki.68-0431   |
| 1.4                                    | $\text{Ag}_2^0/\text{Ag}_3^+ + \text{MnO}_4^- (\text{et})$                                                  | $1.2 \times 10^{10}$                                         | 0.003           | RT                 | —      | pr     | Measured by the rate of depletion of the $\text{MnO}_4^-$ absorption.                                                                                                            | Baxe..65-0385  |
| 1.5                                    | $\text{Ag}_2^+ + \text{O}_2 (\text{et or af})$                                                              | $3.8 \times 10^8$                                            | —               | RT                 | —      | pr     | Product uncertain, but transfers an electron to 1,4-benzoquinone (see Sell.76-1134).                                                                                             | Baxe..65-0393  |
| 1.6                                    | $\text{Ag}_2^+ + 1,4\text{-benzoquinone} \rightarrow \text{Ag}_3^{2+}(?) + (1,4\text{-benzoquinone})^-$     | $(1.5 \pm 0.3) \times 10^9$                                  | —               | $25 \pm 2$         | 5.8    | pr     | Measured by the rate of formation of the semiquinone in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                             | Sell.76-1134   |
| 1.7                                    | $\text{Ag}_2^+ + \text{menaquinone} \rightarrow \text{Ag}_3^{2+}(?) + (\text{menaquinone})^-$               | slow                                                         | —               | —                  | 7.0    | pr     | Only 24% electron transfer, which may be due to side reactions. Solutions contained $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                 | Rao.73-1047    |
| <i>Ag(0) - ammine complexes</i>        |                                                                                                             |                                                              |                 |                    |        |        |                                                                                                                                                                                  |                |
| 1.8                                    | $\text{Ag}^0 + \text{Ag}(\text{NH}_3)_2^+ \rightarrow \text{Ag}_2(\text{NH}_3)_3^+$                         | $5.2 \times 10^9$                                            | —               | RT                 | —      | pr     | $\text{Ag}^0$ generated from $e_{aq}^- + \text{Ag}(\text{NH}_3)_2^+$ - might be same as product of $e_{aq}^- + \text{Ag}^+$ . Product contains unknown number of ammine ligands. | Puki.68-0435   |
| 1.9                                    | $\text{Ag}_2(\text{NH}_3)_3^+ + \text{Ag}_2(\text{NH}_3)_3^+ \rightarrow \text{Ag}_4(\text{NH}_3)_5^{2+} ?$ | $2k = 2.6 \times 10^{10}$                                    | —               | RT                 | —      | pr     | Product uncertain; gives ultimately $\text{Ag}_3^0$ .                                                                                                                            | Puki.68-0435   |
| 1.10                                   | $\text{Ag}_2(\text{NH}_3)_3^+ + \text{Ag}(\text{NH}_3)_2^+ \rightarrow \text{Ag}_3(\text{NH}_3)_4^{2+} ?$   | $10^8$                                                       | —               | RT                 | —      | pr     | Measured from rate of formation of product, nature of which is uncertain.                                                                                                        | Puki.68-0435   |
| <i>Ag(II) - aquo complex</i>           |                                                                                                             |                                                              |                 |                    |        |        |                                                                                                                                                                                  |                |
| 1.11                                   | $\text{Ag}^{2+} + \text{Ag}^{2+} \rightarrow \text{Ag}^+ + \text{Ag}^{3+}$                                  | $1.5 \times 10^9$                                            | —               | RT                 | —      | pr     | —                                                                                                                                                                                | Puki.68-0431   |
| 1.12                                   | $\text{Ag}^{2+} + \text{anisole} \rightarrow \text{Ag}^+ + \text{anisole}^+$                                | $(3.8 \pm 0.4) \times 10^7$                                  | —               | $20 \pm 2$         | nat(?) | pr     | Product characterised by absorption spectrum and esr.                                                                                                                            | O'Ne..75-1171  |

TABLE 1. Silver(0) and Silver(II) reactions — Continued

| No.  | Reaction                                                                                                       | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^a$ | $I$ | $t/^\circ\text{C}$ | pH     | Method | Comments                                              | Ref.          |
|------|----------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|-----|--------------------|--------|--------|-------------------------------------------------------|---------------|
| 1.13 | $\text{Ag}^{2+} + 1,2\text{-dimethoxybenzene} \rightarrow \text{Ag}^+ + (1,2\text{-dimethoxybenzene})^+$       | $(6.0 \pm 0.6) \times 10^7$                                | —   | $20 \pm 2$         | nat(?) | pr     | Product characterised by absorption spectrum and esr. | O'Ne..75-1171 |
| 1.14 | $\text{Ag}^{2+} + 1,3\text{-dimethoxybenzene} \rightarrow \text{Ag}^+ + (1,3\text{-dimethoxybenzene})^+$       | $(6.3 \pm 0.6) \times 10^7$                                | —   | $20 \pm 2$         | nat(?) | pr     | Product characterised by absorption spectrum and esr. | O'Ne..75-1171 |
| 1.15 | $\text{Ag}^{2+} + 1,4\text{-dimethoxybenzene} \rightarrow \text{Ag}^+ + (1,4\text{-dimethoxybenzene})^+$       | $(4.6 \pm 0.5) \times 10^7$                                | —   | $20 \pm 2$         | nat(?) | pr     | Product characterised by absorption spectrum and esr. | O'Ne..75-1171 |
| 1.16 | $\text{Ag}^{2+} + 1,2,3\text{-trimethoxybenzene} \rightarrow \text{Ag}^+ + (1,2,3\text{-trimethoxybenzene})^+$ | $(2.5 \pm 0.3) \times 10^7$                                | —   | $20 \pm 2$         | nat(?) | pr     | Product characterised by absorption spectrum and esr. | O'Ne..75-1171 |
| 1.17 | $\text{Ag}^{2+} + 1,2,4\text{-trimethoxybenzene} \rightarrow \text{Ag}^+ + (1,2,4\text{-trimethoxybenzene})^+$ | $(7.0 \pm 0.7) \times 10^7$                                | —   | $20 \pm 2$         | nat(?) | pr     | Product characterised by absorption spectrum and esr. | O'Ne..75-1171 |
| 1.18 | $\text{Ag}^{2+} + 1,3,5\text{-trimethoxybenzene} \rightarrow \text{Ag}^+ + (1,3,5\text{-trimethoxybenzene})^+$ | $(5.6 \pm 0.6) \times 10^7$                                | —   | $20 \pm 2$         | nat(?) | pr     | Product characterised by absorption spectrum and esr. | O'Ne..75-1171 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 2. Gold(0) and Gold(II) reactions

| No. | Reaction                                                                                                                                                                                | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^a$ | $I$   | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                    | Ref.         |
|-----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|-------|--------------------|-----|--------|-------------------------------------------------------------------------------------------------------------|--------------|
| 2.1 | $\text{Au}(0) \text{ from } \text{Au}(\text{CN})_2^- + e_{\text{aq}}^-$<br>$\text{Au}^0 + \text{Au}^0 \rightarrow \text{Au}_2^0$                                                        | $(3.2 \pm 0.9) \times 10^9$                                | 0.001 | RT                 | 11  | pr     | Product assumed. Solutions contained $9.8 \times 10^{-3} \text{ mol dm}^{-3} \text{ H}_2$ .                 | Ghos.68-0302 |
|     |                                                                                                                                                                                         | $(2.9 \pm 0.7) \times 10^9$                                | 0.1   | RT                 | 13  | pr     |                                                                                                             | Ghos.68-0302 |
| 2.2 | $\text{Au}^0 + \text{Fe}(\text{CN})_6^{3-} \text{ (et?)}$                                                                                                                               | $5.5 \times 10^8$                                          | —     | RT                 | —   | pr     | —                                                                                                           | Ghos.68-0302 |
| 2.3 | $\text{Au}^0 + \text{N}_2\text{O} \text{ (et or O at)}$                                                                                                                                 | $5.5 \times 10^8$                                          | —     | RT                 | —   | pr     | —                                                                                                           | Ghos.68-0302 |
| 2.4 | $\text{Au}^0 + \text{O}_2 \text{ (et or af)}$                                                                                                                                           | $3.6 \times 10^8$                                          | —     | RT                 | —   | pr     | —                                                                                                           | Ghos.68-0302 |
| 2.5 | $\text{Au}(0) \text{ from } \text{Au}(\text{CN})_2^- + \text{H}$<br>$\text{Au}^0 + \text{Au}^0 \rightarrow \text{Au}_2^0$<br>$\text{Au(II) from } \text{Au}(\text{CN})_2^- + \text{OH}$ | $(5.0 \pm 1.0) \times 10^9$                                | 0.015 | RT                 | 2   | pr     | —                                                                                                           | Ghos.68-0302 |
|     |                                                                                                                                                                                         | $(2.4 \pm 0.6) \times 10^8$                                | 0.01  | RT                 | 2   | pr     | Solutions contained $0.1 \text{ mol dm}^{-3} \text{ HCl}$ .                                                 | Ghos.68-0302 |
| 2.6 | $\text{Au}^{\text{II}} + \text{Au}^{\text{II}}$<br>(dis or af)                                                                                                                          | $(4.8 \pm 1.2) \times 10^8$                                | 0.01  | RT                 | 4,7 | pr     | Solutions contained $0.01 \text{ mol dm}^{-3} \text{ KCl}$ .                                                | Ghos.68-0302 |
|     |                                                                                                                                                                                         | $(1.4 \pm 0.3) \times 10^9$                                | 0.01  | 20                 | 2   | pr     | Nature of products —see ref. 70-0580.                                                                       | Baxe.70-0580 |
| 2.7 | $\text{Au}^{\text{II}} + \text{Au}^{\text{II}} \rightarrow \text{Au}^{\text{I}} + \text{Au}^{\text{III}}$                                                                               | $(8.6 \pm 0.7) \times 10^8$                                | 0.011 | 20                 | 2   | pr     | Solutions contained $10^{-3} \text{ mol dm}^{-3} \text{ Cl}^-$ .                                            | Baxe.70-0580 |
|     |                                                                                                                                                                                         | $(1.2 \pm 0.1) \times 10^9$                                | 0.131 | 20                 | 2   | pr     | Solutions contained $10^{-3} \text{ mol dm}^{-3} \text{ Cl}^- + 0.12 \text{ mol dm}^{-3} \text{ NaClO}_4$ . | Baxe.70-0580 |
|     |                                                                                                                                                                                         | $(2.7 \pm 0.6) \times 10^8$                                | 0.02  | 20                 | 2   | pr     | Solutions contained $10^{-3} \text{ mol dm}^{-3} \text{ Cl}^-$ .                                            | Baxe.70-0580 |
|     |                                                                                                                                                                                         | $(2.5 \pm 0.2) \times 10^7$                                | 0.11  | 20                 | 2   | pr     | Solutions contained $10^{-1} \text{ mol dm}^{-3} \text{ Cl}^-$ .                                            | Baxe.70-0580 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 3. Cd(I) reactions

| No.  | Reaction                                                            | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1} \text{ }^a$ | $I$   | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                                                                                                                                                                                                                                       | Ref.         |
|------|---------------------------------------------------------------------|----------------------------------------------------------|-------|--------------------|-----|--------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| 3.1  | $\text{Cd}^+ + \text{BrO}_3^-$ (et)                                 | $(1.25 \pm 0.2) \times 10^8$                             | 0.08  | RT                 | nat | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.68-0855 |
|      |                                                                     | $E_a = 13.4 \pm 1.7 \text{ kJ mol}^{-1}$                 | 0.08  | 3 - 90             | nat | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.70-1228 |
| 3.2  | $\text{Cd}^+ + \text{Cd}^+ \rightarrow \text{Cd}_2^{2+}$            | $2k = \text{ca. } 1.2 \times 10^9$                       | 0.4   | $25 \pm 2$         | nat | pr     | Measured at 300 nm taking $\epsilon_{300} = 8080 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . Rate constant estimated from studies of $\text{Cd}^+$ decay in presence of several different OH scavengers.                                                                                                                                                                                                                                    | Buxt.75-1027 |
|      |                                                                     | $2k = 3.0 \times 10^9$                                   | 0.002 | RT                 | nat | pr     | Measured at 300 nm taking $\epsilon_{300} = 16500 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . Rate constant estimated from computer analysis of $\text{Cd}^+$ decay. Competing reactions taken to be $\text{Cd}^+ + \text{H}_2\text{O}_2$ and $\text{Cd}^+ + \text{R} \cdot$ ( $\text{R} = \text{CH}_3\text{COHCH}_3$ , $\text{CH}_3\text{CHOH}$ , $\text{CH}_2\text{OH}$ ). Product identified from effect of ionic strength on its decay. | Kelm.75-1064 |
|      |                                                                     | $2k = 5.0 \times 10^9$                                   | 0.004 | RT                 | nat | pr     | Measured at 313 nm taking $\epsilon_{301} = 14000 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . Rate constant independent of OH scavenger used.                                                                                                                                                                                                                                                                                               | Bark.75-1153 |
| 3.3  | $\text{Cd}^+ + \text{Co(en)}_2^{3+}$ (et)                           | $(1.6 \pm 0.2) \times 10^9$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.4  | $\text{Cd}^+ + \text{cis-Co(en)}_2\text{Cl}_2^+$ (et)               | $(2.3 \pm 0.3) \times 10^9$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.5  | $\text{Cd}^+ + \text{trans-Co(en)}_2\text{Cl}_2^+$ (et)             | $(2.6 \pm 0.4) \times 10^9$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.6  | $\text{Cd}^+ + \text{Co(en)}_2\text{CO}_3^+$ (et)                   | $(6.7 \pm 1.0) \times 10^8$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.7  | $\text{Cd}^+ + \text{cis-Co(en)}_2\text{F}_2^+$ (et)                | $(6.0 \pm 0.9) \times 10^8$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.8  | $\text{Cd}^+ + \text{Co(en)}_2\text{FH}_2\text{O}^{2+}$ (et)        | $(4.1 \pm 0.6) \times 10^8$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.9  | $\text{Cd}^+ + \text{cis-Co(en)}_2\text{NH}_3\text{Cl}^{2+}$ (et)   | $(1.75 \pm 0.26) \times 10^9$                            | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.10 | $\text{Cd}^+ + \text{cis-Co(en)}_2\text{NH}_3\text{NO}_2^{2+}$ (et) | $(2.8 \pm 0.7) \times 10^9$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.11 | $\text{Cd}^+ + \text{Co(NH}_3)_6^{3+}$ (et)                         | $(1.72 \pm 0.3) \times 10^8$                             | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.12 | $\text{Cd}^+ + \text{Co(NH}_3)_5\text{Br}^{2+}$ (et)                | $(25 \pm 0.4) \times 10^8$                               | 0.08  | RT                 | 4.0 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.13 | $\text{Cd}^+ + \text{Co(NH}_3)_5\text{Cl}^{2+}$ (et)                | $(2.2 \pm 0.3) \times 10^9$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.14 | $\text{Cd}^+ + \text{Co(NH}_3)_5\text{CN}^{2+}$ (et)                | $(9.1 \pm 1.4) \times 10^8$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.15 | $\text{Cd}^+ + \text{Co(NH}_3)_5\text{F}^{2+}$ (et)                 | $(5.4 \pm 0.8) \times 10^8$                              | 0.08  | RT                 | 5-6 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |
| 3.16 | $\text{Cd}^+ + \text{Co(NH}_3)_5\text{fumarate}^+$ (et or af?)      | $(8.3 \pm 2.1) \times 10^8$                              | 0.08  | RT                 | 5-6 | pr     | Products of the reaction have relatively large absorption.                                                                                                                                                                                                                                                                                                                                                                                     | Meye.69-0428 |
| 3.17 | $\text{Cd}^+ + \text{Co(NH}_3)_5\text{H}_2\text{O}^{3+}$ (et)       | $(6.2 \pm 0.9) \times 10^8$                              | 0.08  | RT                 | 4.0 | pr     | -                                                                                                                                                                                                                                                                                                                                                                                                                                              | Meye.69-0428 |

TABLE 3. Cd(I) reactions — Continued

| No.  | Reaction                                                                                         | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>                                                                      | $I$                                                 | $t/^\circ\text{C}$                            | pH                                         | Method                                   | Comments                                                                                                                                                                                                          | Ref.                                                            |
|------|--------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|-----------------------------------------------|--------------------------------------------|------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|
| 3.18 | $\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{OH}^{2+}$<br>(et)                                   | $(9.0 \pm 1.3) \times 10^8$                                                                                                     | 0.08                                                | RT                                            | 7.1                                        | pr                                       | —                                                                                                                                                                                                                 | Meye.69-0428                                                    |
| 3.19 | $\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$<br>(et)                                  | $(1.41 \pm 0.2) \times 10^9$                                                                                                    | 0.08                                                | RT                                            | 5-6                                        | pr                                       | —                                                                                                                                                                                                                 | Meye.69-0428                                                    |
| 3.20 | $\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$<br>(et)                                  | $(1.32 \pm 0.2) \times 10^9$                                                                                                    | 0.08                                                | RT                                            | 5-6                                        | pr                                       | —                                                                                                                                                                                                                 | Meye.69-0428                                                    |
| 3.21 | $\text{Cd}^+ + \text{Co}(\text{NH}_3)_5\text{OOCCH}_3^{2+}$<br>(et)                              | $(9.0 \pm 1.3) \times 10^7$                                                                                                     | 0.08                                                | RT                                            | 5-6                                        | pr                                       | —                                                                                                                                                                                                                 | Meye.69-0428                                                    |
| 3.22 | $\text{Cd}^+ + \text{Cr}^{3+}$                                                                   | $< 10^7$                                                                                                                        | —                                                   | RT                                            | nat                                        | pr                                       | —                                                                                                                                                                                                                 | Baxe..66-0848                                                   |
| 3.23 | $\text{Cd}^+ + \text{CrO}_4^{2-}$ (et)                                                           | $(9.8 \pm 1.0) \times 10^9$                                                                                                     | 0.02*                                               | 25±2                                          | nat                                        | pr                                       | —                                                                                                                                                                                                                 | Buxt..76-1072                                                   |
| 3.24 | $\text{Cd}^+ + \text{Cr}_2\text{O}_7^{2-}$ (et)                                                  | $(1.6 \pm 0.2) \times 10^{10}$                                                                                                  | 0.02*                                               | 25±2                                          | nat                                        | pr                                       | —                                                                                                                                                                                                                 | Buxt..76-1072                                                   |
| 3.25 | $\text{Cd}^+ + \text{Cu}^{2+}$ (et)                                                              | $(1.2 \pm 0.2) \times 10^8$<br>$(1.1 \pm 0.2) \times 10^9$                                                                      | 0.08<br>0.04                                        | RT<br>RT                                      | nat<br>5-8                                 | pr<br>$\gamma$                           | —<br>Measured by competition kinetics using $\text{NO}_3^-$ as competitor and taking $k(\text{Cd}^+ + \text{NO}_3^-) = 3.5 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .                              | Meye.68-0855<br>Fiti70-0117                                     |
| 3.26 | $\text{Cd}^+ + \text{H}_2\text{O}_2 \rightarrow$<br>$\text{Cd}^{2+} + \text{OH}^- + \text{OH}^-$ | $(1.55 \pm 0.2) \times 10^9$<br>$(2.2 \pm 0.2) \times 10^9$<br>$2.8 \times 10^9$<br>$E_a = 9.2 \pm 0.8$<br>$\text{kJ mol}^{-1}$ | —<br>—<br>—<br>—                                    | RT<br>25<br>RT<br>1-30                        | nat<br>nat<br>nat<br>nat                   | pr<br>pr<br>pr<br>pr                     | —<br>—<br>—<br>—<br>Products identified in $\gamma$ -radiolysis studies (see Buxt..73-0039).                                                                                                                      | Meye.68-0855<br>Buxt..76-1072<br>Buxt..67-0062<br>Buxt..76-1072 |
| 3.27 | $\text{Cd}^+ + \text{H}_2\text{O}^+$                                                             | $< 10^8$                                                                                                                        | 0.08                                                | RT                                            | —                                          | pr                                       | —                                                                                                                                                                                                                 | Meye.68-0855                                                    |
| 3.28 | $\text{Cd}^+ + \text{IO}_3^-$ (et)                                                               | $(2.3 \pm 0.3) \times 10^9$<br>$(2.1 \pm 0.2) \times 10^9$                                                                      | 0.08<br>0.04                                        | RT<br>RT                                      | nat<br>5-8                                 | pr<br>$\gamma$                           | —<br>Measured by competition kinetics using $\text{NO}_3^-$ as competitor and taking $k(\text{Cd}^+ + \text{NO}_3^-) = 3.5 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .                              | Meye.68-0855<br>Fiti70-0117                                     |
| 3.29 | $\text{Cd}^+ + \text{MnO}_4^-$ (et)                                                              | $(7.8 \pm 0.8) \times 10^9$<br><br><br><br><br><br><br><br><br>$1.3 \times 10^{10}$                                             | —<br><br><br><br><br><br><br><br><br>$ca.$<br>0.004 | $ca.22$<br><br><br><br><br><br><br><br><br>20 | 7.0<br><br><br><br><br><br><br><br><br>nat | pr<br><br><br><br><br><br><br><br><br>pr | Measured by the rate of depletion of the $\text{MnO}_4^-$ absorption in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.<br>Measured by the rate of depletion of the $\text{MnO}_4^-$ absorption. | Rao.73-1104<br><br><br><br><br><br><br><br><br>Baxe..65-0305    |
| 3.30 | $\text{Cd}^+ + \text{Ni}^{2+}$                                                                   | $< 10^7$                                                                                                                        | —                                                   | RT                                            | nat                                        | pr                                       | —                                                                                                                                                                                                                 | Baxe..66-0848                                                   |
| 3.31 | $\text{Cd}^+ + \text{NO}_3^-$ (et)                                                               | $(2.0 \pm 0.3) \times 10^9$<br>$E_a = 12.5 \pm 1.7$<br>$\text{kJ mol}^{-1}$                                                     | 0.08<br>0.08                                        | RT<br>3-90                                    | nat<br>nat                                 | pr<br>pr                                 | —<br>—                                                                                                                                                                                                            | Meye.68-0855<br>Meye.70-1228                                    |
| 3.32 | $\text{Cd}^+ + \text{NO}_3^-$ (et)                                                               | $(3.5 \pm 0.5) \times 10^8$                                                                                                     | 0.08                                                | RT                                            | nat                                        | pr                                       | —                                                                                                                                                                                                                 | Meye.68-0855                                                    |

TABLE 3. Cd(II) reactions — Continued

| No.  | Reaction                                                                 | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | <i>I</i> | <i>t</i> /°C | pH  | Method | Comments                                                                                                                                                                                                                                                                                                                                          | Ref.          |
|------|--------------------------------------------------------------------------|--------------------------------------------------------------|----------|--------------|-----|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 3.33 | $\text{Cd}^+ + \text{N}_2\text{O} \rightarrow \text{CdO}^+ + \text{N}_2$ | $< 2 \times 10^6$                                            | —        | RT           | nat | pr     | —                                                                                                                                                                                                                                                                                                                                                 | Meye.68-0855  |
|      |                                                                          | $1 \times 10^6$                                              | —        | RT           | nat | pr     | —                                                                                                                                                                                                                                                                                                                                                 | Buxt..67-0062 |
|      |                                                                          | $(3.5 \pm 0.4) \times 10^6$                                  | —        | 25           | nat | pr     | Solutions contain-                                                                                                                                                                                                                                                                                                                                | Buxt..76-1072 |
|      |                                                                          | $E_a = 45.6 \pm 1.3$<br>$\text{kJ mol}^{-1}$                 | —        | 1 - 30       | nat | pr     | ed 0.1 mol dm <sup>-3</sup><br>methanol.<br>Products inferred<br>from $\gamma$ -ray induc-<br>ed chain reaction<br>in the system<br>$\text{Cd}^{2+} + \text{HCO}_2^- + \text{N}_2\text{O}$ .<br>$G(\text{N}_2)$ measured in<br>the system $\text{Cd}^{2+} +$<br>$\text{N}_2\text{O}$ . (see ref.<br>73-0039).                                     |               |
| 3.34 | $\text{Cd}^+ + \text{O}_2$ (et or af)                                    | $(2.4 \pm 0.4) \times 10^9$                                  | —        | RT           | nat | pr     | —                                                                                                                                                                                                                                                                                                                                                 | Meye.68-0855  |
|      |                                                                          | $3.3 \times 10^9$                                            | —        | RT           | nat | pr     | —                                                                                                                                                                                                                                                                                                                                                 | Baxe..66-0848 |
|      |                                                                          | $(3.6 \pm 0.4) \times 10^9$                                  | —        | 25±2         | nat | pr     | Absorption spec-<br>trum of products<br>similar to that of<br>$\text{O}_2^-$ ; but decay<br>slower (see ref.<br>76-1072). Pro-<br>duct transfers an<br>electron to<br><i>p</i> -benzoquinone<br>(see ref. 76-1134).<br>Evidence possibly<br>indicates product<br>to be $\text{CdO}_2^+$ .                                                         | Buxt..76-1072 |
| 3.35 | $\text{Cd}^+ + \text{OH} \rightarrow \text{Cd}^{2+} + \text{OH}^-$       | $ca. 8 \times 10^9$                                          | —        | 25           | nat | pr     | Estimated from de-<br>cay of $\text{Cd}^+$ in ab-<br>sence of OH sca-<br>vengers taking in-<br>to account the<br>major competing<br>reaction $\text{Cd}^+ + \text{Cd}^+$ .                                                                                                                                                                        | Buxt.75-1027  |
|      |                                                                          | $1.8 \times 10^{10}$                                         | —        | RT           | nat | pr     | Experimentally de-<br>termined rate con-<br>stant for the decay<br>of $\text{Cd}^+$ in the ab-<br>sence of OH scaven-<br>gers. Not correct-<br>ed for $\text{Cd}^+ + \text{Cd}^+$<br>or other competing<br>reactions.                                                                                                                             | Baxe..66-0848 |
|      |                                                                          | $2 \times 10^{10}$                                           | —        | RT           | nat | pr     | Estimated from<br>computer analysis<br>of the decay of<br>the optical absorp-<br>tion and conduc-<br>tivity of $\text{Cd}^+$ in<br>the absence of OH<br>scavengers, taking<br>$\text{Cd}^+ + \text{Cd}^+$ and<br>$\text{Cd}^+ + \text{H}_2\text{O}_2$ as the<br>competing reac-<br>tions. Products<br>identified from<br>conductivity<br>changes. | Kelm..75-1064 |

TABLE 3. Cd(I) reactions — Continued

| No.  | Reaction.                                                                                                                                     | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$    | $t/^\circ\text{C}$ | pH         | Method   | Comments                                                                                                                   | Ref.                          |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|--------|--------------------|------------|----------|----------------------------------------------------------------------------------------------------------------------------|-------------------------------|
| 3.36 | $\text{Cd}^+ + \text{Pb}^{2+} (\text{et})$                                                                                                    | $7.5 \times 10^7$                                            | —      | RT                 | nat        | pr       | —                                                                                                                          | Baxe..66-0848                 |
| 3.37 | $\text{Cd}^+ + \text{Ru}(\text{NH}_3)_6^{2+} (\text{et})$                                                                                     | $(2.2 \pm 0.3) \times 10^9$                                  | 0.08   | RT                 | nat        | pr       | —                                                                                                                          | Nav..70-1229                  |
| 3.38 | $\text{Cd}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow$<br>$\text{Cd}^{2+} + \text{SO}_4^- + \text{SO}_4^{2-}$                                  | $(2.4 \pm 0.2) \times 10^9$                                  | 0.02*  | $25 \pm 2$         | nat        | pr       | Product identification: $\text{SO}_4^-$ observed to form at same rate as $\text{Cd}^+$ decayed.                            | Buxt..76-1072                 |
| 3.39 | $\text{Cd}^+ + \text{Zn}^{2+}$                                                                                                                | $< 10^7$                                                     | —      | RT                 | nat        | pr       | —                                                                                                                          | Baxe..66-0848                 |
| 3.40 | $\text{Cd}^+ + \cdot\text{CH}_2\text{OH} \rightarrow \text{CdCH}_2\text{OH}^+$                                                                | $2 \times 10^8$                                              | —      | RT                 | nat        | pr       | Product inferred from conductivity measurements.                                                                           | Kelm..75-1064                 |
| 3.41 | $\text{Cd}^+ + \text{CH}_3\text{CHOH} \rightarrow$<br>$\text{CdCH}_3\text{CHOH}^+$                                                            | $< 2 \times 10^8$<br>$(1.3 \pm 0.7) \times 10^9$             | —<br>— | RT<br>RT           | nat<br>nat | pr<br>pr | —<br>Product inferred from conductivity measurements.                                                                      | Bark.75-1153<br>Kelm..75-1064 |
| 3.42 | $\text{Cd}^+ + \cdot\text{CHOHCH}_2\text{OH}$                                                                                                 | $< 2 \times 10^8$                                            | —      | RT                 | nat        | pr       | —                                                                                                                          | Bark.75-1153                  |
| 3.43 | $\text{Cd}^+ + \text{CH}_3\text{COHCH}_3 \rightarrow$<br>$\text{CdCH}_3\text{COHCH}_3^+$                                                      | $< 2 \times 10^8$<br>$(2.4 \pm 1.2) \times 10^9$             | —<br>— | RT<br>RT           | nat<br>nat | pr<br>pr | —<br>Product inferred from conductivity measurements.                                                                      | Bark.75-1153<br>Kelm..75-1064 |
| 3.44 | $\text{Cd}^+ + \cdot\text{CHOHCHOHCH}_2\text{OH}$                                                                                             | $< 2 \times 10^8$                                            | —      | RT                 | nat        | pr       | —                                                                                                                          | Bark.75-1153                  |
| 3.45 | $\text{Cd}^+ + \cdot\text{CH}_2(\text{CH}_3)_2\text{COH} \rightarrow$<br>$\text{Cd}^{2+} + (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{OH}^-$ | $ca. 1 \times 10^9$                                          | —      | RT                 | nat        | pr       | Isobutene detected as product.                                                                                             | Kelm..75-1064                 |
| 3.46 | $\text{Cd}^+ + \cdot(\text{CH}_2\text{CH}_2\text{O})_n(\text{CHCH}_2\text{O})\cdot$                                                           | $< 2 \times 10^8$<br>$< 2 \times 10^8$                       | —<br>— | RT<br>RT           | nat<br>nat | pr<br>pr | —<br>Radical from polyethylene glycol (mw $10^4$ ) + OH.                                                                   | Bark.75-1153<br>Bark.75-1153  |
| 3.47 | $\text{Cd}^+ + \text{allyl alcohol}$                                                                                                          | $< 5 \times 10^7$                                            | —      | $25 \pm 2$         | nat        | pr       | —                                                                                                                          | Buxt..76-1072                 |
| 3.48 | $\text{Cd}^+ + 9,10\text{-anthraquinone} \rightarrow \text{Cd}^{2+} +$<br>$(9,10\text{-anthraquinone})^-$                                     | $(1.03 \pm 0.1) \times 10^9$                                 | —      | $ca. 22$           | 7.0        | pr       | Measured by the rate of formation of the semiquinone in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.   | Rao.73-1104                   |
| 3.49 | $\text{Cd}^+ + \text{benzophenone} \rightarrow$<br>$\text{Cd}^{2+} + (\text{benzophenone})^-$                                                 | $1.0 \times 10^9$                                            | —      | RT                 | 7.0        | pr       | Measured by the rate of formation of the ketyl radical in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. | Rao.75-1032                   |
| 3.50 | $\text{Cd}^+ + 1,4\text{-benzoquinone} \rightarrow$<br>$\text{Cd}^{2+} + (1,4\text{-benzoquinone})^-$                                         | $(4.1 \pm 0.8) \times 10^9$                                  | —      | $25 \pm 2$         | 5.4        | pr       | Measured by the rate of formation of the semiquinone in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.       | Sell.76-1134                  |
|      |                                                                                                                                               | $4.4 \times 10^9$                                            | —      | RT                 | 7.0        | pr       | Measured in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                               | Rao.75-1032                   |
|      |                                                                                                                                               | $(7.7 \pm 0.8) \times 10^9$                                  | —      | $ca. 22$           | 7.0        | pr       | Measured in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                               | Rao.73-1104                   |

TABLE 3. Cd(I) reactions — Continued

| No.                                               | Reaction                                                                                                                       | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>          | $I$  | $t/^\circ\text{C}$ | pH   | Method | Comments                                                                                                                       | Ref.                     |
|---------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------|------|--------------------|------|--------|--------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| 3.51                                              | $\text{Cd}^+ + 2\text{-hydroxy-1,4-naphthoquinone} \rightarrow \text{Cd}^{2+} + (2\text{-hydroxy-1,4-naphthoquinone})^-$       | $(3.57 \pm 0.4) \times 10^9$                                        | —    | ca. 22             | 7.0  | pr     | Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.        | Rao.73-1104              |
| 3.52                                              | $\text{Cd}^+ + \text{menaquinone} \rightarrow \text{Cd}^{2+} + (\text{menaquinone})^-$                                         | $(4.6 \pm 0.5) \times 10^9$                                         | —    | RT                 | 7.0  | pr     | Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.        | Rao.73-1047, Rao.75-1032 |
|                                                   |                                                                                                                                | $(4.68 \pm 0.5) \times 10^9$                                        | —    | ca. 22             | 7.0  | pr     | Measured in the presence of ca. 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                    | Rao.73-1104              |
| 3.53                                              | $\text{Cd}^+ + \text{NAD}^+ \rightarrow \text{Cd}^{2+} + \text{NAD}^\bullet$                                                   | $(2.9 \pm 0.3) \times 10^9$                                         | —    | ca. 22             | 7.0  | pr     | Measured by the rate of formation of NAD <sup>•</sup> in the presence of ca. 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.       | Rao.73-1104              |
| 3.54                                              | $\text{Cd}^+ + 1,4\text{-naphthoquinone-2-sulphonate} \rightarrow \text{Cd}^{2+} + (1,4\text{-naphthoquinone-2-sulphonate})^-$ | $(7.35 \pm 0.7) \times 10^9$                                        | —    | ca. 22             | 7.0  | pr     | Measured by the rate of formation of the semiquinone in the presence of ca. 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.        | Rao.73-1104              |
| 3.55                                              | $\text{Cd}^+ + \text{PNDA (et)}$                                                                                               | $1.4 \times 10^{10}$                                                | —    | RT                 | nat  | pr     | —                                                                                                                              | Dain.68-0066             |
| 3.56                                              | $\text{Cd}^+ + \text{riboflavin} \rightarrow \text{Cd}^{2+} + (\text{riboflavin})^-$                                           | $(5.10 \pm 0.5) \times 10^9$                                        | —    | ca. 22             | 7.0  | pr     | Measured by the rate of formation of the reduced riboflavin in the presence of ca. 1 mol dm <sup>-3</sup> 2-methyl-2-propanol. | Rao.73-1104              |
| <i>Cd(I) complexes</i>                            |                                                                                                                                |                                                                     |      |                    |      |        |                                                                                                                                |                          |
| <i>CdEDTA<sup>3-</sup></i>                        |                                                                                                                                |                                                                     |      |                    |      |        |                                                                                                                                |                          |
| 3.57                                              | $\text{CdEDTA}^{3-} + \text{BrO}_3^- \text{ (et)}$                                                                             | $(8.9 \pm 1.8) \times 10^6$                                         | 0.16 | RT                 | 11.3 | pr     | —                                                                                                                              | Meye.70-1228             |
|                                                   |                                                                                                                                | $E_a = 4.6 \pm 1.2$ kJ mol <sup>-1</sup>                            | 0.16 | 3-90               | 11.3 | pr     | —                                                                                                                              | Meye.70-1228             |
| 3.58                                              | $\text{CdEDTA}^{3-} + \text{CdEDTA}^{3-} \text{ (et or af)}$                                                                   | $'k'/\epsilon_{350} = (5.8 \pm 1.5) \times 10^3$ cm s <sup>-1</sup> | 0.16 | RT                 | 11.3 | pr     | Unclear whether $k$ or $2k$ .                                                                                                  | Meye.70-1228             |
|                                                   |                                                                                                                                | $'k' = (4 \pm 2) \times 10^7$                                       | 0.16 | RT                 | 11.3 | pr     | Unclear whether $k$ or $2k$ .                                                                                                  | Meye.70-1228             |
| 3.59                                              | $\text{CdEDTA}^{3-} + \text{IO}_3^- \text{ (et)}$                                                                              | $(2.7 \pm 0.6) \times 10^8$                                         | 0.16 | RT                 | 11.3 | pr     | —                                                                                                                              | Meye.70-1228             |
| 3.60                                              | $\text{CdEDTA}^{3-} + \text{NO}_2^- \text{ (et)}$                                                                              | $(3.2 \pm 0.6) \times 10^8$                                         | 0.16 | RT                 | 11.3 | pr     | —                                                                                                                              | Meye.70-1228             |
|                                                   |                                                                                                                                | $E_a = 8.4 \pm 1.2$ kJ mol <sup>-1</sup>                            | 0.16 | 3-90               | 11.3 | pr     | —                                                                                                                              | Meye.70-1228             |
| 3.61                                              | $\text{CdEDTA}^{3-} + \text{NO}_2^- \text{ (et)}$                                                                              | $(1.66 \pm 0.3) \times 10^7$                                        | 0.16 | RT                 | 11.3 | pr     | —                                                                                                                              | Meye.70-1228             |
| <i>Cd(en)<sub>n</sub><sup>+</sup> (n unknown)</i> |                                                                                                                                |                                                                     |      |                    |      |        |                                                                                                                                |                          |
| 3.62                                              | $\text{Cd(en)}_n^+ + \text{BrO}_3^- \text{ (et)}$                                                                              | $(1.28 \pm 0.3) \times 10^8$                                        | 0.64 | RT                 | 11.4 | pr     | —                                                                                                                              | Meye.70-1228             |
| 3.63                                              | $\text{Cd(en)}_n^+ + \text{IO}_3^- \text{ (et)}$                                                                               | $(2.5 \pm 0.5) \times 10^8$                                         | 0.64 | RT                 | 11.4 | pr     | —                                                                                                                              | Meye.70-1228             |
| 3.64                                              | $\text{Cd(en)}_n^+ + \text{NO}_2^- \text{ (et)}$                                                                               | $(1.12 \pm 0.2) \times 10^8$                                        | 0.64 | RT                 | 11.4 | pr     | —                                                                                                                              | Meye.70-1228             |
| 3.65                                              | $\text{Cd(en)}_n^+ + \text{NO}_3^- \text{ (et)}$                                                                               | $(4.5 \pm 0.9) \times 10^8$                                         | 0.64 | RT                 | 11.4 | pr     | —                                                                                                                              | Meye.70-1228             |

TABLE 3. Cd(I) reactions — Continued

| No.                            | Reaction                                                                                                                                                         | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^a$                   | $I$  | $t/^\circ\text{C}$ | pH   | Method | Comments                                          | Ref.          |
|--------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------|------|--------------------|------|--------|---------------------------------------------------|---------------|
| <i>Cd(gly)</i>                 |                                                                                                                                                                  |                                                                              |      |                    |      |        |                                                   |               |
| 3.66                           | $\text{Cd(gly)} + \text{BrO}_3^- \text{ (et)}$                                                                                                                   | $(6.1 \pm 1.2) \times 10^7$                                                  | 0.21 | RT                 | 10.5 | pr     | —                                                 | Meye.70-1228  |
| 3.67                           | $\text{Cd(gly)} + \text{IO}_3^- \text{ (et)}$                                                                                                                    | $(1.8 \pm 0.4) \times 10^8$                                                  | 0.21 | RT                 | 10.5 | pr     | —                                                 | Meye.70-1228  |
| 3.68                           | $\text{Cd(gly)} + \text{NO}_2^- \text{ (et)}$                                                                                                                    | $(8.5 \pm 1.7) \times 10^8$                                                  | 0.21 | RT                 | 10.5 | pr     | —                                                 | Meye.70-1228  |
| 3.69                           | $\text{Cd(gly)} + \text{NO}_3^- \text{ (et)}$                                                                                                                    | $(2.4 \pm 0.5) \times 10^8$                                                  | 0.21 | RT                 | 10.5 | pr     | —                                                 | Meye.70-1228  |
| <i>CdNTA<sup>2-</sup></i>      |                                                                                                                                                                  |                                                                              |      |                    |      |        |                                                   |               |
| 3.70                           | $\text{CdNTA}^{2-} + \text{BrO}_3^- \text{ (et)}$                                                                                                                | $(1.02 \pm 0.2) \times 10^7$                                                 | 0.10 | RT                 | 10.7 | pr     | —                                                 | Meye.70-1228  |
| 3.71                           | $\text{CdNTA}^{2-} + \text{CdNTA}^{2-}$<br>(et or af)                                                                                                            | $k'/\epsilon_{\text{NaO}} = (1.2 \pm 0.4) \times 10^5$<br>$\text{cm s}^{-1}$ | 0.10 | RT                 | 10.7 | pr     | Unclear whether $k$ or $2k$ .                     | Meye.70-1228  |
|                                |                                                                                                                                                                  | $k' = (8 \pm 4) \times 10^8$                                                 | 0.10 | RT                 | 10.7 | pr     | Unclear whether $k$ or $2k$ .                     | Meye.70-1228  |
| 3.72                           | $\text{CdNTA}^{2-} + \text{IO}_3^- \text{ (et)}$                                                                                                                 | $(6.1 \pm 1.2) \times 10^8$                                                  | 0.10 | RT                 | 10.7 | pr     | —                                                 | Meye.70-1228  |
| 3.73                           | $\text{CdNTA}^{2-} + \text{NO}_2^- \text{ (et)}$                                                                                                                 | $(4.2 \pm 0.8) \times 10^7$                                                  | 0.10 | RT                 | 10.7 | pr     | —                                                 | Meye.70-1228  |
| 3.74                           | $\text{CdNTA}^{2-} + \text{NO}_3^- \text{ (et)}$                                                                                                                 | $(4.5 \pm 0.9) \times 10^7$                                                  | 0.10 | RT                 | 10.7 | pr     | —                                                 | Meye.70-1228  |
| <i>Cd(I)-radical complexes</i> |                                                                                                                                                                  |                                                                              |      |                    |      |        |                                                   |               |
| 3.75                           | $\text{CdCH}_3\text{CHOH}^+ + \text{H}_2\text{O} \rightarrow$<br>$\text{Cd}^{2+} + \text{CH}_3\text{CH}_2\text{OH} + \text{OH}^-$                                | $257 \text{ s}^{-1}$                                                         | —    | RT                 | nat  | pr     | Products inferred from conductivity measurements. | Kelm..75-1064 |
| 3.76                           | $\text{CdCH}_3\text{COHCH}_3^+ + \text{H}_2\text{O} \rightarrow$<br>$\text{Cd}^{2+} + \text{CH}_3\text{CHOHCH}_3 + \text{OH}^-$                                  | $161 \text{ s}^{-1}$                                                         | —    | RT                 | nat  | pr     | Products inferred from conductivity measurements. | Kelm..75-1064 |
| 3.77                           | $\text{Cd}_2^{2+} + \cdot\text{CH}_2(\text{CH}_3)_2\text{COH} \rightarrow$<br>$\text{Cd}^+ + \text{Cd}^{2+} + (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{OH}^-$ | $\text{ca. } 1 \times 10^9$                                                  | —    | RT                 | nat  | pr     | Isobutene detected as product.                    | Kelm..75-1064 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 4. Cobalt(I) reactions

| No.  | Reaction                                                                                      | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$          | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                        | Ref.          |
|------|-----------------------------------------------------------------------------------------------|------------------------------------------------------------|--------------|--------------------|-----|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 4.1  | <sup>Co<sup>3+</sup>aq</sup><br>Co <sup>3+</sup> + Br <sub>2</sub> <sup>-</sup> (et)          | $(1.0 \pm 0.3) \times 10^{10}$                             | -            | RT                 | nat | f.ph.  | Competing reactions Br <sub>2</sub> <sup>-</sup> + Br <sub>2</sub> <sup>-</sup> and Co <sup>3+</sup> + Co <sup>3+</sup> not considered.                                                         | Thor.70-7726  |
| 4.2  | Co <sup>3+</sup> + BrO <sub>3</sub> <sup>-</sup> (et)                                         | $(4.8 \pm 0.5) \times 10^8$                                | 0.019*       | 25±2               | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
|      |                                                                                               | $(7.1 \pm 1.1) \times 10^8$                                | → 0          | 25±2               | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
| 4.3  | Co <sup>3+</sup> + Cd <sup>2+</sup>                                                           | < 10 <sup>7</sup>                                          | -            | RT                 | nat | pr     | -                                                                                                                                                                                               | Baxe..66-0848 |
| 4.4  | Co <sup>3+</sup> + Co <sup>3+</sup> (et or af)                                                | $2k < 4 \times 10^9$                                       | 0.019*       | 25±2               | nat | pr     | Estimated at 370 nm taking $\epsilon_{370} = 2080 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ .                                                                                                | Buxt.75-1027  |
| 4.5  | Co <sup>3+</sup> + Cu <sup>2+</sup> (et)                                                      | $(4.1 \pm 0.4) \times 10^8$                                | 0.019*       | 25±2               | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
|      |                                                                                               | $(1.06 \pm 0.36) \times 10^{10}$                           | 0.04         | RT                 | 5-8 | γ      | Measured by competition kinetics using NO <sub>3</sub> <sup>-</sup> as competitor and taking $k(\text{Co}^{3+} + \text{NO}_3^-) = 1.8 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . | Fiti70-0117   |
| 4.6  | Co <sup>3+</sup> + H <sub>2</sub> O <sub>2</sub> →<br>Co <sup>2+</sup> + OH + OH <sup>-</sup> | $(1.6 \pm 0.2) \times 10^8$                                | -            | 25                 | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
|      |                                                                                               | $1.9 \times 10^8$                                          | -            | RT                 | nat | pr     | -                                                                                                                                                                                               | Buxt..67-0062 |
|      |                                                                                               | $E_a = 13.0 \pm 1.0 \text{ kJ mol}^{-1}$                   | -            | 1 - 30             | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
|      |                                                                                               |                                                            |              |                    |     |        | Products identified in γ-radiolysis studies (see ref. 73-0039).                                                                                                                                 |               |
| 4.7  | Co <sup>3+</sup> + IO <sub>3</sub> <sup>-</sup> (et)                                          | $(4.3 \pm 0.4) \times 10^8$                                | 0.019*       | 25±2               | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
|      |                                                                                               | $(4.9 \pm 0.8) \times 10^8$                                | 0.04         | RT                 | 5-8 | γ      | Measured by competition kinetics using NO <sub>3</sub> <sup>-</sup> as competitor and taking $k(\text{Co}^{3+} + \text{NO}_3^-) = 1.8 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ . | Fiti70-0117   |
| 4.8  | Co <sup>3+</sup> + MnO <sub>4</sub> <sup>-</sup> (et)                                         | $1.06 \times 10^{10}$                                      | ca.<br>0.004 | 20                 | nat | pr     | Measured by the rate of depletion of the MnO <sub>4</sub> <sup>-</sup> absorption.                                                                                                              | Baxe..65-0385 |
| 4.9  | Co <sup>3+</sup> + N <sub>2</sub> O → CoO <sup>2+</sup> + N <sub>2</sub>                      | $7 \times 10^8$                                            | -            | RT                 | nat | γ      | Estimated from N <sub>2</sub> yields in the γ-radiolysis of Co <sup>2+</sup> + N <sub>2</sub> O solutions.                                                                                      | Buxt..67-0062 |
|      |                                                                                               | $(1.0 \pm 0.1) \times 10^9$                                | -            | 25±2               | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
|      |                                                                                               |                                                            |              |                    |     |        | Products inferred from γ-ray induced chain reaction in the system Co <sup>2+</sup> + HCO <sub>2</sub> <sup>-</sup> + N <sub>2</sub> O. (see ref. 73-0039).                                      |               |
| 4.10 | Co <sup>3+</sup> + NO <sub>3</sub> <sup>-</sup> (et)                                          | $(1.8 \pm 0.2) \times 10^9$                                | 0.019        | 25±2               | nat | pr     | -                                                                                                                                                                                               | Buxt..76-1072 |
| 4.11 | Co <sup>3+</sup> + Ni <sup>2+</sup>                                                           | < 10 <sup>7</sup>                                          | -            | RT                 | nat | pr     | -                                                                                                                                                                                               | Baxe..66-0848 |

TABLE 4. Cobalt(II) reactions — Continued

| No.  | Reaction                                                                                                | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$   | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                         | Ref.          |
|------|---------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-------|--------------------|-----|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 4.12 | $\text{Co}^+ + \text{O}_2$ (et or af)                                                                   | $(6.0 \pm 0.6) \times 10^9$                                  | —     | $25 \pm 2$         | nat | pr     | Absorption of products similar to that of $\text{O}_2^-$ but decay slower (see ref. 76-1072). Product transfers an electron to 1,4-benzoquinone (see ref. 76-1134). Evidence possibly indicates product to be $\text{CoO}_2^+$ . | Buxt.76-1072  |
| 4.13 | $\text{Co}^+ + \text{OH}$ (et)                                                                          | $ca. 8 \times 10^9$                                          | —     | $25 \pm 2$         | nat | pr     | Estimated from decay of $\text{Co}^+$ in absence of OH scavengers, taking into account the major competing reaction $\text{Co}^+ + \text{Co}^+$ .                                                                                | Buxt.75-1027  |
| 4.14 | $\text{Co}^+ + \text{Ph}^{2+}$                                                                          | $< 10^7$                                                     | —     | RT                 | nat | pr     | —                                                                                                                                                                                                                                | Baxe..66-0848 |
| 4.15 | $\text{Co}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Co}^{2+} + \text{SO}_4^- + \text{SO}_4^{2-}$ | $(2.8 \pm 0.5) \times 10^9$                                  | 0.019 | $25 \pm 2$         | nat | pr     | Formation of $\text{SO}_4^-$ inferred from the absorption produced on pulse radiolysis of solutions of $\text{Co}^{2+} + \text{S}_2\text{O}_8^{2-}$ .                                                                            | Buxt.76-1072  |
| 4.16 | $\text{Co}^+ + \text{Zn}^{2+}$                                                                          | $< 10^7$                                                     | —     | RT                 | nat | pr     | —                                                                                                                                                                                                                                | Baxe..66-0848 |
| 4.17 | $\text{Co}^+ + \text{allyl alcohol} \rightarrow (\text{Co-allyl alcohol})^+$                            | $ca. 10^9$                                                   | —     | $25 \pm 2$         | nat | pr     | Product characterised by its absorption spectrum.                                                                                                                                                                                | Buxt.76-1072  |
| 4.18 | $\text{Co}^+ + 9,10\text{-anthraquinone} \rightarrow \text{Co}^{2+} + (9,10\text{-anthraquinone})^-$    | $(1.05 \pm 0.1) \times 10^9$                                 | —     | $ca. 22$           | nat | pr     | Measured by the rate of formation of the semiquinone in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                                                         | Rao.73-1104   |
| 4.19 | $\text{Co}^+ + \text{benzophenone} \rightarrow \text{Co}^{2+} + (\text{benzophenone})^-$                | $2.5 \times 10^9$                                            | —     | RT                 | 7.0 | pr     | Measured by the rate of formation of the ketyl radical in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                                                       | Rao.75-1032   |
| 4.20 | $\text{Co}^+ + 1,4\text{-benzoquinone} \rightarrow \text{Co}^{2+} + (1,4\text{-benzoquinone})^-$        | $4.0 \times 10^9$                                            | —     | RT                 | 7.0 | pr     | Measured by the rate of formation of the semiquinone in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                                                         | Rao.75-1032   |
|      |                                                                                                         | $(5.1 \pm 0.5) \times 10^9$                                  | —     | $25 \pm 2$         | 4.7 | pr     | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                                         | Sell.76-1134  |
|      |                                                                                                         | $(7.35 \pm 0.7) \times 10^9$                                 | —     | $ca. 22$           | 7.0 | pr     | Measured in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                                     | Rao.73-1104   |

TABLE 4. Cobalt(I) reactions — Continued

| No.                                                                                               | Reaction                                                                                                                                                                                                        | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$   | $t/^\circ\text{C}$ | pH            | Method | Comments                                                                                                                                                    | Ref.                       |
|---------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|-------|--------------------|---------------|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------|
| 4.21                                                                                              | $\text{Co}^+ + \text{menaquinone} \rightarrow \text{Co}^{2+} + (\text{menaquinone})^-$                                                                                                                          | $(4.0 \pm 0.4) \times 10^9$                                | —     | RT                 | 7.3           | pr     | Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                             | Rao.73-1047<br>Rao.75-1032 |
|                                                                                                   |                                                                                                                                                                                                                 | $(4.1 \pm 0.1) \times 10^9$                                | —     | <i>ca.</i> 22      | 7.0           | pr     | Measured in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                         | Rao.73-1104                |
| 4.22                                                                                              | $\text{Co}^+ + 1,4\text{-naphthoquinone-2-sulphonate} \rightarrow \text{Co}^{2+} + (1,4\text{-naphthoquinone-2-sulphonate})^-$                                                                                  | $(6.83 \pm 0.7) \times 10^9$                               | —     | <i>ca.</i> 22      | 7.3           | pr     | Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                             | Rao.73-1104                |
| 4.23                                                                                              | $\text{Co}^+ + \text{riboflavin} \rightarrow \text{Co}^{2+} + (\text{riboflavin})^-$                                                                                                                            | $(2.55 \pm 0.3) \times 10^9$                               | —     | <i>ca.</i> 22      | 7.0           | pr     | Measured by the rate of formation of the reduced riboflavin in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                      | Rao.73-1104                |
| <i>Co(I) complexes</i>                                                                            |                                                                                                                                                                                                                 |                                                            |       |                    |               |        |                                                                                                                                                             |                            |
| 4.24                                                                                              | $\text{Co}(\text{CN})_5^{4-} \text{ (from } \text{Co}(\text{CN})_5^{3-} + e_{\text{aq}}^-)$<br>$\text{Co}(\text{CN})_5^{4-} + \text{H}_2\text{O} \rightarrow \text{Co}(\text{CN})_5\text{H}^{3-} + \text{OH}^-$ | $(1.1 \pm 0.1) \times 10^8 \text{ s}^{-1}$                 | —     | 20                 | <i>ca.</i> 13 | pr     | Measured in the presence of <i>ca.</i> $0.1 \text{ mol dm}^{-3}$ $\text{H}_2$ . Proton transfer mechanism implied from isotope effect (compare entry 4.25). | Vene.71-0097               |
| 4.25                                                                                              | $\text{Co}(\text{CN})_5^{4-} + \text{D}_2\text{O} \rightarrow \text{Co}(\text{CN})_5\text{D}^{3-} + \text{OD}^-$                                                                                                | $(1.9 \pm 0.2) \times 10^8 \text{ s}^{-1}$                 | —     | 20                 | <i>ca.</i> 13 | pr     | Measured in $\text{D}_2\text{O}$ in the presence of <i>ca.</i> $0.1 \text{ mol dm}^{-3}$ $\text{H}_2$ .                                                     | Vene.71-0097               |
| <i>CoL<sup>+</sup> (L = 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)</i> |                                                                                                                                                                                                                 |                                                            |       |                    |               |        |                                                                                                                                                             |                            |
| 4.26                                                                                              | $\text{CoL}^+ + \text{H}_2\text{O} \rightarrow \text{CoLH}^{2+} + \text{OH}^-$                                                                                                                                  | 20                                                         | 0.001 | RT                 | 9-10          | pr     | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                               | Tait..76-1001              |
| 4.27                                                                                              | $\text{CoL}^+ + \text{H}_3\text{O}^+ \rightarrow \text{CoLH}^{2+} + \text{H}_2\text{O}$                                                                                                                         | $1.2 \times 10^9$                                          | 0.015 | RT                 | 3.5-4.2       | pr     | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                               | Tait..76-1001              |

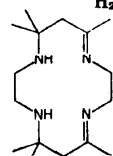


TABLE 4. Cobalt(I) reactions — Continued

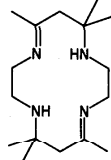
| No.                                                                                                                                                                                                          | Reaction                                                                               | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$            | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                   | Ref.          |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|--------------------------------------------------------------|----------------|--------------------|-----|--------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 4.28                                                                                                                                                                                                         | $\text{CoL}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{CoLH}^+ + \text{HPO}_4^{2-}$ | $3.0 \times 10^7$                                            | 0.005<br>-0.01 | RT                 | 5.5 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                                                                               | Tait..76-1001 |
| 4.29                                                                                                                                                                                                         | $\text{CoL}^+ + \text{N}_2\text{O (et)}$                                               | $9.0 \times 10^6$                                            | 0.01           | RT                 | 9.2 | pr     | Reaction possibly involves two electron oxidation to $\text{Co(III)}$ complex.                                                                                                                             | Tait..76-1001 |
| 4.30                                                                                                                                                                                                         | $\text{CoL}^+ + \text{O}_2 \rightarrow \text{CoLO}_2^+$                                | $9.0 \times 10^8$                                            | 0.02           | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Reaction does not involve the formation of $\text{CoL}^{2+}$ , assumed therefore to involve the coordination of the $\text{O}_2$ . | Tait..76-1001 |
| <p><math>\text{CoL}^+</math> (<math>L = 5,7,7,12,14,14</math>-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).</p>  |                                                                                        |                                                              |                |                    |     |        |                                                                                                                                                                                                            |               |
| 4.31                                                                                                                                                                                                         | $\text{CoL}^+ + \text{Co(bpy)}_3^{3+} \text{ (et)}$                                    | $1.2 \times 10^9$                                            | ca.<br>0.02    | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                    | Tait..76-1001 |
| 4.32                                                                                                                                                                                                         | $\text{CoL}^+ + \text{Co(en)}_3^{3+} \text{ (et)}$                                     | $7.9 \times 10^6$                                            | ca.<br>0.02    | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                    | Tait..76-1001 |
| 4.33                                                                                                                                                                                                         | $\text{CoL}^+ + \text{Co(NH}_3)_6^{3+} \text{ (et)}$                                   | $7.5 \times 10^6$                                            | ca.<br>0.02    | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                    | Tait..76-1001 |
| 4.34                                                                                                                                                                                                         | $\text{CoL}^+ + \text{CoL}^{2+} \text{ (et)}$                                          | $4.0 \times 10^6$                                            | ca.<br>0.02    | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                    | Tait..76-1001 |
| 4.35                                                                                                                                                                                                         | $\text{CoL}^+ + \text{CoL}^{2+} \text{ (et)}$                                          | $6.7 \times 10^6$                                            | ca.<br>0.02    | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                    | Tait..76-1001 |
| <p>(<math>L' = 2,3,9,10</math>-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,2,8,10-tetraene)</p>                                                                                                            |                                                                                        |                                                              |                |                    |     |        |                                                                                                                                                                                                            |               |
| 4.36                                                                                                                                                                                                         | $\text{CoL}^+ + \text{Cr(bpy)}_3^{3+} \text{ (et)}$                                    | $1.2 \times 10^9$                                            | ca.<br>0.02    | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                    | Tait..76-1001 |

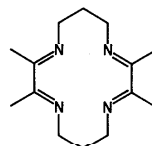
TABLE 4. Cobalt(I) reactions — Continued

| No.  | Reaction                                                                               | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$             | $t/^\circ\text{C}$ | pH      | Method | Comments                                                                                                                                                                                               | Ref.          |
|------|----------------------------------------------------------------------------------------|--------------------------------------------------------------|-----------------|--------------------|---------|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 4.37 | $\text{CoL}^+ + \text{Fe}(\text{bpy})_3^{3+} (\text{et})$                              | $2.3 \times 10^7$                                            | ca.<br>0.02     | RT                 | 9.2     | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                | Tait..76-1001 |
| 4.38 | $\text{CoL}^+ + \text{H}_2\text{O} \rightarrow \text{CoLH}^{2+} + \text{OH}^-$         | 48                                                           | 0.001           | RT                 | 9-10    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                                                                           | Tait..76-1001 |
| 4.39 | $\text{CoL}^+ + \text{H}_3\text{O}^+ \rightarrow \text{CoLH}^+ + \text{H}_2\text{O}$   | $3.1 \times 10^9$                                            | 0.015           | RT                 | 3.5-4.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                                                                           | Tait..76-1001 |
| 4.40 | $\text{CoL}^+ + \text{HPO}_4^{2-} \rightarrow \text{CoLH}^{2+} + \text{PO}_4^{3-}$     | $1.0 \times 10^5$                                            | 0.06-<br>0.3    | RT                 | 10.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                                                                           | Tait..76-1001 |
| 4.41 | $\text{CoL}^+ + \text{H}_2\text{PO}_4^- \rightarrow \text{CoLH}^+ + \text{HPO}_4^{2-}$ | $9.8 \times 10^7$                                            | 0.005-<br>0.01  | RT                 | 5.5     | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                                                                           | Tait..76-1001 |
| 4.42 | $\text{CoL}^+ + \text{NH}_4^+ \rightarrow \text{CoLH}^+ + \text{NH}_3$                 | $6.8 \times 10^5$                                            | 0.015-<br>0.1   | RT                 | 7.0     | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                                                                           | Tait..76-1001 |
| 4.43 | $\text{CoL}^+ + \text{N}_2\text{O} (\text{et})$                                        | $3.9 \times 10^7$                                            | 0.01            | RT                 | 9.2     | pr     | Reaction possibly involves two electron oxidation to Co(III) complex.                                                                                                                                  | Tait..76-1001 |
| 4.44 | $\text{CoL}^+ + \text{O}_2 \rightarrow \text{CoLO}_2^+$                                | $1.7 \times 10^9$                                            | 0.02            | RT                 | 9.2     | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Reaction does not involve formation of $\text{CoL}^{2+}$ , assumed therefore to involve the coordination of the $\text{O}_2$ . | Tait..76-1001 |
| 4.45 | $\text{CoL}^+ + \text{Ru}(\text{NH}_3)_6^{2+} (\text{et})$                             | $4.0 \times 10^8$                                            | 0.016-<br>0.028 | RT                 | 9.2     | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                | Tait..76-1001 |

TABLE 4. Cobalt(II) reactions — Continued

| No.  | Reaction                                                                                                                         | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$         | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                  | Ref.          |
|------|----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|-------------|--------------------|-----|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 4.46 | $\text{CoL}^+ + \text{Ru}(\text{NH}_3)_5\text{NO}^{3+} (\text{et})$                                                              | $3.9 \times 10^7$                                          | 0.016–0.028 | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                   | Tait..76–1001 |
| 4.47 | $\text{CoL}^+ + \text{acetic acid} \rightarrow \text{CoLH}^+ + \text{CH}_3\text{COO}^-$                                          | $7.5 \times 10^7$                                          | 0.01–0.05   | RT                 | 4.8 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. See ref. for evidence for proton transfer mechanism.                                              | Tait..76–1001 |
| 4.48 | $\text{CoL}^+ + 9,10\text{-anthraquinone-2-sulphonate} \rightarrow \text{CoL}^{2+} + (9,10\text{-anthraquinone-2-sulphonate})^-$ | $4.4 \times 10^9$                                          | 0.004       | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption.                                             | Tait..76–1001 |
| 4.49 | $\text{CoL}^+ + 3\text{-benzoylpyridine} (\text{et} + ?)$                                                                        | $4.6 \times 10^8$                                          | 0.004       | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Only 50% electron transfer to the 3-benzoylpyridine. Other reaction pathway(s) not characterised. | Tait..76–1001 |
| 4.50 | $\text{CoL}^+ + \text{fluorenone} \rightarrow \text{CoL}^{2+} + (\text{fluorenone})^-$                                           | $4.3 \times 10^9$                                          | 0.004       | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Ketyl radical product characterised by its absorption.                                            | Tait..76–1001 |
| 4.51 | $\text{CoL}^+ + \text{menaquinone} \rightarrow \text{CoL}^{2+} + (\text{menaquinone})^-$                                         | $4.6 \times 10^9$                                          | 0.004       | RT                 | 9.2 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption.                                             | Tait..76–1001 |
| 4.52 | $\text{CoL}^+ + \text{methyl iodide} (\text{et})$                                                                                | $4.7 \times 10^8$                                          | 0.015       | RT                 | 9.2 | pr     | No evidence for substitution ( $\text{S}_\text{N}2$ ) reaction pathway.                                                                                                   | Tait..76–1001 |

$\text{CoL}^+$  ( $L = 2,3,9,10\text{-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene}$ )



|      |                                                           |                   |             |    |     |    |                                                                         |               |
|------|-----------------------------------------------------------|-------------------|-------------|----|-----|----|-------------------------------------------------------------------------|---------------|
| 4.53 | $\text{CoL}^+ + \text{Co}(\text{bpy})_3^{3+} (\text{et})$ | $8.5 \times 10^7$ | 0.016–0.028 | RT | 6.5 | pr | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. | Tait..76–1001 |
|------|-----------------------------------------------------------|-------------------|-------------|----|-----|----|-------------------------------------------------------------------------|---------------|

TABLE 4. Cobalt(I) reactions — Continued

| No.  | Reaction                                                                                                                             | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$         | $t/^\circ\text{C}$ | pH        | Method | Comments                                                                                                                                                                                           | Ref.          |
|------|--------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-------------|--------------------|-----------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 4.54 | $\text{CoL}^+ + \text{Cr}(\text{bpy})_3^{3+} (\text{et})$                                                                            | $1.6 \times 10^8$                                            | 0.016–0.028 | RT                 | 6.5       | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                            | Tait..76–1001 |
| 4.55 | $\text{CoL}^+ + \text{H}_3\text{O}^+ \rightarrow \text{CoLH}^{2+} + \text{H}_2\text{O}$                                              | $1.6 \times 10^8$                                            | 0.06–0.6    | RT                 | 0.25–1.25 | pr     | Measured in the presence of 2 mol $\text{dm}^{-3}$ 2-propanol. See ref. for evidence for proton transfer mechanism.                                                                                | Tait..76–1001 |
| 4.56 | $\text{CoL}^+ + \text{O}_2 \rightarrow \text{CoLO}_2^+$                                                                              | $1.1 \times 10^9$                                            | 0.02        | RT                 | 6.5       | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Reaction does not involve formation of $\text{CoL}^{2+}$ , assumed therefore to involve the coordination of $\text{O}_2$ . | Tait..76–1001 |
| 4.57 | $\text{CoL}^+ + \text{acetic acid} \rightarrow \text{CoLH}^{2+} + \text{CH}_3\text{COO}^-$                                           | $6.2 \times 10^4$                                            | 0.01–0.05   | RT                 | 4.8       | pr     | Measured in the presence of 2 mol $\text{dm}^{-3}$ 2-propanol. See ref. for evidence for proton transfer mechanism.                                                                                | Tait..76–1001 |
| 4.58 | $\text{CoL}^+ + 9,10\text{-anthraquinone-2,6-sulphonate} \rightarrow \text{CoL}^{2+} + (9,10\text{-anthraquinone-2,6-sulphonate})^-$ | $3.8 \times 10^9$                                            | 0.004       | RT                 | 6.5       | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption.                                                                      | Tait..76–1001 |
| 4.59 | $\text{CoL}^+ + \text{indigosulphonate} \rightarrow \text{CoL}^{2+} + (\text{indigosulphonate})^-$                                   | $4.9 \times 10^9$                                            | 0.004       | RT                 | 6.5       | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Radical anion product characterised by its absorption.                                                                     | Tait..76–1001 |
| 4.60 | $\text{CoL}^+ + \text{riboflavin} \rightarrow \text{CoL}^{2+} + (\text{riboflavin})^-$                                               | $1.0 \times 10^9$                                            | 0.004       | RT                 | 6.5       | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Radical anion product characterised by its absorption.                                                                     | Tait..76–1001 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions

| No.                                                                           | Reaction                                                                                                                                    | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$     | $t/^\circ\text{C}$ | pH      | Method   | Comments                                                                                                                                                                                                             | Ref.         |
|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|---------|--------------------|---------|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| <i>Cr(I) Reactions</i>                                                        |                                                                                                                                             |                                                              |         |                    |         |          |                                                                                                                                                                                                                      |              |
| $\text{Cr}_{\text{aq}}^{+}$                                                   |                                                                                                                                             |                                                              |         |                    |         |          |                                                                                                                                                                                                                      |              |
| 5.1                                                                           | $\text{Cr}^{+} + \text{H}_2\text{O}$                                                                                                        | $< 5 \times 10^8 \text{ s}^{-1}$                             | -       | $22 \pm 2$         | 3.0-4.3 | pr       | Estimated from first order, dose dependent decay of $\text{Cr}^{+}$ . Major competing reactions thought to be $\text{Cr}^{+} + \text{H}_2\text{O}_2$ . $\text{H}_2$ detected as product ( $G = 2.9$ at pH 3.4).      | Cohe.74-1142 |
| <i>CrH<sup>2+</sup> (from H + Cr<sup>2+</sup>)</i>                            |                                                                                                                                             |                                                              |         |                    |         |          |                                                                                                                                                                                                                      |              |
| 5.2                                                                           | $\text{CrH}^{2+} + \text{H}_2\text{O}$                                                                                                      | $< 1 \text{ s}^{-1}$                                         | -       | $22 \pm 2$         | 0-2     | pr       | -                                                                                                                                                                                                                    | Cohe.74-1142 |
| 5.3                                                                           | $\text{CrH}^{2+} + \text{H}_3\text{O}^{+} \rightarrow \text{Cr}^{3+} + \text{H}_2 + \text{H}_2\text{O}$                                     | $(1.8 \pm 0.2) \times 10^4$                                  | var     | $22 \pm 2$         | 0-2     | pr       | $G(\text{H}_2) = 3.8$ at pH 0-2.                                                                                                                                                                                     | Cohe.74-1142 |
| <i>Cr(II) reactions (includes only those measured by radiolytic methods).</i> |                                                                                                                                             |                                                              |         |                    |         |          |                                                                                                                                                                                                                      |              |
| $\text{Cr}_{\text{aq}}^{2+}$                                                  |                                                                                                                                             |                                                              |         |                    |         |          |                                                                                                                                                                                                                      |              |
| 5.4                                                                           | $\text{Cr}^{2+} + \text{Br}_2^{-} \rightarrow \text{CrBr}^{2+} + \text{Br}^{-}$                                                             | $(1.9 \pm 0.2) \times 10^9$                                  | 0.2     | $22 \pm 3$         | 1       | pr       | Reaction occurs by inner sphere diffusion controlled mechanism. $G(\text{CrBr}^{2+}) = 2.4$ in $\gamma$ -radiolysis experiments.                                                                                     | Laur.74-1104 |
| 5.5                                                                           | $\text{Cr}^{2+} + \text{Cl}_2^{-} \rightarrow \text{CrCl}^{2+} + \text{Cl}^{-} \text{ (a) or } \text{Cr}^{3+} + 2\text{Cl}^{-} \text{ (b)}$ | $(2.4 \pm 0.3) \times 10^9$                                  | 0.2     | $22 \pm 3$         | 1       | pr       | Reaction occurs by parallel mechanisms involving inner-sphere (path a) and outer sphere (b) diffusion control with approximately equal probability. $G(\text{CrCl}^{2+}) = 1.4$ in $\gamma$ -radiolysis experiments. | Laur.74-1104 |
| 5.6                                                                           | $\text{Cr}^{2+} + \text{I}_2^{-} \rightarrow \text{CrI}^{2+} + \text{I}^{-}$                                                                | $(1.5 \pm 0.2) \times 10^9$                                  | 0.2     | $22 \pm 3$         | 1       | pr       | Reaction occurs by inner sphere diffusion controlled mechanism. $\text{CrI}^{2+}$ characterised by flash photolysis and $\gamma$ -radiolysis experiments. $G(\text{CrI}^{2+}) = 0.85$ at $0^\circ\text{C}$ .         | Laur.74-1104 |
| 5.7                                                                           | $\text{Cr}^{2+} + \text{MnO}_4^{-} \text{ (et)}$                                                                                            | $3.7 \times 10^9$                                            | ca.0.01 | 20                 | nat     | pr       | Measured by the rate of depletion of the $\text{MnO}_4^{-}$ absorption.                                                                                                                                              | Baxe.65-0385 |
| 5.8                                                                           | $\text{Cr}^{2+} + \text{N}_2\text{O}$                                                                                                       | $< 10^9$                                                     | -       | 25                 | nat     | $\gamma$ | Estimated from the values of $G(\text{N}_2)$ measured in the $\gamma$ -radiolysis of $\text{Cr}^{2+} + \text{N}_2\text{O}$ solutions.                                                                                | Sell72-0844  |

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

| No.  | Reaction                                                                                                                                    | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$      | $t/^\circ\text{C}$ | pH      | Method    | Comments                                                                                                                                                                                                        | Ref.            |
|------|---------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|----------|--------------------|---------|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|
| 5.9  | $\text{Cr}^{3+} + \text{O}_2 \rightarrow \text{CrO}_2^{2+}$                                                                                 | $(1.6 \pm 0.2) \times 10^8$                                | —        | $25 \pm 2$         | 2.6–4.3 | pr        | Measured from the rate of formation of $\text{CrO}_2^{2+}$ in the presence of $0.5 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. Product characterised by its absorption spectrum and by conductivity measurements. | Sell.76–1134    |
|      |                                                                                                                                             | $(1.6 \pm 0.2) \times 10^8$                                | —        | RT                 | 1–3     | pr        | Measured from the rate of formation of $\text{CrO}_2^{2+}$ .                                                                                                                                                    | Ilan..75–1215   |
|      |                                                                                                                                             | $(1.9 \pm 0.3) \times 10^8$                                | —        | $25 \pm 2$         | 3.4     | pr (comp) | Measured by competition with 1,4-benzoquinone taking $k(\text{Cr}^{2+} + \text{C}_6\text{H}_4\text{O}_2) = 3.2 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ .                                        | Sell.76–1134    |
| 5.10 | $\text{Cr}^{2+} + \cdot\text{CONH}_2 \rightarrow \text{CrCONH}_2^{2+}$                                                                      | $(6.5 \pm 0.7) \times 10^8$                                | —        | $22 \pm 2$         | 0–4.5   | pr        | Measured by the rate of formation of the product in the presence of $1 \text{ mol dm}^{-3}$ formamide. Product characterised by its absorption spectrum and decay kinetics.                                     | Cohe.74–1146    |
| 5.11 | $\text{Cr}^{2+} + \cdot\text{CH}_2\text{OH} \rightarrow \text{CrCH}_2\text{OH}^{2+}$                                                        | $1.6 \times 10^8$                                          | —        | $22 \pm 2$         | 0–1     | pr        | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146    |
| 5.12 | $\text{Cr}^{2+} + \text{CO}_2^- \rightarrow \text{CrCO}_2^+$                                                                                | $(1.1 \pm 0.1) \times 10^9$                                | ca. 0.04 | $25 \pm 2$         | 1.4     | pr        | Measured by rate of formation of the product in the presence of $1 \text{ mol dm}^{-3}$ formic acid. Product characterised by its spectrum and decay kinetics.                                                  | Elli....73–1057 |
| 5.13 | $\text{Cr}^{2+} + \cdot\text{CH}_2\text{CHO} \rightarrow \text{CrCH}_2\text{CHO}^{2+} \text{ or } \text{CrCH}_2\text{CH}(\text{OH})_2^{2+}$ | $3.5 \times 10^8$                                          | —        | $22 \pm 2$         | 0–1     | pr        | Measured by the rate of formation of the product, which may be in the form of an acetal.                                                                                                                        | Cohe.74–1146    |
| 5.14 | $\text{Cr}^{2+} + \cdot\text{CH}_2\text{COOH} \rightarrow \text{CrCH}_2\text{COOH}^{2+}$                                                    | $2.5 \times 10^8$                                          | —        | $22 \pm 2$         | 0–1     | pr        | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146    |
| 5.15 | $\text{Cr}^{2+} + \cdot\text{CHOH.COOH} \rightarrow \text{CrCHOH.COOH}^{2+}$                                                                | $1.4 \times 10^8$                                          | —        | $22 \pm 2$         | 0–1     | pr        | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146    |

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

| No.  | Reaction                                                                                                                                       | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | <i>I</i> | <i>t</i> /°C | pH      | Method | Comments                                                                                                                                                                                                        | Ref.         |
|------|------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|----------|--------------|---------|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| 5.16 | $\text{Cr}^{3+} + \text{CH}_3\text{CHOH} \rightarrow \text{CrCH}(\text{CH}_3)\text{OH}^{2+}$                                                   | $7.9 \times 10^7$                                            | —        | $22 \pm 2$   | 0–1     | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146 |
| 5.17 | $\text{Cr}^{3+} + \cdot\text{CHOHCH}_2\text{OH} \rightarrow \text{CrCH}_2\text{CHO}^{2+} \text{ or } \text{CrCH}_2\text{CH}(\text{OH})_2^{2+}$ | $1.5 \times 10^8$                                            | —        | $22 \pm 2$   | 3.0–4.5 | pr     | Measured by the rate of formation of the product. Product is identical to that formed in the reaction $\text{Cr}^{3+} + \text{CH}_3\text{CHO}$ (see entry 5.13).                                                | Cohe.74–1146 |
| 5.18 | $\text{Cr}^{3+} + \cdot\text{CH}(\text{COOH})_2 \rightarrow \text{CrCH}(\text{COOH})_2^{2+}$                                                   | $6.0 \times 10^7$                                            | —        | $22 \pm 2$   | 0–1     | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146 |
| 5.19 | $\text{Cr}^{3+} + \text{CH}_3\text{CHCOOH} \rightarrow \text{CrCH}(\text{CH}_3)\text{COOH}^{2+}$                                               | $1.1 \times 10^8$                                            | —        | $22 \pm 2$   | 0–1     | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146 |
| 5.20 | $\text{Cr}^{3+} + \text{CH}_3\text{C}(\text{OH})\text{COOH} \rightarrow \text{CrCOH}(\text{CH}_3)\text{COOH}^{2+}$                             | $9.2 \times 10^7$                                            | —        | $22 \pm 2$   | 0–1     | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146 |
| 5.21 | $\text{Cr}^{3+} + \cdot\text{CH}_2\text{N}(\text{CH}_3)\text{CHO} \rightarrow \text{CrCH}_2\text{N}(\text{CH}_3)\text{CHO}^{2+}$               | $(1.1 \pm 0.1) \times 10^8$                                  | —        | $22 \pm 2$   | 0–4.5   | pr     | Measured by the rate of formation of the product in the presence of $1 \text{ mol dm}^{-3}$ $\text{CH}_3\text{N}(\text{CH}_3)\text{CHO}$ . Product characterised by its absorption spectrum and decay kinetics. | Cohe.74–1146 |
| 5.22 | $\text{Cr}^{3+} + (\text{CH}_3)_2\text{COH} \cdot \rightarrow \text{CrCOH}(\text{CH}_3)_2^{2+}$                                                | $5.1 \times 10^7$                                            | —        | $22 \pm 2$   | 0–1     | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146 |
| 5.23 | $\text{Cr}^{3+} + \cdot\text{R} \rightarrow \text{CrR}^{3+}$<br>$\cdot\text{R}$ = radical from dioxane<br>(H abstraction)                      | $1.0 \times 10^8$                                            | —        | $22 \pm 2$   | 0–1     | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146 |
| 5.24 | $\text{Cr}^{3+} + \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH} \rightarrow \text{CrCH}_2\text{C}(\text{CH}_3)_2\text{OH}^{2+}$             | $1.0 \times 10^8$                                            | —        | $22 \pm 2$   | 0–1     | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.                                                                                          | Cohe.74–1146 |

TABLE 5. Chromium(I), chromium(II) and chromium(V) reactions — Continued

| No.  | Reaction                                                                                                                                         | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>  | $I$   | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                       | Ref.         |
|------|--------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|-------|--------------------|-----|--------|--------------------------------------------------------------------------------------------------------------------------------|--------------|
| 5.25 | $\text{Cr}^{3+} + \text{CH}_3\text{CHOCH}_2\text{CH}_3 \rightarrow \text{CrCH}(\text{CH}_3)\text{OCH}_2\text{CH}_3^{2+}$                         | $3.4 \times 10^7$                                             | —     | $22 \pm 2$         | 0–1 | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.         | Cohe.74–1146 |
| 5.26 | $\text{Cr}^{3+} + \text{CH}_3\text{C}(\text{CH}_3)_2\text{COOH} \rightarrow \text{CrCH}_2\text{C}(\text{CH}_3)_2\text{COOH}^{2+}$                | $1.1 \times 10^8$                                             | —     | $22 \pm 2$         | 0–1 | pr     | Measured by the rate of formation of the product. Product characterised by its absorption spectrum and decay kinetics.         | Cohe.74–1146 |
| 5.27 | $\text{Cr}^{3+} + \text{anthraquinone-2,6-disulphonate} \rightarrow \text{Cr}^{3+} + (\text{anthraquinone-2,6-disulphonate})^-$                  | $(2.8 \pm 0.3) \times 10^8$                                   | —     | <i>ca.</i> 22      | 7.0 | pr     | Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> 1 mol dm <sup>-3</sup> 2-methyl-2-propanol. | Rao.75–1032  |
| 5.28 | $\text{Cr}^{3+} + 1,4\text{-benzoquinone} \rightarrow \text{Cr}^{3+} + (1,4\text{-benzoquinone})^-$                                              | $(3.2 \pm 0.3) \times 10^8$                                   | —     | $25 \pm 2$         | 3.4 | pr     | Measured by the rate of formation of the semiquinone in the presence of 0.5 mol dm <sup>-3</sup> 2-methyl-2-propanol.          | Sell.76–1134 |
|      |                                                                                                                                                  | $(3.5 \pm 0.4) \times 10^8$                                   | —     | <i>ca.</i> 22      | 7.0 | pr     | Measured by the rate of formation of the semiquinone in the presence of <i>ca.</i> 1 mol dm <sup>-3</sup> 2-methyl-2-propanol. | Rao.75–1032  |
| 5.29 | $\text{Cr}^{3+} + \text{tetra-nitromethane} \rightarrow \text{Cr}^{3+} + \text{NO}_2 + \text{C}(\text{NO}_2)_3^-$                                | $(1.2 \pm 0.2) \times 10^8$                                   | —     | $25 \pm 2$         | 3.4 | pr     | Measured by the rate of formation of the nitroform anion in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.        | Sell.76–1134 |
| 5.30 | $\text{Cr}^{\text{IV}} \text{ (from } \text{CrO}_4^{2-} + e_{\text{aq}}^-)$<br>$\text{Cr}^{\text{V}} + \text{Cr}^{\text{V}} \text{ (dis or af)}$ | $2k/\epsilon_{400} = (7 \pm 3) \times 10^6 \text{ cm s}^{-1}$ | 0.003 | 25                 | nat | pr     | —                                                                                                                              | Sell72–0844  |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 6. Copper(I) and copper(III) reactions

| No.  | Reaction                                                                                                                | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>                                                                     | $I$         | $t/^\circ\text{C}$ | pH              | Method   | Comments                                                                                                                                                                                                                                                  | Ref.          |
|------|-------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|-------------|--------------------|-----------------|----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 6.1  | $\text{Cu}^+ + \text{Cu}(\text{OH})_2^+ \text{ (et)}$                                                                   | $(1.8 \pm 0.6) \times 10^9$                                                                                                      | 0.003       | 25                 | 4.8             | pr       | See comments under entry 6.37.                                                                                                                                                                                                                            | Sell72-0844   |
|      |                                                                                                                         | $(1.6 \pm 0.5) \times 10^9$                                                                                                      | 0.003       | 25                 | 6               | pr       | See comments under entry 6.37.                                                                                                                                                                                                                            | Sell72-0844   |
| 6.2  | $\text{Cu}^+ + \text{MnO}_4^- \text{ (et)}$                                                                             | $(3.6 \pm 1.2) \times 10^9$                                                                                                      | 0.002       | RT                 | nat             | pr       | -                                                                                                                                                                                                                                                         | Meye71-0174   |
|      |                                                                                                                         | $5 \times 10^9$                                                                                                                  | ca.<br>0.08 | 20                 | 2               | pr       | Measured by the rate of depletion of the $\text{MnO}_4^-$ absorption. Dependence of $k$ on $[\text{Cu}^{2+}]$ detected.                                                                                                                                   | Baxe..65-0385 |
|      |                                                                                                                         | $(6.4 \pm 0.6) \times 10^9$                                                                                                      | 0.004       | 25                 | nat             | pr       | Measured by the rate of depletion of the $\text{MnO}_4^-$ absorption.                                                                                                                                                                                     | Sell72-0844   |
| 6.3  | $\text{Cu}^+ + \text{N}_2\text{O}$                                                                                      | $< 10^9$                                                                                                                         | -           | 25                 | nat             | $\gamma$ | Estimated from $\text{N}_2$ yields in the $\gamma$ -radiolysis of $\text{Cu}^{2+} + \text{N}_2\text{O}$ solutions. Identity of product inferred from its absorption spectrum.                                                                             | Sell72-0844   |
| 6.4  | $\text{Cu}^+ + \cdot\text{CH}_2\text{OH} \rightleftharpoons \text{CuCH}_2\text{OH}^+$                                   | $k_t \text{ ca. } 10^{10}$                                                                                                       | -           | RT                 | 4.5             | pr       | Rate constants estimated from rate of growth and decay of $\text{CuCH}_2\text{OH}^+$ .                                                                                                                                                                    | Buxt.77-1500  |
|      |                                                                                                                         | $k_r \text{ ca. } 10^6 \text{ s}^{-1}$                                                                                           | -           | RT                 | 4.5             | pr       | Identity of product inferred from its absorption spectrum.                                                                                                                                                                                                | Buxt.77-1500  |
| 6.5  | $\text{Cu}^+ + (\text{CH}_3)_2\text{COH} \rightarrow \text{CuCOH}(\text{CH}_3)_2^+$                                     | ca. $6 \times 10^9$                                                                                                              | -           | RT                 | 4.5             | pr       | Estimated from dependence of decay of absorption attributed to $\text{CuOH}(\text{CH}_3)_2^+$ on $[\text{H}^+]$ (see entry 6.5).                                                                                                                          | Buxt.77-1500  |
| 6.6  | $\text{CuCOH}(\text{CH}_3)_2^+ + \text{H}^+ \rightarrow \text{Cu}^+ + \text{products}$                                  | $3.2 \times 10^7$                                                                                                                | -           | RT                 | 3-4.5           | pr       | Estimated from yields of $\text{Cu}^+$ in $\gamma$ -radiolysis of $\text{Cu}^{2+} + \text{C}_2\text{H}_4$ solutions. Products inferred from data for entry 6.8.                                                                                           | Buxt.77-1500  |
| 6.7  | $\text{Cu}^+ + \cdot\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{OH}^- + \text{Cu}^{2+}$ | $1.9 \times 10^{10}$                                                                                                             | -           | RT                 | 4.5             | $\gamma$ | Product inferred from its absorption spectrum. Estimated from yields of $\text{Cu}^+$ in the $\gamma$ -radiolysis of $\text{Cu}^{2+} + 2$ -methyl-2-propanol + $\text{C}_2\text{H}_4$ solutions. Final product is $\text{CH}_2=\text{C}(\text{CH}_3)_2$ . | Buxt.77-1500  |
| 6.8  | $\text{Cu}^+ + \cdot\text{CH}_2(\text{CH}_2)_2\text{COH} \rightarrow \text{CuCH}_2(\text{CH}_2)_2\text{COH}^+$          | $2.6 \times 10^9$                                                                                                                | -           | RT                 | 4.5             | $\gamma$ | Measured from the effect of [acrylamide] on the yield and rate of formation of $\text{Cu}$ -acrylamide $^+$ .                                                                                                                                             | Buxt.76-1186  |
| 6.9  | $\text{Cu}^+ + \text{acrylamide} \rightleftharpoons \text{Cu-acrylamide}^+$                                             | $K = (2.1 \pm 0.1) \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$<br>$k_t = 2 \times 10^9$<br>$k_r = 1.1 \times 10^8 \text{ s}^{-1}$ | -           | $25 \pm 2$         | 4<br>2.5<br>2.5 | pr       | Estimated from the non-formation of benzosemiquinone in the pulse radiolysis of $\text{Cu}^{2+} + \text{benzoquinone}$ solutions.                                                                                                                         | Sell.76-1134  |
| 6.10 | $\text{Cu}^+ + \text{benzoquinone}$                                                                                     | $< 10^9$                                                                                                                         | -           | $25 \pm 2$         | 4.9             | pr       |                                                                                                                                                                                                                                                           |               |

TABLE 6. Copper(I) and copper(III) reactions — Continued

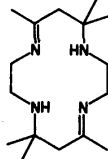
| No.                                                                                                                                                                                                                                                                                         | Reaction                                                                                                                    | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>    | $I$         | $t/^\circ\text{C}$ | pH   | Method   | Comments                                                                                                                                      | Ref.           |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------|-------------|--------------------|------|----------|-----------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| 6.11                                                                                                                                                                                                                                                                                        | $\text{Cu}^+ + \text{ethylene} \rightleftharpoons \text{Cu-ethylene}^+$                                                     | $K = (2.22 \pm 0.1) \times 10^8 \text{ dm}^3 \text{mol}^{-1}$ | —           | $25 \pm 2$         | 4    | $\gamma$ | Measured from the effect of admitting ethylene to solutions of Cu-acrylamide <sup>+</sup> (see entry 6.9).                                    | Buxt..76-1186  |
| 6.12                                                                                                                                                                                                                                                                                        | $\text{Cu}^+ + \text{fumaric acid} \rightleftharpoons \text{Cu-fumaric acid}^+$                                             | $k_t = (1.7 \pm 0.4) \times 10^8$                             | —           | $22 \pm 2$         | 3.65 | pr       | Measured from the rate of formation of the product in the presence of 1 mol dm <sup>-3</sup> methanol.                                        | Meye75-1092    |
|                                                                                                                                                                                                                                                                                             |                                                                                                                             | $k_r = (2.4 \pm 0.4) \times 10^8 \text{ s}^{-1}$              | —           | $22 \pm 2$         | 3.65 | pr       |                                                                                                                                               |                |
|                                                                                                                                                                                                                                                                                             |                                                                                                                             | $K = (7.1 \pm 2.0) \times 10^8 \text{ dm}^3 \text{mol}^{-1}$  | —           | $22 \pm 2$         | 3.65 | pr       | Measured from the effect of [fumaric acid] on the yield of Cu-fumaric acid <sup>+</sup> – in the presence of 1 mol dm <sup>-3</sup> methanol. | Meye75-1092    |
|                                                                                                                                                                                                                                                                                             |                                                                                                                             | $K = (9.0 \pm 2.0) \times 10^8 \text{ dm}^3 \text{mol}^{-1}$  | —           | $22 \pm 2$         | 3.65 | pr       |                                                                                                                                               |                |
| 6.13                                                                                                                                                                                                                                                                                        | $\text{Cu}^+ + \text{iso-butene} \rightleftharpoons \text{Cu-iso-butene}^+$                                                 | $K = (2.7 \pm 0.1) \times 10^4 \text{ dm}^3 \text{mol}^{-1}$  | —           | $25 \pm 2$         | 4    | $\gamma$ | Measured from the effect of admitting iso-butene to solutions of Cu-acrylamide <sup>+</sup> .                                                 | Buxt..76-1186  |
| 6.14                                                                                                                                                                                                                                                                                        | $\text{Cu}^+ + \text{maleic acid} \rightleftharpoons \text{Cu-maleic acid}^+$                                               | $k_t = (2.0 \pm 0.4) \times 10^8$                             | —           | $22 \pm 2$         | 3.65 | pr       | Measured from the rate of formation of the product in the presence of 1 mol dm <sup>-3</sup> methanol.                                        | Meye75-1092    |
|                                                                                                                                                                                                                                                                                             |                                                                                                                             | $k_r = (1.8 \pm 0.4) \times 10^8 \text{ s}^{-1}$              | —           | $22 \pm 2$         | 3.65 | pr       |                                                                                                                                               |                |
|                                                                                                                                                                                                                                                                                             |                                                                                                                             | $K = (1.1 \pm 0.3) \times 10^4 \text{ dm}^3 \text{mol}^{-1}$  | —           | $22 \pm 2$         | 3.65 | pr       | Measured from the effect of [maleic acid] on the yield of Cu-maleic acid <sup>+</sup> in the presence of 1 M methanol.                        | Meye75-1092    |
|                                                                                                                                                                                                                                                                                             |                                                                                                                             | $K = (1.3 \pm 0.2) \times 10^4 \text{ dm}^3 \text{mol}^{-1}$  | —           | $22 \pm 2$         | 3.65 | pr       |                                                                                                                                               |                |
| 6.15                                                                                                                                                                                                                                                                                        | $\text{Cu}^+ + \text{tetraniro-} \\ \text{methane} \rightarrow \text{Cu}^{2+} + \\ \text{NO}_2 + \text{C}(\text{NO}_2)_3^-$ | $(4.2 \pm 0.4) \times 10^8$                                   | —           | RT                 | —    | pr       | Measured from the rate of formation of the nitroform anion.                                                                                   | Asmu...64-0133 |
|                                                                                                                                                                                                                                                                                             |                                                                                                                             | $(4.7 \pm 0.5) \times 10^8$                                   | —           | $25 \pm 2$         | 4.9  | pr       | Measured from the rate of formation of the nitroform anion.                                                                                   | Sell.76-1134   |
| <div><div><div><math>\text{Cu(I) Complexes}</math></div><div><math>\text{CuL}^+ \text{ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)}</math></div></div><div></div></div> |                                                                                                                             |                                                               |             |                    |      |          |                                                                                                                                               |                |
| 6.16                                                                                                                                                                                                                                                                                        | $\text{CuL}^+ + \text{Co}(\text{bpy})_3^{3+} \text{ (et)}$                                                                  | $(1.2 \pm 0.1) \times 10^7$                                   | 0.016–0.028 | RT                 | 7.0  | pr       | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76-1039  |
| 6.17                                                                                                                                                                                                                                                                                        | $\text{CuL}^+ + \text{CoL}'(\text{OH})_2(\text{OH})^{2+}$                                                                   | $< 10^8$                                                      | 0.016–0.028 | RT                 | 7.0  | pr       | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76-1039  |
| (L' = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene).                                                                                                                                                                                                                |                                                                                                                             |                                                               |             |                    |      |          |                                                                                                                                               |                |

TABLE 6. Copper(I) and copper(III) reactions — Continued

| No.  | Reaction                                                                                                                                    | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$         | $t/^\circ\text{C}$ | pH    | Method | Comments                                                                                                                                      | Ref.          |
|------|---------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|-------------|--------------------|-------|--------|-----------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 6.18 | $\text{CuL}^+ + \text{Co(en)}_3^{3+}$                                                                                                       | $< 10^3$                                                   | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76–1039 |
| 6.19 | $\text{CuL}^+ + \text{Co}(\text{NH}_3)_6^{3+}$                                                                                              | $< 10^3$                                                   | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76–1039 |
| 6.20 | $\text{CuL}^+ + \text{CoL}(\text{OH})_2^+$                                                                                                  | $< 10^3$                                                   | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76–1039 |
| 6.21 | (L' = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,7,10-tetraene).<br>$\text{CuL}^+ + \text{Cr}(\text{bpy})_3^{3+} (\text{et})$ | $(3.7 \pm 0.4) \times 10^4$                                | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76–1039 |
| 6.22 | $\text{CuL}^+ + \text{Fe}(\text{bpy})_3^{3+}$                                                                                               | $< 10^3$                                                   | 0.016–0.028 | RT                 | 7.0   | pr     | Estimated in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                      | Tait..76–1039 |
| 6.23 | $\text{CuL}^+ + \text{H}_3\text{O}^+ (\text{pt})$                                                                                           | $(5.0 \pm 0.5) \times 10^4$                                | 0.06–0.3    | RT                 | <1.25 | pr     | Reaction may involve proton transfer to the metal centre to give a hydrido complex.                                                           | Tait..76–1039 |
| 6.24 | $\text{CuL}^+ + \text{H}_2\text{PO}_4^-$                                                                                                    | $< 10^4$                                                   | 0.01–0.1    | RT                 | 5.50  | pr     | –                                                                                                                                             | Tait..76–1039 |
| 6.25 | $\text{CuL}^+ + \text{N}_2\text{O} (\text{et or O at})$                                                                                     | $(1.7 \pm 0.2) \times 10^4$                                | –           | RT                 | 7.0   | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol. Reaction possibly involves two electron oxidation to Cu(III) complex. | Tait..76–1039 |
| 6.26 | $\text{CuL}^+ + \text{O}_2 \rightarrow \text{CuLO}_2^+$                                                                                     | $(2.6 \pm 0.3) \times 10^7$                                | –           | RT                 | 7.0   | pr     | Product does not transfer an electron to 1,4-benzoquinone, and identified therefore as O <sub>2</sub> adduct.                                 | Tait..76–1039 |
| 6.27 | $\text{CuL}^+ + \text{Ru}(\text{NH}_3)_6^{3+} (\text{et})$                                                                                  | $(7.2 \pm 0.7) \times 10^4$                                | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76–1039 |
| 6.28 | $\text{CuL}^+ + \text{Ru}(\text{NH}_3)_5\text{NO}^{3+}$                                                                                     | $< 10^3$                                                   | 0.016–0.028 | RT                 | 7.0   | pr     | Estimated in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                      | Tait..76–1039 |
| 6.29 | $\text{CuL}^+ + \text{acetic acid}$                                                                                                         | $< 10^4$                                                   | 0.015–0.06  | RT                 | 4.85  | pr     | Estimated in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                      | Tait..76–1039 |
| 6.30 | $\text{CuL}^+ + 9,10\text{-anthraquinone-2,6-disulphonate} (\text{et})$                                                                     | $(4.3 \pm 0.4) \times 10^9$                                | 0.004       | RT                 | 7.0   | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                       | Tait..76–1039 |

TABLE 6. Copper(I) and copper(III) reactions — Continued

| No.                                                                                                                                  | Reaction                                                             | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>                                                                                                                                                                     | $I$   | $t/^\circ\text{C}$ | pH   | Method | Comments                                                                                                                                                                                                                                                           | Ref.          |
|--------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|--------------------|------|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| 6.31                                                                                                                                 | $\text{CuL}^+ + 9,10\text{-anthraquinone-2-sulphonate (et)}$         | $(1.1 \pm 0.1) \times 10^8$                                                                                                                                                                                                    | 0.004 | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                                                                            | Tait..76-1039 |
| 6.32                                                                                                                                 | $\text{CuL}^+ + 1,4\text{-benzoquinone (et)}$                        | $(2.6 \pm 0.3) \times 10^8$                                                                                                                                                                                                    | 0.004 | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                                                                            | Tait..76-1039 |
| 6.33                                                                                                                                 | $\text{CuL}^+ + 3\text{-benzoylpyridine}$                            | no reaction observed                                                                                                                                                                                                           | 0.004 | RT                 | 7.0  | pr     | —                                                                                                                                                                                                                                                                  | Tait..76-1039 |
| 6.34                                                                                                                                 | $\text{CuL}^+ + \text{eosin Y}$                                      | no reaction observed                                                                                                                                                                                                           | 0.004 | RT                 | 7.0  | pr     | —                                                                                                                                                                                                                                                                  | Tait..76-1039 |
| 6.35                                                                                                                                 | $\text{CuL}^+ + \text{fluorescein}$                                  | no reaction observed                                                                                                                                                                                                           | 0.004 | RT                 | 7.0  | pr     | —                                                                                                                                                                                                                                                                  | Tait..76-1039 |
| 6.36                                                                                                                                 | $\text{CuL}^+ + \text{methyl iodide (et or S}_N2\text{)}$            | $(3.1 \pm 0.3) \times 10^8$                                                                                                                                                                                                    | 0.01  | RT                 | 9.2  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                                                                            | Tait..76-1039 |
| <i>Cu(III) Reactions</i>                                                                                                             |                                                                      |                                                                                                                                                                                                                                |       |                    |      |        |                                                                                                                                                                                                                                                                    |               |
| <i>Cu(III) aquo ion (<math>\text{Cu(OH)}_3</math>, <math>\text{Cu(OH)}_2^+</math> and <math>\text{CuOH}^{2+}</math>)<sup>b</sup></i> |                                                                      |                                                                                                                                                                                                                                |       |                    |      |        |                                                                                                                                                                                                                                                                    |               |
| 6.37                                                                                                                                 | $\text{CuOH}^{2+} \rightleftharpoons \text{Cu(OH)}_2^+ + \text{H}^+$ | $\text{pK} = 2.4 \pm 0.2$                                                                                                                                                                                                      | var   | 25                 | 0.6  | pr     | Degree of hydrolysis deduced from conductivity experiments (see ref. 70-0512).<br>Note: $\text{pK}$ of this value is also in keeping with the data of Baxendale <i>et al</i> (ref. 65-0394) and of Meyerstein (ref. 71-0174) taking into account equilibrium 6.39. | Sell72-0844   |
| 6.38                                                                                                                                 | $\text{Cu(OH)}_2^+ \rightleftharpoons \text{CuOH}^+ + \text{OH}^-$   | $\text{pK} = 3.05 \pm 0.05$                                                                                                                                                                                                    | var   | RT                 | 2-7  | pr     | —                                                                                                                                                                                                                                                                  | Baxe..65-0394 |
|                                                                                                                                      |                                                                      | $k_t = (4.2 \pm 1.4) \times 10^4 \text{ s}^{-1}$<br>and $K = 1.3 \times 10^{-4} \text{ dm}^3 \text{mol}^{-1}$<br>$k_t = (2.8 \pm 1.0) \times 10^4 \text{ s}^{-1}$<br>and $K = 9.0 \times 10^{-5} \text{ dm}^3 \text{mol}^{-1}$ | var   | RT                 | 3.50 | pr     | Estimated from decay of $\text{Cu}^{\text{III}}$ in the presence of $\text{Br}^-$ , $\text{CH}_3\text{OH}$ , $\text{H}_2\text{O}_2$ etc. Values of $k_t$ taken to be same as $k(\text{Cu}^{2+} + \text{OH})$ .                                                     | Baxe..65-0394 |
| 6.39                                                                                                                                 | $\text{Cu(OH)}_2^+ \rightleftharpoons \text{Cu(OH)}_3 + \text{H}^+$  | $\text{pK} > 6$                                                                                                                                                                                                                | var   | 25                 | 0-6  | pr     | —                                                                                                                                                                                                                                                                  | Sell72-0844   |
| 6.40                                                                                                                                 | $\text{Cu(OH)}_2^+ + \text{Cu}^+ \text{ (et)}$                       | $(1.8 \pm 0.6) \times 10^8$                                                                                                                                                                                                    | 0.003 | 25                 | 4.8  | pr     | Estimated from decay of $\text{Cu}^{\text{III}}$ in deaerated solutions.                                                                                                                                                                                           | Sell72-0844   |
|                                                                                                                                      |                                                                      | $(1.6 \pm 0.5) \times 10^8$                                                                                                                                                                                                    | 0.003 | 25                 | 6    | pr     | Possibly some contribution from $\text{Cu(OH)}_3 + \text{Cu}^+$ .                                                                                                                                                                                                  | Sell72-0844   |
|                                                                                                                                      |                                                                      | $(3.6 \pm 1.2) \times 10^8$                                                                                                                                                                                                    | 0.002 | RT                 | nat  | pr     | Possibly some contribution from $\text{Cu(OH)}_3 + \text{Cu}^+$ .                                                                                                                                                                                                  | Meye71-0174   |
| 6.41                                                                                                                                 | $\text{Cu(OH)}_2^+ + \text{Cu(gly)}^+ \text{ (et?)}$                 | $(8.1 \pm 0.5) \times 10^7$                                                                                                                                                                                                    | 0.004 | RT                 | 5.5  | pr     | —                                                                                                                                                                                                                                                                  | Meye71-0775   |

TABLE 6. Copper(I) and copper(III) reactions — Continued

| No.                                                                                                                                                                   | Reaction                                                                              | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$         | $t/^\circ\text{C}$ | pH        | Method | Comments                                                                                                                                            | Ref.        |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|--------------------------------------------------------------|-------------|--------------------|-----------|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 6.42                                                                                                                                                                  | $\text{Cu}(\text{OH})_2^+ + \text{Cu}(\text{OH})_2^+$<br>(af)                         | $2k = (4.6 \pm 0.6) \times 10^7$                             | 0.002       | RT                 | 6         | pr     | Estimated from the decay of $\text{Cu}^{\text{III}}$ in $\text{Na}_2\text{O}$ saturated solutions.                                                  | Meye71-0174 |
|                                                                                                                                                                       |                                                                                       | $2k < 5 \times 10^7$                                         | 0.004       | 25                 | 6         | pr     | Possibly some contribution from $\text{Cu}(\text{OH})_2^+ + \text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2 + \text{Cu}(\text{OH})_2$ .         | Sell72-0844 |
| 6.43                                                                                                                                                                  | $\text{Cu}(\text{OH})_2^+ + \text{CuNO}_2^+$ (et)                                     | $ca. 3 \times 10^9$                                          | $ca. 0.002$ | RT                 | 5.2       | pr     | Estimated from decay of $\text{Cu}^{\text{III}}$ in presence of $\text{NO}_2^-$ .                                                                   | Meye71-0174 |
| 6.44                                                                                                                                                                  | $\text{Cu}(\text{OH})_2^+ + \text{mena-quinone (?)}$                                  | $(2.0 \pm 0.2) \times 10^9$                                  | —           | RT                 | 9.0, 10.6 | pr     | 40% of $\text{Cu}^{\text{III}}$ claimed to react by electron transfer. $\text{Cu}^{\text{III}}$ formed by $\text{OH} + \text{Cu}(\text{ClO}_4)_2$ . | Rao.73-1047 |
|                                                                                                                                                                       |                                                                                       | —                                                            | —           | RT                 | 8.0       | pr     | 20.3% electron transfer. $\text{Cu}^{\text{III}}$ formed by $\text{OH} + \text{CuSO}_4$ .                                                           | Rao.73-1047 |
|                                                                                                                                                                       |                                                                                       | —                                                            | —           |                    | 10.6      | pr     | 39% electron transfer. $\text{Cu}^{\text{III}}$ formed by $\text{OH} + \text{CuSO}_4$ .                                                             | Rao.73-1047 |
| <i>Cu(III) Complexes.</i> (The precise nature of these complexes is uncertain: all were formed by OH oxidation of the corresponding $\text{Cu}^{\text{II}}$ complex). |                                                                                       |                                                              |             |                    |           |        |                                                                                                                                                     |             |
| 6.45                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\text{NH}_3)_n + \text{Cu}^{\text{III}}(\text{NH}_3)_n$ (af?) | $2k = (3.0 \pm 0.5) \times 10^7$                             | $< 0.008$   | RT                 | 11.1      | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.46                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\alpha\text{-alanine})_2$<br>(int et?)                        | $(8.0 \pm 2.4) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 6.3       | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.47                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\beta\text{-alanine})_2$<br>(int et?)                         | $(7.0 \pm 2.1) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 5.8       | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.48                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\alpha\text{-amino-n-butyric acid})_2$ (int et?)              | $(5.0 \pm 1.5) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 6.1       | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.49                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\beta\text{-amino-n-butyric acid})_2$ (int et?)               | $(4.5 \pm 1.3) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 6.0       | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.50                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\gamma\text{-amino-n-butyric acid})_2$ (int et?)              | $(1.2 \pm 0.4) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 4.8       | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.51                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\alpha\text{-amino-iso-butyric acid})_2$<br>(int et?)         | $(1.5 \pm 0.5) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 6.2       | pr     | —                                                                                                                                                   | Meye71-0775 |
|                                                                                                                                                                       |                                                                                       | $(2.5 \pm 0.8) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 7.3       | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.52                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\text{en})_n$ (int et?)                                       | $< 3 \text{ s}^{-1}$                                         | 0.002       | RT                 | 5.8       | pr     | —                                                                                                                                                   | Meye71-0775 |
|                                                                                                                                                                       |                                                                                       | $120 \text{ s}^{-1}$                                         | 0.002       | RT                 | 11.6      | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.53                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\text{en})_n + \text{Cu}^{\text{III}}(\text{en})_n$ (af?)     | $2k = 5.5 \times 10^8$                                       | 0.002       | RT                 | 5.8       | pr     | —                                                                                                                                                   | Meye71-0775 |
|                                                                                                                                                                       |                                                                                       | $2k = 3.9 \times 10^7$                                       | 0.002       | RT                 | 11.6      | pr     | —                                                                                                                                                   | Meye71-0775 |
| 6.54                                                                                                                                                                  | $\text{Cu}^{\text{III}}(\text{gly})_2$ (int et?)                                      | $(6.0 \pm 2.0) \times 10^8 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 6.1       | pr     | —                                                                                                                                                   | Meye71-0775 |
|                                                                                                                                                                       |                                                                                       | $(2.2 \pm 0.7) \times 10^4 \text{ s}^{-1}$                   | $< 0.002$   | RT                 | 7.5       | pr     | —                                                                                                                                                   | Meye71-0775 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

<sup>b</sup>The form of  $\text{Cu}^{\text{III}}$  reacting reinterpreted from original references according to equilibria 6.37 and 6.39.

TABLE 7. Europium(II) reactions

| Reaction                                                             | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $I$                   | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                  | Ref.         |
|----------------------------------------------------------------------|-------------------------------------------------|-----------------------|--------------------|-----|--------|---------------------------------------------------------------------------------------------------------------------------|--------------|
| (Includes only those rate constants measured by pulse radiolysis).   |                                                 |                       |                    |     |        |                                                                                                                           |              |
| $\text{Eu}^{2+} + \text{BrO}_3^-$                                    | $< 10^4$                                        | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{Co}(\text{NH}_3)_6\text{Cl}^{2+}$<br>(et-is) | $90 \pm 9$                                      | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      | $(4.7 \pm 0.5) \times 10^3$                     | 1.0                   | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      | $(5.3 \pm 0.5) \times 10^3$                     | (NaClO <sub>4</sub> ) | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Co}(\text{NH}_3)_6\text{CN}^{2+}$            | $< 30$                                          | (NaCl)                | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Co}(\text{NH}_3)_6\text{F}^{2+}$<br>(et-is)  | $(2.8 \pm 0.3) \times 10^3$                     | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      | $(1.5 \pm 0.2) \times 10^4$                     | 1.0                   | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      | $(2.4 \pm 0.2) \times 10^4$                     | (NaClO <sub>4</sub> ) | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Co}(\text{NH}_3)_6\text{OH}^{2+}$<br>(et-is) | ca. 100                                         | (NaCl)                | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Co}(\text{NH}_3)_6\text{N}_3^{2+}$           | $< 30$                                          | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Co}(\text{NH}_3)_6\text{NCS}^{2+}$           | $< 10$                                          | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Cu}^{2+}$                                    | $< 10^4$                                        | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{H}_2\text{O}_2$                              | $< 10^4$                                        | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{IO}_3^-$                                     | $< 10^4$                                        | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{MnO}_4^-$ (et)                               | $6.5 \times 10^3$                               | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{NO}_2^-$ (et)                                | $6.2 \times 10^3$                               | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{NO}_3^-$                                     | $< 10^4$                                        | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{N}_2\text{O}$                                | $< 10^4$                                        | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{O}_2$                                        | $< 10^4$                                        | ca.                   | RT                 | nat | pr     | —                                                                                                                         | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{OH}^-$ (et)                                  | $9 \times 10^3$                                 | —                     | RT                 | nat | pr     | Measured from the rate of decay of $\text{Eu}^{2+}$ in the absence of OH scavengers. Major competing reaction is OH + OH. | Fara.72-0065 |
| $\text{Eu}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Br}^{2+}$<br>(et-is) | $(1.3 \pm 0.2) \times 10^3$                     | —                     | RT                 | 2   | pr     | —                                                                                                                         | Pika.73-1084 |
|                                                                      | $3.8 \times 10^3$                               | —                     | RT                 | nat | pr     | —                                                                                                                         | Gord65-0799  |
|                                                                      | ca. $3 \times 10^3$                             | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Cl}^{2+}$<br>(et-is) | $(1.5 \pm 0.2) \times 10^4$                     | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Ru}(\text{NH}_3)_6\text{H}_3\text{O}^{2+}$   | $< 2 \times 10^3$                               | 0.3                   | 25                 | 2   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Ru}(\text{NH}_3)_6^{2+}$<br>(et-is)          | ca. $1 \times 10^3$                             | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      | $(2.3 \pm 0.2) \times 10^3$                     | 1.0                   | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      | $(1.5 \pm 0.5) \times 10^4$                     | (NaClO <sub>4</sub> ) | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
| $\text{Eu}^{2+} + \text{Ru}(\text{NH}_3)_6\text{OH}^{2+}$<br>(et-is) | $(6.0 \pm 0.6) \times 10^4$                     | (NaCl)                | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      | $(1.0 \pm 0.1) \times 10^5$                     | 0.06                  | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |
|                                                                      |                                                 | 0.3                   | 25                 | 6   | pr     | —                                                                                                                         | Fara.73-0107 |

ata source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 8. Iron(II) and iron(III) radical complex reactions

| No. | Reaction                                                                                            | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>                                                                                                                             | $I$                                                                                                                                                                                          | $t/^\circ\text{C}$   | pH                                       | Method               | Comments                                                                                                                              | Re       |
|-----|-----------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|------------------------------------------|----------------------|---------------------------------------------------------------------------------------------------------------------------------------|----------|
| 8.1 | $\text{FeH}^{2+} + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2$                              | $(1.06 \pm 0.1) \times 10^4$                                                                                                                                                             | 0.1–1.0                                                                                                                                                                                      | 19–24                | 0.1–1.0                                  | pr                   | $\text{H}_2$ product characterised by vpc; $\text{Fe}^{3+}$ by its absorption spectrum. $\text{Fe}^{\text{III}}$ detected as product. | Jays...6 |
| 8.2 | $\text{FeHO}_2^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}_2^-$                                     | $(1.8 \pm 0.1) \times 10^3 \text{ s}^{-1}$<br>$E_a = 8.8 \pm 0.8 \text{ kJ mol}^{-1}$                                                                                                    | 1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )                                                                                                                                                 | 20, 25               | 0.1–0.3                                  | pr                   |                                                                                                                                       | Jays...5 |
| 8.3 | $\text{FeHO}_2^{2+} + \text{Fe}^{3+} \rightleftharpoons \text{FeHO}_2\text{Fe}^{4+}$                | $K = 22 \pm 2 \text{ dm}^3 \text{ mol}^{-1}$<br>$K = 27 \pm 2 \text{ dm}^3 \text{ mol}^{-1}$<br>$K = 33 \pm 1 \text{ dm}^3 \text{ mol}^{-1}$<br>$K = 37.5 \text{ dm}^3 \text{ mol}^{-1}$ | 1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )<br>1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )<br>1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )<br>1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> ) | 20<br>25<br>30<br>40 | 0.1–0.3<br>0.1–0.3<br>0.1–0.3<br>0.1–0.3 | pr<br>pr<br>pr<br>pr | Measured from the effect of $[\text{Fe}^{\text{II}}]$ on the absorption of $\text{FeHO}_2\text{Fe}^{4+}$ .                            | Jays...5 |
| 8.4 | $\text{FeHO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeHO}_2\text{SO}_4$                 | $K = 90 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$                                                                                                                                            | 1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )                                                                                                                                                 | 22 ± 1               | 0.1–0.3                                  | pr                   | Measured from the effect of $[\text{SO}_4^{2-}]$ on the absorption of $\text{FeHO}_2\text{Fe}^{4+}$ .                                 | Jays...5 |
| 8.5 | $\text{FeHO}_2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{HO}_2^- + \text{Fe}^{2+}$           | $(1.8 \pm 0.1) \times 10^4 \text{ s}^{-1}$<br>$(2.5 \pm 0.1) \times 10^4 \text{ s}^{-1}$<br>$E_a = 47.7 \pm 4.6 \text{ kJ mol}^{-1}$                                                     | 1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )<br>1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )<br>1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )                                                 | 20<br>25             | 0.1–0.3<br>0.1–0.3                       | pr<br>pr             | $\text{Fe}^{\text{III}}$ detected as product.                                                                                         | Jays...5 |
| 8.6 | $\text{FeHO}_2\text{Fe}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{FeHO}_2\text{FeSO}_4^{2+}$ | $K = 100 \pm 20 \text{ dm}^3 \text{ mol}^{-1}$                                                                                                                                           | 1.0 (HClO <sub>4</sub> /NaClO <sub>4</sub> )                                                                                                                                                 | 22 ± 1               | 0.1–0.3                                  | pr                   | Measured from the effect of $[\text{SO}_4^{2-}]$ on the absorption of $\text{FeHO}_2\text{Fe}^{4+}$ .                                 | Jays...5 |
| 8.7 | $\text{FeHO}_2\text{SO}_4 \rightarrow \text{FeSO}_4^+ + \text{HO}_2^-$                              | $ca. 10^4 \text{ s}^{-1}$                                                                                                                                                                | —                                                                                                                                                                                            | 22 ± 1               | 0.1–0.3                                  | pr                   | $\text{FeSO}_4^+$ characterised by its absorption spectrum.                                                                           | Jays...5 |
| 8.8 | $\text{FeHO}_2\text{FeSO}_4^{2+} \rightarrow \text{FeSO}_4\text{Fe}^{3+} + \text{HO}_2^-$           | $ca. 10^4 \text{ s}^{-1}$                                                                                                                                                                | —                                                                                                                                                                                            | 22 ± 1               | 0.1–0.3                                  | pr                   | $\text{FeSO}_4\text{Fe}^{3+}$ characterised by its absorption spectrum.                                                               | Jays...5 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for 2k).

TABLE 9. Mercury(0) and mercury(I) reactions

| Reaction                                                                                                                                            | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$                                                                                                   | $I$                                | $t/^\circ\text{C}$   | pH                         | Method               | Comments                                                                                                                                                                                                                                                                                                                                                                                                         | Ref.                                                             |
|-----------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|----------------------|----------------------------|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|
| $\text{Hg}^0 + \text{Hg}^{2+} \rightarrow \text{Hg}_2^{2+}$                                                                                         | $(5.9 \pm 0.6) \times 10^8$                                                                                                                       | —                                  | RT                   | 3–4                        | pr                   | Measured from the pH dependence of the formation of $\text{Hg}_2^{2+}$ .                                                                                                                                                                                                                                                                                                                                         | Fuji..73–1080                                                    |
| $\text{Hg}^0 + \text{HgOH}^+ \rightarrow \text{Hg}_2^{2+} + \text{OH}^-$                                                                            | $(5.0 \pm 0.5) \times 10^8$                                                                                                                       | —                                  | RT                   | 3–4                        | pr                   | Measured from the pH dependence of the formation of $\text{Hg}_2^{2+}$ .                                                                                                                                                                                                                                                                                                                                         | Fuji..73–1080                                                    |
| $\text{Hg}^0 + \text{Hg}(\text{OH})_2 \rightarrow \text{Hg}_2^{2+} + 2\text{OH}^-$                                                                  | $< 5 \times 10^7$                                                                                                                                 | —                                  | RT                   | 3–4                        | pr                   | Measured from the pH dependence of the formation of $\text{Hg}_2^{2+}$ . See also comments for entry 9.6.                                                                                                                                                                                                                                                                                                        | Fuji..73–1080                                                    |
| $\text{Hg}_2^{2+} + \text{Hg}_2^{2+} (\text{et?})$                                                                                                  | $2k = (1.4 \pm 0.2) \times 10^{10}$                                                                                                               | $< 0.017$                          | RT                   | 1.9                        | pr                   | Rate constant calculated taking $\epsilon_{222} = 9000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .                                                                                                                                                                                                                                                                                                          | Fara.72–0290                                                     |
| $\text{Hg}_2^{2+}$<br><i>Hg<sub>2</sub><sup>2+</sup> (and hydrolysed forms)</i><br>$\text{Hg}_2^{2+} \rightleftharpoons \text{HgOH}^+ + \text{H}^+$ | $pK = 5.1$                                                                                                                                        | var                                | RT                   | 4–7                        | pr                   | Measured from the effect of pH on the absorption spectrum of $\text{Hg}_2^{2+}$ . Transient product formed, whose decay is dependent on $[\text{Hg}_2^{2+}]$ , and which gives $\text{Hg}_2^{2+}$ . These results taken to indicate that $\text{Hg}^+ + \text{Hg}^+$ results in dismutation. Rate constants calculated taking $\epsilon_{222} = 1.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . | Fuji...75–1044                                                   |
| $\text{Hg}^+ + \text{Hg}^+ \rightarrow \text{Hg}^0 + \text{Hg}_2^{2+}$                                                                              | $2k = (4.9 \pm 0.5) \times 10^9$<br>$2k = (5.2 \pm 0.5) \times 10^9$                                                                              | $\rightarrow 0$<br>$\rightarrow 0$ | RT<br>RT             | 2.0<br>4.3                 | pr<br>pr             | Products not characterised, but reaction considered to involve dimerisation. Rate constant calculated taking $\epsilon_{222} = 7800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .                                                                                                                                                                                                                             | Fuji..73–1080                                                    |
| $\text{Hg}^+ + \text{Hg}^+ (\rightarrow \text{Hg}_2^{2+})$                                                                                          | $2k = (8.0 \pm 1.0) \times 10^9$                                                                                                                  | $< 0.017$                          | RT                   | 1.9                        | pr                   | Products not characterised, but reaction considered to involve dimerisation. Rate constant calculated taking $\epsilon_{222} = 7800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .                                                                                                                                                                                                                             | Fara.72–0290                                                     |
| $\text{HgOH} + \text{HgOH} \rightarrow \text{Hg}_2\text{O} + \text{H}_2\text{O}$<br>or $\text{Hg}_2(\text{OH})_2$                                   | $2k = (4.4 \pm 0.4) \times 10^9$                                                                                                                  | $< 0.1$                            | RT                   | —                          | pr                   | Products identified from pH dependence of their absorption spectra. Rate constant calculated taking $\epsilon_{222} = 5300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .                                                                                                                                                                                                                                      | Fuji...75–1044                                                   |
| $\text{Hg}^1 + \text{Hg}^1$                                                                                                                         | $2k = (4.9 \pm 1.0) \times 10^9$<br>$2k = (5.1 \pm 1.0) \times 10^9$<br>$2k = (3.5 \pm 0.7) \times 10^9$<br>$2k = \text{ca. } 1.1 \times 10^{10}$ | —<br>—<br>—<br>—                   | RT<br>RT<br>RT<br>RT | 1.2<br>3.15<br>4.8<br>10.2 | pr<br>pr<br>pr<br>pr | —<br>—<br>—<br>—                                                                                                                                                                                                                                                                                                                                                                                                 | Pika..75–1218<br>Pika..75–1218<br>Pika..75–1218<br>Pika..75–1218 |

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

| No.                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Reaction                                                                                                        | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$                         | $t/^\circ\text{C}$ | pH       | Method   | Comments                                                                                                                                           | Ref.                 |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|-----------------------------|--------------------|----------|----------|----------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| 9.8                                                                                                                                                                                                                                                                                                                                                                                                                                                          | $\text{Hg}^{\text{I}} + \text{Hg}^{\text{I}}$                                                                   | $2k = \text{ca. } 1.5 \times 10^{10}$                      | —                           | RT                 | 11.0     | pr       | —                                                                                                                                                  | Pika..75-            |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                 | $2k = (7.0 \pm 1.4) \times 10^{10}$                        | 1(KOH)                      | RT                 | 14       | pr       | —                                                                                                                                                  | Pika..75-            |
| 9.9                                                                                                                                                                                                                                                                                                                                                                                                                                                          | $\text{Hg}^{\text{I}} + \text{O}_2$ (et or as)                                                                  | $(4.0 \pm 0.6) \times 10^8$                                | + data at intermediate pH's | RT                 | 2.7      | pr       | —                                                                                                                                                  | Pika..75-            |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                 | $(1.2 \pm 0.2) \times 10^8$                                | —                           | RT                 | 11.2     | pr       | —                                                                                                                                                  | Pika..75-            |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                 | $(1.6 \pm 0.2) \times 10^8$                                | 1(KOH)                      | RT                 | 14       | pr       | —                                                                                                                                                  | Pika..75-            |
| Note: A change in mechanism of the decay of $\text{Hg}^{\text{I}}$ aquo ions is observed on increasing the pH. There appears to be no good understanding of why this should be, and we suggest, therefore, that the reaction mechanisms written above should be viewed with caution. Note also that the spectral data for $\text{Hg}^{\text{I}}$ obtained by Faraggi and Amozig (ref. 72-0290) and by Fujita <i>et al.</i> (ref. 73-1080) do not correspond. |                                                                                                                 |                                                            |                             |                    |          |          |                                                                                                                                                    |                      |
| <i>Hg(I) Complexes</i>                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                 |                                                            |                             |                    |          |          |                                                                                                                                                    |                      |
| <i>HgBr and related species</i>                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                 |                                                            |                             |                    |          |          |                                                                                                                                                    |                      |
| 9.10                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgBr} + \text{HgBr} \rightarrow \text{Hg}_2\text{Br}_2$                                                  | $2k = 8 \times 10^8$                                       | —                           | RT                 | —        | pr       | Product characterised by its absorption spectrum.                                                                                                  | Jung..76             |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                                                                                                 | $2k = (1.0 \pm 0.1) \times 10^{10}$                        | —                           | RT                 | —        | pr       | —                                                                                                                                                  | Fuji...76-           |
| 9.11                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgBr} + \text{O}_2 \rightarrow \text{HgBrO}_2$                                                           | $> 10^8$                                                   | —                           | RT                 | —        | pr       | Product characterised by conductivity experiments and non-formation of $\text{O}_2^{\cdot-}/\text{HO}_2$ absorption.                               | Jung..76             |
| 9.12                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgBr} + 1,4\text{-benzoquinone} \rightarrow \text{HgBr}^+ + (1,4\text{-benzoquinone})^-$                 | $> 10^8$                                                   | —                           | RT                 | 5-5.5    | pr       | Benzosemiquinone product characterised by its absorption spectrum.                                                                                 | Jung..76             |
| 9.13                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgBr} + \text{tetranitromethane} \rightarrow \text{HgBr}^+ + \text{C(NO}_2)_3^- + \text{NO}_2$           | $2.2 \times 10^8$                                          | —                           | RT                 | —        | pr       | Nitroform anion product characterised by its absorption spectrum.                                                                                  | Jung..76             |
| 9.14                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgBrO}_2 + 1,4\text{-benzoquinone} \rightarrow \text{HgBr}^+ + \text{O}_2 + (1,4\text{-benzoquinone})^-$ | $7 \times 10^8$                                            | —                           | RT                 | —        | pr       | Benzosemiquinone product characterised by its absorption spectrum.                                                                                 | Jung..76             |
| 9.15                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgCl} + \text{HgCl} \rightarrow \text{Hg}_2\text{Cl}_2$                                                  | $2k = (8.0 \pm 0.5) \times 10^8$                           | —                           | RT                 | —        | pr       | Product characterised by its absorption spectrum, and gravimetrically giving $G(\text{Hg}_2\text{Cl}_2) = 3.0$ in solutions containing 2-propanol. | Nash.7               |
| 9.16                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgCl} + \text{O}_2 \rightarrow \text{HgClO}_2$                                                           | $(1.0 \pm 0.3) \times 10^8$                                | —                           | RT                 | —        | pr       | Product characterised by conductivity experiments and non-formation of $\text{O}_2^{\cdot-}/\text{HO}_2$ absorption.                               | Nash.7               |
| 9.17                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgCl} + \text{OH}^- \rightarrow \text{HgCl} + \text{OH}^-$                                               | $\text{ca. } 10^{10}$                                      | —                           | RT                 | —        | pr       | Products characterised by conductivity experiments.                                                                                                | Nash.7               |
| 9.18                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgCl} + 1,4\text{-benzoquinone} \rightarrow \text{HgCl}^+ + (1,4\text{-benzosemiquinone})^-$             | $3.0 \times 10^8$<br>$(3.9 \pm 0.4) \times 10^8$           | —                           | RT<br>$25 \pm 2$   | —<br>5.1 | pr<br>pr | Benzosemiquinone product characterised by its absorption spectrum.                                                                                 | Jung..76<br>Sell.76- |
| 9.19                                                                                                                                                                                                                                                                                                                                                                                                                                                         | $\text{HgCl} + \text{tetranitromethane} \rightarrow \text{HgCl}^+ + \text{C(NO}_2)_3^- + \text{NO}_2$           | $(4.5 \pm 0.3) \times 10^8$                                | —                           | RT                 | 5-5.5    | pr       | Nitroform anion product characterised by its absorption spectrum.                                                                                  | Nash.7               |

TABLE 9. Mercury(0) and mercury(I) reactions — Continued

| Reaction                                                                                                                 | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $I$     | $t/^\circ\text{C}$ | pH | Method   | Comments                                                                                                                                                                                                                       | Ref.                           |
|--------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|---------|--------------------|----|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|
| $\text{HgClO}_2 + 1,4\text{-benzoquinone} \rightarrow \text{HgCl}^+ + \text{O}_2 + (1,4\text{-benzosemiquinone})^-$      | $7 \times 10^9$                                 | —       | RT                 | —  | pr       | Benzosemiquinone product characterised by its absorption spectrum.                                                                                                                                                             | Jung..76-1042                  |
| $\text{HgCN} + \text{HgCN} \rightarrow \text{Hg}_2(\text{CN})_2$                                                         | $2k = (3.4 \pm 0.5) \times 10^9$                | $< 0.2$ | RT                 | —  | pr       | Product characterised by its absorption spectrum and decay to give $\text{Hg}^0$ and $\text{Hg}(\text{CN})_2$ . Rate constant calculated taking $\epsilon_{\text{max}} = 3800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . | Fuji...75-1203                 |
| $\text{HgCN} + \text{O}_2 \rightarrow \text{HgCN}^+ + \text{O}_2^-$                                                      | $2k = 1.2 \times 10^{10}$<br>$4 \times 10^9$    | —       | RT<br>RT           | —  | pr<br>pr | $\text{O}_2^-$ product characterised by its absorption spectrum, lifetime in neutral solution, and conductivity measurements.                                                                                                  | Jung..76-1042<br>Jung..76-1042 |
| $\text{HgCN} + \text{OH} \text{ (et)}$                                                                                   | $3.1 \times 10^9$                               | —       | RT                 | —  | pr       | Estimated from initial decay of $\text{HgCN}$ in the absence of OH scavengers.                                                                                                                                                 | Fuji...75-1203                 |
| $\text{HgCN} + \cdot\text{CH}_2\text{OH}$                                                                                | $4.0 \times 10^9$                               | —       | RT                 | —  | pr       | Estimated from initial decay of $\text{HgCN}$ in the presence of methanol.                                                                                                                                                     | Fuji...75-1203                 |
| $\text{HgCN} + \text{CH}_3\text{CHOH} \text{ (et to HgCN?)}$                                                             | $3.9 \times 10^9$                               | —       | RT                 | —  | pr       | Estimated from initial decay of $\text{HgCN}$ in the presence of ethanol.                                                                                                                                                      | Fuji...75-1203                 |
| $\text{HgCN} + (\text{CH}_3)_2\text{CHOH} \rightarrow \text{Hg}^0 + \text{CN}^- + \text{CH}_3\text{COCH}_3 + \text{H}^+$ | $2.4 \times 10^9$                               | —       | RT                 | —  | pr       | Estimated from initial decay of $\text{HgCN}$ in the presence of 2-propanol. $G(\text{acetone}) = 3.0$ measured.                                                                                                               | Fuji...75-1203                 |
| $\text{HgCN} + \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH} \text{ (af?)}$                                           | $1.6 \times 10^9$                               | —       | RT                 | —  | pr       | Estimated from initial decay of $\text{HgCN}$ in the presence of 2-methyl-2-propanol. Isobutene <i>not</i> detected as product.                                                                                                | Fuji...75-1203                 |
| $\text{HgCN} + 1,4\text{-benzoquinone} \rightarrow \text{HgCN}^+ + (1,4\text{-benzoquinone})^-$                          | $3.5 \times 10^9$                               | —       | RT                 | —  | pr       | Benzosemiquinone product characterised by its absorption spectrum.                                                                                                                                                             | Jung..76-1042                  |
| $\text{HgCN} + \text{tetranitromethane} \rightarrow \text{HgCN}^+ + \text{C}(\text{NO}_2)_4^- + \text{NO}_2$             | $3.1 \times 10^9$                               | —       | RT                 | —  | pr       | Nitroform anion product characterised by its absorption spectrum.                                                                                                                                                              | Jung..76-1042                  |
| $\text{HgI} + \text{HgI} \rightarrow \text{Hg}_2\text{I}_2$                                                              | $2k = 5.0 \times 10^9$                          | —       | RT                 | —  | pr       | Product characterised by its absorption spectrum.                                                                                                                                                                              | Jung..76-1042                  |

TABLE 9. Mercury(0) and mercury(II) reactions — Continued

| No.  | Reaction                                                                                                          | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ * | $I$ | $t/^\circ\text{C}$ | pH | Method | Comments                                                                                                          | Ref.     |
|------|-------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|-----|--------------------|----|--------|-------------------------------------------------------------------------------------------------------------------|----------|
| 9.31 | $\text{HgI} + \text{O}_2 \rightarrow \text{HgIO}_2$                                                               | $> 10^9$                                          | —   | RT                 | —  | pr     | Product characterised by conductivity experiments and non-formation of $\text{O}_2^-$ / $\text{HO}_2$ absorption. | Jung..76 |
| 9.32 | $\text{HgI} + 1,4\text{-benzoquinone} \rightarrow \text{HgI}^+ + (1,4\text{-benzoquinone})^-$                     | $> 10^9$                                          | —   | RT                 | —  | pr     | Benzosemiquinone product characterised by its absorption spectrum.                                                | Jung..76 |
| 9.33 | $\text{HgI} + \text{tetranitromethane} \rightarrow \text{HgI}^+ + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$        | $1.4 \times 10^9$                                 | —   | RT                 | —  | pr     | Nitroform anion product characterised by its absorption spectrum.                                                 | Jung..76 |
| 9.34 | $\text{HgSCN} + \text{HgSCN} \rightarrow \text{Hg}_2(\text{SCN})_2$                                               | $2k = 6.0 \times 10^9$                            | —   | RT                 | —  | pr     | Product characterised by its absorption spectrum.                                                                 | Jung..76 |
| 9.35 | $\text{HgSCN} + \text{O}_2 \rightarrow \text{HgSCNO}_2$                                                           | $> 10^9$                                          | —   | RT                 | —  | pr     | Product characterised by conductivity experiments and non-formation of $\text{O}_2^-$ / $\text{HO}_2$ absorption. | Jung..76 |
| 9.36 | $\text{HgSCN} + 1,4\text{-benzoquinone} \rightarrow \text{HgSCN}^+ + (1,4\text{-benzoquinone})^-$                 | $> 10^9$                                          | —   | RT                 | —  | pr     | Benzosemiquinone product characterised by its absorption spectrum.                                                | Jung..76 |
| 9.37 | $\text{HgSCN} + \text{tetranitromethane} \rightarrow \text{HgSCN}^+ + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$    | $2.8 \times 10^9$                                 | —   | RT                 | —  | pr     | Nitroform anion product characterised by its absorption spectrum.                                                 | Jung..76 |
| 9.38 | $\text{HgSCNO}_2 + 1,4\text{-benzoquinone} \rightarrow \text{HgSCN}^+ + \text{O}_2 + (1,4\text{-benzoquinone})^-$ | $1.0 \times 10^9$                                 | —   | RT                 | —  | pr     | Benzosemiquinone product characterised by its absorption spectrum.                                                | Jung..76 |

\*If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 10. Indium(II) reactions

| No.  | Reaction                                                               | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}^a$ | $I$                         | $t/^\circ\text{C}$ | pH  | Method   | Comments                                                                                                                                           | Ref.                      |
|------|------------------------------------------------------------------------|-------------------------------------------------|-----------------------------|--------------------|-----|----------|----------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------|
| 10.1 | $\overset{\text{In}^{2+}}{\text{In}^{2+}} + \text{In}^{3+}$ (et or af) | $2k = \text{ca. } 1.2 \times 10^9$              | 0.7<br>( $\text{LiClO}_4$ ) | RT                 | 3   | pr       | Reinterpreted from data in ref. 76-1087.                                                                                                           | Tayl.69-0971              |
|      |                                                                        | $2k = (1.6 \pm 0.2) \times 10^9$                | 0.0075                      | 25                 | 3.6 | pr       | Measured in the presence of 1 mol/dm <sup>3</sup> 2-methyl-2-propanol taking $\epsilon_{250} = 7000 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . | R.M. Sellers, unpub. data |
| 10.2 | $\text{In}^{2+} + \text{OH}^-$ (et)                                    | $2k = (4.9 \pm 0.7) \times 10^9$                | -                           | 25                 | 3.6 | pr       | Measured from the initial decay of $\text{In}^{2+}$ in the absence of OH scavengers.                                                               | R.M. Sellers, unpub. data |
| 10.3 | $\text{In}^{2+} + \text{N}_2\text{O}$                                  | $< 10^6$                                        | -                           | 25                 | nat | $\gamma$ | Estimated from the values of $G(\text{N}_3)$ measured in the $\gamma$ -radiolysis of $\text{In}^{3+} + \text{N}_2\text{O}$ solutions.              | Sell72-0844               |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 11. Iridium(II) reactions

| No.  | Reaction                                                                                                               | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}^a$ | $I$    | $t/^\circ\text{C}$ | pH | Method | Comments | Ref.        |
|------|------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|--------|--------------------|----|--------|----------|-------------|
| 11.1 | $\overset{\text{Ir}^{II} \text{ (from } e_{\text{aq}}^- + \text{IrCl}_6^{3-})}{\text{Ir}^{II}} + \text{Ir}^{II}$ (dis) | $2k = (3.3 \pm 0.4) \times 10^9$                | 0.0018 | RT                 | -  | pr     | -        | Bros73-1066 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 12. Manganese(II) reactions

| No.  | Reaction                                                                      | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}^a$ | $I$                        | $t/^\circ\text{C}$ | pH  | Method   | Comments                                                                                                                                                                                           | Ref.        |
|------|-------------------------------------------------------------------------------|-------------------------------------------------|----------------------------|--------------------|-----|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------|
| 12.1 | $\overset{\text{Mn}^{2+}_{\text{aq}}}{\text{Mn}^{2+}} + \text{Cu}^{2+}$ (et?) | $k_{\text{rel}} = 1.6 \pm 0.2$                  | 2.0<br>( $\text{MnSO}_4$ ) | RT                 | 5-8 | $\gamma$ | Measured by competition kinetics using $\text{NO}_3^-$ as competitor in the presence of 0.5 mol dm <sup>-3</sup> $\text{MnSO}_4$ . Rate constant relative to $k(\text{Mn}^{2+} + \text{NO}_3^-)$ . | Fiti70-0117 |
| 12.2 | $\text{Mn}^{2+} + \text{IO}_3^-$ (et?)                                        | $k_{\text{rel}} = 1.4 \pm 0.1$                  | 2.0<br>( $\text{MnSO}_4$ ) | RT                 | 5-8 | $\gamma$ | Measured by competition kinetics using $\text{NO}_3^-$ as competitor in the presence of 0.5 mol dm <sup>-3</sup> $\text{MnSO}_4$ . Rate constant relative to $k(\text{Mn}^{2+} + \text{NO}_3^-)$ . | Fiti70-0117 |
| 12.3 | $\text{Mn}^{2+} + \text{NO}_3^-$ (et?)                                        | see entries 12.1 and 12.2.                      |                            |                    |     |          |                                                                                                                                                                                                    |             |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 13. Molybdenum reactions

| No.  | Reaction                                                                                                     | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>         | $I$ | $t/^\circ\text{C}$ | pH | Method | Comments                                                                                                                                                                                                                                                                                                                                                                                                       | Ref.           |
|------|--------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------|-----|--------------------|----|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| 13.1 | $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^-$ (from $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4 + e^-$ in methanol) |                                                                      |     |                    |    |        |                                                                                                                                                                                                                                                                                                                                                                                                                |                |
|      | $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^- + [\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^-$ (dis?)               | $k' = (4.5 \pm 1.0) \times 10^9$<br>$k' = (2.5 \pm 1.0) \times 10^9$ | -   | RT                 | -  | pr     | Measured from decay of Mo(1 1/2) species in methanol. Two decay processes observed, one of which believed to be a dismutation reaction. Rate constant (unclear whether $k$ or $2k$ ) calculated taking $\epsilon_{780} = 2600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Note that if the slower process does not involve the Mo(1 1/2) species, the value of $\epsilon$ , and hence $k$ , is incorrect. | Baxe...76-1003 |
| 13.2 | $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]^- + \text{O}_2$ (af?)                                               | $(5.9 \pm 0.3) \times 10^9$                                          | -   | RT                 | -  | pr     | Measured in Methanol. Starting material $[\text{Mo}_2(\text{O}_2\text{CCF}_3)_4]$ not regenerated, so reaction does not involve electron transfer.                                                                                                                                                                                                                                                             | Baxe...76-1003 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 14. Nickel(II) and nickel(III) reactions

| Reaction                                                                                       | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ | $I$   | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                                   | Ref.           |
|------------------------------------------------------------------------------------------------|-----------------------------------------------|-------|--------------------|-----|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| $\text{Ni}^{2+} + \text{BrO}_3^-$                                                              | $< 8.4 \times 10^6$                           | 0.08  | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Meye.68-0855   |
| $\text{Ni}^{2+} + \text{Cd}^{2+}$                                                              | $< 10^7$                                      | —     | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Baxe..66-0848  |
| $\text{Ni}^{2+} + \text{Co(en)}_3^{3+}$                                                        | $< 5 \times 10^6$                             | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{cis-Co(en)}_3\text{Cl}_3^{3+} \text{ (et)}$                            | $(5.9 \pm 0.9) \times 10^6$                   | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{trans-Co(en)}_3\text{Cl}_3^{3+} \text{ (et)}$                          | $(8.3 \pm 2.1) \times 10^6$                   | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(en)}_3\text{CO}_3^{3+}$                                             | $< 5 \times 10^6$                             | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{cis-Co(en)}_3\text{F}_3^{3+}$                                          | $< 5 \times 10^6$                             | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(en)}_3\text{FH}_2\text{O}^{3+}$                                     | $(4.7 \pm 0.7) \times 10^6$                   | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{cis-Co(en)}_3\text{NH}_2\text{Cl}_2^{3+} \text{ (et)}$                 | $(3.3 \pm 0.8) \times 10^6$                   | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{cis-Co(en)}_3\text{NH}_2\text{NO}_2^{3+} \text{ (et)}$                 | $< 5 \times 10^6$                             | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{B}_3^{3+} \text{ (et)}$                               | $(1.05 \pm 0.2) \times 10^6$                  | 0.08  | RT                 | 4.0 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{Cl}_3^{3+} \text{ (et)}$                              | $(6.5 \pm 1.0) \times 10^6$                   | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{CN}^{3+} \text{ (et)}$                                | $(3.3 \pm 0.8) \times 10^6$                   | 0.08  | RT                 | 5-6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{F}_3^{3+}$                                            | $< 5 \times 10^6$                             | 0.08  | RT                 | 4.0 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{H}_2\text{O}^{3+}$                                    | $(1.3 \pm 0.3) \times 10^6$                   | 0.08  | RT                 | 7.6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{OH}^{3+} \text{ (et)}$                                | $(5.8 \pm 1.5) \times 10^6$                   | 0.08  | RT                 | 7.6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{N}_3^{3+} \text{ (et)}$                               | $(4.1 \pm 1.0) \times 10^6$                   | 0.08  | RT                 | 7.6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{NCS}^{3+} \text{ (et)}$                               | $< 5 \times 10^6$                             | 0.08  | RT                 | 5.6 | pr     | —                                                                                                                                                                                                                                          | Meye.69-0428   |
| $\text{Ni}^{2+} + \text{Co(NH}_3)_6\text{OOCCH}_3^{3+}$                                        | $< 10^7$                                      | —     | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Baxe..66-0848  |
| $\text{Ni}^{2+} + \text{Cr}^{3+}$                                                              | $< 2.4 \times 10^7$                           | 0.08  | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Meye.68-0855   |
| $\text{Ni}^{2+} + \text{Cu}^{2+}$                                                              | $(3.2 \pm 0.3) \times 10^7$                   | —     | 25                 | nat | pr     | —                                                                                                                                                                                                                                          | Buxt..76-1072  |
| $\text{Ni}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Ni}^{3+} + \text{OH}^- + \text{OH}^-$ | $(4.3 \pm 0.6) \times 10^7$                   | —     | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Meye.68-0855   |
|                                                                                                | $2.1 \times 10^8$                             | —     | RT                 | nat | pr     | Products identified in $\gamma$ -radiolysis studies (see ref. 73-0039).                                                                                                                                                                    | Buxt..67-0062  |
| $\text{Ni}^{2+} + \text{H}_2\text{O}^+$                                                        | $< 10^8$                                      | 0.08  | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Meye.68-0855   |
| $\text{Ni}^{2+} + \text{IO}_3^- \text{ (et)}$                                                  | $(2.2 \pm 0.3) \times 10^8$                   | 0.08  | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Meye.68-0855   |
| $\text{Ni}^{2+} + \text{MnO}_4^- \text{ (et)}$                                                 | $7.5 \times 10^8$                             | 0.005 | RT                 | nat | pr     | Measured by the rate of depletion of the $\text{MnO}_4^-$ absorption.                                                                                                                                                                      | Baxe..65-0385  |
| $\text{Ni}^{2+} + \text{Ni}^{2+}$                                                              | slow ( $< 10^8$ )                             | var   | RT                 | nat | pr     | Estimated from decay of $\text{Ni}^{2+}$ in presence and absence of OH scavengers.                                                                                                                                                         | Kelme..74-1037 |
| $\text{Ni}^{2+} + \text{NO}_3^- \text{ (et)}$                                                  | $(1.5 \pm 0.2) \times 10^8$                   | 0.08  | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Meye.68-0855   |
| $\text{Ni}^{2+} + \text{NO}_3^-$                                                               | $< 1.4 \times 10^8$                           | 0.08  | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Meye.68-0855   |
| $\text{Ni}^{2+} + \text{Na}_2\text{O} \rightarrow \text{NiO}^+ + \text{N}_2$                   | $6.3 \times 10^8$                             | —     | RT                 | nat | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ $\text{NiSO}_4$ .                                                                                                                                                                       | Meye.68-0855   |
|                                                                                                | $(9.1 \pm 0.9) \times 10^8$                   | —     | 25 + 2             | nat | pr     | Measured in the presence of 0.5 mol $\text{dm}^{-3}$ $\text{NiSO}_4$ .                                                                                                                                                                     | Buxt..76-1072  |
|                                                                                                | $5.1 \times 10^7$                             | —     | RT                 | nat | pr     | —                                                                                                                                                                                                                                          | Buxt..67-0062  |
|                                                                                                | $E_a = 40.6 \pm 3.8 \text{ kJ mol}^{-1}$      | —     | 1-30               | nat | pr     | —                                                                                                                                                                                                                                          | Buxt..67-0062  |
|                                                                                                |                                               |       |                    |     |        | Products inferred from $\gamma$ -ray induced chain reaction in the system $\text{Ni}^{2+} + \text{HCO}_3^- + \text{Na}_2\text{O}$ . $G(\text{N}_2)$ also measured in $\text{Ni}^{2+} + \text{Na}_2\text{O}$ solutions. (see ref. 73-0039). |                |

TABLE 14. Nickel(II) and nickel(III) reactions — Continued

| No.   | Reaction                                                                                                                                       | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$                | $t/^\circ\text{C}$ | pH         | Method   | Comments                                                                                                                                                                                                                                                                         | Ref.                 |
|-------|------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|--------------------|--------------------|------------|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------|
| 14.31 | $\text{Ni}^{2+} + \text{OH}^- \rightarrow \text{Ni}^{3+} + \text{OH}^-$                                                                        | $2 \times 10^{10}$                                           | —                  | RT                 | nat        | pr       | Measured from a computer fit of the decay of $\text{Ni}^{3+}$ in the absence of OH scavengers assuming competing reactions to be $\text{OH}^- + \text{OH}$ and $\text{Ni}^{3+} + \text{H}_2\text{O}_2$ . Product identified by conductivity measurements (but see ref. 75-1027). | Kelm...74-           |
| 14.32 | $\text{Ni}^{2+} + \text{O}_2 \rightarrow \text{NiO}_2^+$                                                                                       | $(1.4 \pm 0.2) \times 10^8$<br>$2.2 \times 10^8$             | —<br>—             | RT<br>RT           | nat<br>nat | pr<br>pr | —<br>—<br>Product characterised by its absorption spectrum (ref. 76-1072), reactivity with tetra-nitromethane and lack of reactivity with 1,4-benzoquinone (ref. 76-1134).                                                                                                       | Meye.68<br>Baxe..66- |
| 14.33 | $\text{Ni}^{2+} + \text{Pb}^{2+}$                                                                                                              | $< 10^7$                                                     | —                  | RT                 | nat        | pr       | —                                                                                                                                                                                                                                                                                | Baxe..66-            |
| 14.34 | $\text{Ni}^{2+} + \text{Ru}(\text{NH}_3)_6^{3+} (\text{et})$                                                                                   | $(4.0 \pm 0.6) \times 10^8$                                  | 0.08               | RT                 | nat        | pr       | —                                                                                                                                                                                                                                                                                | Navo.70              |
| 14.35 | $\text{Ni}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Ni}^{3+} + \text{SO}_4^- + \text{SO}_4^{2-}$                                     | $(1.5 \pm 0.2) \times 10^8$                                  | 0.049              | $25 \pm 2$         | nat        | pr       | $\text{SO}_4^-$ product characterised by its absorption spectrum and decay kinetics.                                                                                                                                                                                             | Tait..76-            |
| 14.36 | $\text{Ni}^{2+} + \text{Zn}^{2+}$                                                                                                              | $< 10^7$                                                     | —                  | RT                 | nat        | pr       | —                                                                                                                                                                                                                                                                                | Baxe..66-            |
| 14.37 | $\text{Ni}^{2+} + \cdot\text{CH}_2\text{OH} \rightarrow \text{NiCH}_2\text{OH}^+$                                                              | $4.2 \times 10^9$                                            | —                  | RT                 | nat        | pr       | Product characterised by its absorption spectrum and conductivity measurements.                                                                                                                                                                                                  | Kelm...74-           |
| 14.38 | $\text{Ni}^{2+} + \text{CO}_3^{2-} \rightarrow \text{NiCO}_3$                                                                                  | $6.6 \times 10^9$                                            | $4 \times 10^{-4}$ | RT                 | nat        | pr       | Product characterised by its absorption spectrum and conductivity measurements.                                                                                                                                                                                                  | Kelm...74-           |
| 14.39 | $\text{Ni}^{2+} + \cdot\text{C}_2\text{H}_5\text{OH} \rightarrow \text{NiC}_2\text{H}_5\text{OH}^+$                                            | $2.3 \times 10^9$                                            | $4 \times 10^{-4}$ | RT                 | nat        | pr       | Product characterised by its absorption spectrum and conductivity measurements.                                                                                                                                                                                                  | Kelm...74-           |
| 14.40 | $\text{Ni}^{2+} + \text{CH}_3\text{COHCH}_3 \rightarrow \text{NiCOH}(\text{CH}_3)_2$                                                           | $1.4 \times 10^9$                                            | $4 \times 10^{-4}$ | RT                 | nat        | pr       | Product characterised by its absorption spectrum and conductivity measurements.                                                                                                                                                                                                  | Kelm...74-           |
| 14.41 | $\text{Ni}^{2+} + \text{H}_2\text{C}(\text{CH}_3)_2\text{OH}^- \rightarrow \text{Ni}^{3+} + \text{OH}^- + \text{CH}_2=\text{C}(\text{CH}_3)_2$ | $2 \times 10^9$                                              | $4 \times 10^{-4}$ | RT                 | nat        | pr       | Isobutene detected as product; $\text{OH}^-$ detected by conductivity measurements.                                                                                                                                                                                              | Kelm...74-           |
| 14.42 | $\text{Ni}^{2+} + \cdot\text{C}_5\text{H}_9 \rightarrow \text{NiC}_5\text{H}_9^+$<br>( $\cdot\text{C}_5\text{H}_9$ = cyclopentyl radical)      | $2.8 \times 10^9$                                            | $4 \times 10^{-4}$ | RT                 | nat        | pr       | Product characterised by its absorption spectrum and conductivity measurements.                                                                                                                                                                                                  | Kelm...74-           |

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

| Reaction                                                                                                                                                | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ | $I$                                | $t/^\circ\text{C}$ | pH         | Method   | Comments                                                                                                                 | Ref.                       |
|---------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------|------------------------------------|--------------------|------------|----------|--------------------------------------------------------------------------------------------------------------------------|----------------------------|
| $\text{Ni}^+ + \text{allyl alcohol} \rightarrow \text{Ni-allyl alcohol}^+$                                                                              | $ca. 10^6$                                    | —                                  | $25 \pm 2$         | nat        | pr       | —                                                                                                                        | Buxt..76-1072              |
| $\text{Ni}^+ + 1,4\text{-benzoquinone} \rightarrow \text{Ni}^{2+} + (1,4\text{-benzoquinone})^-$                                                        | $(2.3 \pm 0.5) \times 10^6$                   | —                                  | 25                 | 6.0        | pr       | Measured by the rate of formation of the semiquinone in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.     | Sell.76-1134               |
| $\text{Ni}^+ + \text{menaquinone} \rightarrow \text{Ni}^{2+} + (\text{menaquinone})^-$                                                                  | $(2.5 \pm 0.3) \times 10^6$                   | —                                  | $ca. 25$<br>RT     | 7.0<br>7.0 | pr<br>pr | Measured by the rate of formation of the semiquinone in the presence of $ca. 1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. | Rao.75-1032<br>Rao.73-1047 |
| $\text{Ni}^+ + \text{tetranitromethane} \rightarrow \text{Ni}^{2+} + \text{C}(\text{NO}_2)_3^- + \text{NO}_2$                                           | $(1.4 \pm 0.2) \times 10^6$                   | —                                  | $25 \pm 2$         | 5.9        | pr       | Measured by the rate of formation of the nitroform anion in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. | Sell.76-1134               |
| <i>Ni(I) Complexes</i>                                                                                                                                  |                                               |                                    |                    |            |          |                                                                                                                          |                            |
| $\text{Ni}^{\text{II}}\text{-cyano complexes}$<br>$\text{Ni}(\text{CN})_5^{3-} + \text{Ni}(\text{CN})_5^{3-} \rightarrow \text{Ni}_2(\text{CN})_8^{4-}$ | $2k = (1.5 \pm 0.2) \times 10^6$              | 0.1<br>( $\text{HCO}_2\text{Na}$ ) | $20 \pm 2$         | —          | pr       | Product characterised by its absorption spectrum.                                                                        | Mula....74-1072            |
| $\text{Ni}(\text{CN})_5^{3-} \rightarrow \text{Ni}(\text{CN})_5^{3-} + \text{CN}^-$                                                                     | $(8.1 \pm 1.0) \times 10^5 \text{ s}^{-1}$    | 0.1<br>( $\text{HCO}_2\text{Na}$ ) | $20 \pm 2$         | —          | pr       | $\text{Ni}(\text{CN})_5^{3-}$ characterised by its absorption spectrum.                                                  | Mula....74-1072            |
| $\text{NiL}^+ (L = 5,5,7,12,12,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradecane}).$                                                                |                                               |                                    |                    |            |          |                                                                                                                          |                            |
| $\text{NiL}^+ + \text{Co}(\text{bpy})_3^{3+}$                                                                                                           | $(1.3 \pm 0.1) \times 10^6$                   | 0.016–0.028                        | RT                 | 7.0        | pr       | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                 | Tait..76-1039              |
| $\text{NiL}^+ + \text{CoL}'(\text{OH})_2(\text{OH})_2^{2+} (\text{et})$                                                                                 | $(1.1 \pm 0.1) \times 10^6$                   | 0.016–0.028                        | RT                 | 7.0        | pr       | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                 | Tait..76-1039              |
| $(L' = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene}).$                                                                   |                                               |                                    |                    |            |          |                                                                                                                          |                            |
| $\text{NiL}^+ + \text{Co}(\text{en})_3^{3+} (\text{et})$                                                                                                | $(1.1 \pm 0.1) \times 10^6$                   | 0.016–0.028                        | RT                 | 7.0        | pr       | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                 | Tait..76-1039              |
| $\text{NiL}^+ + \text{Co}(\text{NH}_3)_6^{3+} (\text{et})$                                                                                              | $(1.9 \pm 0.2) \times 10^6$                   | 0.016–0.028                        | RT                 | 7.0        | pr       | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                 | Tait..76-1039              |
| $\text{NiL}^+ + \text{CoL}'(\text{OH})_2^{2+} (\text{et})$                                                                                              | $(1.7 \pm 0.2) \times 10^7$                   | 0.016–0.028                        | RT                 | 7.0        | pr       | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                 | Tait..76-1039              |
| $(L' = 2,2,0,10\text{-tetramethyl-1,4,9,11-tetraazacyclotetradeca-1,3,9,10-tetraene}).$                                                                 |                                               |                                    |                    |            |          |                                                                                                                          |                            |

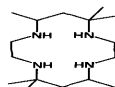


TABLE 14. Nickel(I) and nickel(III) reactions — Continued

| No.   | Reaction                                                               | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$         | $t/^\circ\text{C}$ | pH    | Method | Comments                                                                                                                                                                                                  | Ref.      |
|-------|------------------------------------------------------------------------|------------------------------------------------------------|-------------|--------------------|-------|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 14.54 | $\text{NiL}^+ + \text{Cr}(\text{bpy})_3^{3+}$ (et)                     | $(7.7 \pm 0.8) \times 10^8$                                | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.55 | $\text{NiL}^+ + \text{Fe}(\text{bpy})_3^{3+}$ (et)                     | $(6.4 \pm 0.6) \times 10^7$                                | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.56 | $\text{NiL}^+ + \text{H}_2\text{O}^+$ (pt)                             | $(1.1 \pm 0.1) \times 10^8$                                | 0.06–0.3    | RT                 | <1.25 | pr     | Reaction may involve proton transfer to the metal centre to give a hydrido complex.                                                                                                                       | Tait.,76- |
| 14.57 | $\text{NiL}^+ + \text{H}_2\text{PO}_4^-$ (pt)                          | < $10^4$                                                   | 0.01–0.1    | RT                 | 5.50  | pr     | —                                                                                                                                                                                                         | Tait.,76- |
| 14.58 | $\text{NiL}^+ + \text{NaO}$ (et or O at)                               | $(3.9 \pm 0.4) \times 10^7$                                | —           | RT                 | 7.0   | pr     | Reaction possibly involves two electron oxidation to Ni(III) complex.                                                                                                                                     | Tait.,76- |
| 14.59 | $\text{NiL}^+ + \text{O}_2 \rightarrow \text{NiL}^{3+} + \text{O}_2^-$ | $(1.6 \pm 0.2) \times 10^8$                                | —           | RT                 | 7.0   | pr     | Product transforms an electron to 1,4-benzoquinone but not menaquinone, and identified therefore as $\text{O}_2^-$ , although $\text{O}_2$ adduct, $\text{NiLO}_2^+$ could conceivably react in same way. | Tait.,76  |
| 14.60 | $\text{NiL}^+ + \text{Ru}(\text{NH}_3)_6^{3+}$ (et)                    | $(3.8 \pm 0.4) \times 10^8$                                | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.61 | $\text{NiL}^+ + \text{Ru}(\text{NH}_3)_6\text{NO}^{3+}$ (et)           | $(7.4 \pm 0.7) \times 10^7$                                | 0.016–0.028 | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.62 | $\text{NiL}^+ + \text{acetic acid}$ (pt)                               | $(1.2 \pm 0.1) \times 10^4$                                | 0.015–0.06  | RT                 | 4.85  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.63 | $\text{NiL}^+ + 9,10\text{-anthraquinone-2,6-disulphonate}$ (et)       | $(4.8 \pm 0.5) \times 10^8$                                | 0.004       | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.64 | $\text{NiL}^+ + 1,4\text{-benzoquinone}$ (et)                          | $(4.8 \pm 0.5) \times 10^8$                                | 0.004       | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.65 | $\text{NiL}^+ + 3\text{-benzoylpyridine}$ (et)                         | $(2.5 \pm 0.3) \times 10^8$                                | 0.004       | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.66 | $\text{NiL}^+ + \text{fluorescein}$ (et)                               | $(3.2 \pm 0.3) \times 10^8$                                | 0.004       | RT                 | 7.0   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |
| 14.67 | $\text{NiL}^+ + \text{methyl iodide}$ (et or $\text{S}_{\text{N}}2$ )  | $(4.6 \pm 0.5) \times 10^8$                                | 0.01        | RT                 | 9.2   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                   | Tait.,76- |

TABLE 14. Nickel(II) and nickel(III) reactions — Continued

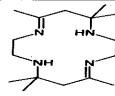
| Reaction                                                                                                                                                                                 | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $I$         | $t/^\circ\text{C}$ | pH     | Method | Comments                                                                                                                                                                                                           | Ref.          |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|-------------|--------------------|--------|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| $\text{NiL}^+$ ( $L = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene}$ ).  |                                                 |             |                    |        |        |                                                                                                                                                                                                                    |               |
| $\text{NiL}^+ + \text{Co}(\text{bpy})_3^{3+}$ (et)                                                                                                                                       | $(1.3 \pm 0.1) \times 10^6$                     | 0.016–0.028 | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| $\text{NiL}^+ + \text{CoL}'(\text{OH})_2(\text{OH})_2^{3+}$ (et)                                                                                                                         | $(2.6 \pm 0.3) \times 10^6$                     | 0.016–0.028 | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| ( $L' = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene}$ ).<br>$\text{NiL}^+ + \text{Co}(\text{en})_3^{3+}$ (et)                                             | $(1.1 \pm 0.1) \times 10^6$                     | 0.016–0.028 | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| $\text{NiL}^+ + \text{Co}(\text{NH}_3)_6^{3+}$ (et)                                                                                                                                      | $(1.9 \pm 0.2) \times 10^6$                     | 0.016–0.028 | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| $\text{NiL}^+ + \text{CoL}'(\text{OH})_2^{3+}$ (et)                                                                                                                                      | $(3.6 \pm 0.4) \times 10^7$                     | 0.016–0.028 | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| ( $L' = 2,3,9,10\text{-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene}$ ).<br>$\text{NiL}^+ + \text{Cr}(\text{bpy})_3^{3+}$                                               | $(1.1 \pm 0.1) \times 10^6$                     | 0.016–0.028 | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| $\text{NiL}^+ + \text{Fe}(\text{bpy})_3^{3+}$ (et)                                                                                                                                       | $(2.2 \pm 0.2) \times 10^6$                     | 0.016–0.028 | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| $\text{NiL}^+ + \text{H}_2\text{O}^+$ (pt)                                                                                                                                               | $(1.5 \pm 0.1) \times 10^6$                     | 0.06–0.3    | RT                 | < 1.25 | pr     | Reaction may involve proton transfer to the metal centre to give a hydrido complex.                                                                                                                                | Tait..76–1039 |
| $\text{NiL}^+ + \text{H}_2\text{PO}_4^-$ (pt)                                                                                                                                            | $(2.4 \pm 0.2) \times 10^6$                     | 0.01–0.1    | RT                 | 5.50   | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                            | Tait..76–1039 |
| $\text{NiL}^+ + \text{NaO}$ (et or O at)                                                                                                                                                 | $(1.8 \pm 0.2) \times 10^7$                     | —           | RT                 | 7.0    | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Reaction possibly involves two electron oxidation to $\text{Ni}^{\text{III}}$ complex.                                                     | Tait..76–1039 |
| $\text{NiL}^+ + \text{O}_2 \rightarrow \text{NiL}^{2+} + \text{O}_2^-$                                                                                                                   | $(1.7 \pm 0.2) \times 10^6$                     | —           | RT                 | 7.0    | pr     | Product transfers an electron to 1,4-benzoquinone but not menaquinone, and identified therefore as $\text{O}_2^-$ , although $\text{O}_2$ adduct $\text{NiL}(\text{O}_2)^+$ , could conceivably react in same way. | Tait..76–1039 |

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

| No.   | Reaction                                                                                                                                          | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ a | $I$         | $t/^\circ\text{C}$ | pH   | Method | Comments                                                                                                                                              | Ref.      |
|-------|---------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|-------------|--------------------|------|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 14.79 | $\text{NiL}^+ + \text{Ru}(\text{NH}_3)_6^{3+}$ (et)                                                                                               | $(4.5 \pm 0.5) \times 10^8$                       | 0.016–0.028 | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.80 | $\text{NiL}^+ + \text{Ru}(\text{NH}_3)_6\text{NO}^{2+}$ (et)                                                                                      | $(3.5 \pm 0.4) \times 10^7$                       | 0.016–0.028 | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.81 | $\text{NiL}^+ + \text{acetic acid}$ (pt)                                                                                                          | $(1.9 \pm 0.2) \times 10^8$                       | 0.015–0.06  | RT                 | 4.85 | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.82 | $\text{NiL}^+ + 9,10\text{-anthraquinone-2,6-disulphonate}$ (et)                                                                                  | $(5.0 \pm 0.5) \times 10^8$                       | 0.004       | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.83 | $\text{NiL}^+ + 1,4\text{-benzoquinone}$ (et)                                                                                                     | $(3.8 \pm 0.4) \times 10^8$                       | 0.004       | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.84 | $\text{NiL}^+ + 3\text{-benzoylpyridine}$ (et)                                                                                                    | $(7.5 \pm 0.8) \times 10^8$                       | 0.004       | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.85 | $\text{NiL}^+ + \text{eosin Y}$ (et)                                                                                                              | $(2.7 \pm 0.3) \times 10^8$                       | 0.004       | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.86 | $\text{NiL}^+ + \text{fluorescein}$ (et)                                                                                                          | $(3.3 \pm 0.3) \times 10^8$                       | 0.004       | RT                 | 7.0  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.87 | $\text{NiL}^+ + \text{methyl iodide}$ (et or $\text{S}_{\text{N}}2$ )                                                                             | $(1.3 \pm 0.1) \times 10^8$                       | 0.01        | RT                 | 9.2  | pr     | Measured in the presence of 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                               | Tait..76- |
| 14.88 | <i>Ni(I) radical complexes</i><br>$\text{NiCH}_3\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{Ni}^{2+} + \text{CH}_3\text{OH} + \text{OH}^-$ | $7 \text{ s}^{-1}$                                | —           | RT                 | nat  | pr     | Products characterised by conductivity experiments.                                                                                                   | Kelm...74 |
| 14.89 | $\text{NiCH}_3\text{OH}^+ + \text{H}_2\text{O}_2$ (et?)                                                                                           | $7.3 \times 10^8$                                 | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.90 | $\text{NiCO}_3 + \text{H}_2\text{O}$                                                                                                              | $< 1 \text{ s}^{-1}$                              | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.91 | $\text{NiC}_6\text{H}_4\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{Ni}^{2+} + \text{C}_6\text{H}_5\text{OH} + \text{OH}^-$                 | $5 \text{ s}^{-1}$                                | —           | RT                 | nat  | pr     | Products characterised by conductivity experiments.                                                                                                   | Kelm...74 |
| 14.92 | $\text{NiC}_6\text{H}_4\text{OH}^+ + \text{H}_2\text{O}_2$ (et?)                                                                                  | $2.3 \times 10^4$                                 | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.93 | $\text{NiCOH}(\text{CH}_3)_2 + \text{H}_2\text{O}$                                                                                                | $< 1 \text{ s}^{-1}$                              | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.94 | $\text{NiCOH}(\text{CH}_3)_2 + \text{H}_2\text{O}_2$                                                                                              | $1.1 \times 10^8$                                 | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.95 | $\text{NiC}_6\text{H}_4\text{OC}_6\text{H}_5 + \text{H}_2\text{O}$                                                                                | $< 1 \text{ s}^{-1}$                              | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.96 | $\text{NiC}_6\text{H}_4\text{OC}_6\text{H}_5 + \text{H}_2\text{O}_2$                                                                              | $1.3 \times 10^8$                                 | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.97 | $\text{NiC}_6\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{Ni}^{2+} + \text{C}_6\text{H}_5\text{OH} + \text{OH}^-$                            | $49 \text{ s}^{-1}$                               | —           | RT                 | nat  | pr     | Products characterised by conductivity experiments.                                                                                                   | Kelm...74 |
| 14.98 | $\text{NiC}_6\text{H}_5 + \text{H}_2\text{O}_2$<br>( $\text{C}_6\text{H}_5$ = cyclopentyl radical)                                                | $< 5 \times 10^8$                                 | —           | RT                 | nat  | pr     | —                                                                                                                                                     | Kelm...74 |
| 14.99 | $\text{NiO}_2^+ \text{NiO}_2\text{H}^{2+}$<br>$\text{NiO}_2^+ \rightarrow \text{Ni}^{2+} + \text{O}_2^-$                                          | $780 \pm 80 \text{ s}^{-1}$                       | —           | $25 \pm 2$         | 5.7  | pr     | Measured from the rate of formation of the nitroform anion in solutions containing tetra-nitromethane and 1 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. | Sell.76   |

TABLE 14. Nickel(I) and nickel(III) reactions — Continued

|                                                                                                                                                                                                                                                   | Reaction                                                                        | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>              | $I$  | $t/^\circ\text{C}$ | pH      | Method | Comments                                                                                                                                                                  | Ref.         |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------|------|--------------------|---------|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| 0                                                                                                                                                                                                                                                 | $\text{NiO}_2^+ + \text{H}^+ \rightleftharpoons \text{NiO}_2\text{H}^{2+}$      | $K = 2000 \pm 1200 \text{ M}^{-1}$<br>(i.e. $\text{p}K_a = 3.2 \pm 0.3$ ) | 0.04 | $25 \pm 2$         | 3.0–5.7 | pr     | Measured from the pH dependence of the rate of formation of the nitroform anion in solutions containing tetranitromethane and 1 mol dm <sup>-3</sup> 2-methyl-2-propanol. | Sell.76-1134 |
| 1                                                                                                                                                                                                                                                 | $\text{NiO}_2\text{H}^{2+} \rightarrow \text{Ni}^{2+} + \text{HO}_2$            | $> 2800 \text{ s}^{-1}$                                                   | —    | $25 \pm 2$         | 3.0     | pr     | Estimated from the rate of formation of the nitroform anion in solutions containing tetranitromethane and 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                     | Sell.76-1134 |
| <i>Ni(III) complexes</i>                                                                                                                                                                                                                          |                                                                                 |                                                                           |      |                    |         |        |                                                                                                                                                                           |              |
| 2                                                                                                                                                                                                                                                 | $\text{Ni}^{\text{III}}(\text{NH}_3)_n + \text{N}_2\text{H}_4$                  | $(4 \pm 1) \times 10^6$                                                   | —    | RT                 | 11.3    | pr     | —                                                                                                                                                                         | Lati.72-0460 |
| 3                                                                                                                                                                                                                                                 | $\text{Ni}^{\text{III}}(\text{NH}_3)_n + \text{Ni}^{\text{III}}(\text{NH}_3)_n$ | $2k < 3.5 \times 10^7$                                                    | —    | RT                 | 11.3    | pr     | —                                                                                                                                                                         | Lati.72-0460 |
| Rate constants for the decay of $\text{Ni}^{\text{III}}(\text{en})_n$ and $\text{Ni}^{\text{III}}(\text{gly})_n$ are given in tables III and IV respectively of ref. 72-0461. These rate constants cannot be attributed to any specific reaction. |                                                                                 |                                                                           |      |                    |         |        |                                                                                                                                                                           |              |

<sup>a</sup> data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 15. Lead(II) reactions

| No.  | Reaction                                                                                            | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} *$ | $I$ | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                      | Ref.           |
|------|-----------------------------------------------------------------------------------------------------|---------------------------------------------------|-----|--------------------|-----|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| 15.1 | $\text{Pb}^{2+} + \text{Cd}^{2+}$                                                                   | $< 10^7$                                          | —   | RT                 | nat | pr     | —                                                                                                                                                                                                             | Baxe..66       |
| 15.2 | $\text{Pb}^{2+} + \text{Cu}^{2+}$                                                                   | $< 10^7$                                          | —   | RT                 | nat | pr     | —                                                                                                                                                                                                             | Baxe..66       |
| 15.3 | $\text{Pb}^{2+} + \text{Ni}^{2+}$                                                                   | $< 10^7$                                          | —   | RT                 | nat | pr     | —                                                                                                                                                                                                             | Baxe..66       |
| 15.4 | $\text{Pb}^{2+} + \text{O}_2 \rightarrow \text{Pb}^{3+} + \text{O}_2^-$                             | $3.9 \times 10^9$                                 | —   | RT                 | nat | pr     | Product transfers an electron to 1,4-benzoquinone and tentatively identified as $\text{O}_2^-$ . (Ref. 76-1134).                                                                                              | Baxe..66       |
| 15.5 | $\text{Pb}^{2+} + \text{OH}^-$ (et)                                                                 | $7.7 \times 10^9$                                 | —   | RT                 | nat | pr     | Reinterpreted from data in ref. 66-0848 on decay of $\text{Pb}^{2+}$ in the absence of OH scavengers. Principal competing reaction, $\text{Pb}^{2+} + \text{Pb}^{2+}$ , not taken into account.               | Baxe..66       |
| 15.6 | $\text{Pb}^{2+} + \text{Zn}^{2+}$                                                                   | $< 10^7$                                          | —   | RT                 | nat | pr     | —                                                                                                                                                                                                             | Baxe..66       |
| 15.7 | $\text{Pb}^{2+} + 1,4\text{-benzoquinone} \rightarrow \text{Pb}^{3+} + (1,4\text{-benzoquinone})^-$ | $(4.1 \pm 0.8) \times 10^9$                       | —   | $25 \pm 2$         | 6.3 | pr     | Lead(II) acetate salt used, $\text{Pb}^{2+}$ may be complexed to acetate. Measured from the rate of formation of the benzosemiquinone product in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. | Sell.76        |
| 15.8 | $\text{Pb}^{2+} + \text{menaquinone} \rightarrow \text{Pb}^{3+} + (\text{menaquinone})^-$           | $(3.7 \pm 0.4) \times 10^9$                       | —   | RT                 | 7.2 | pr     | Measured by the rate of formation of the semiquinone in the presence of ca. $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                                      | Rao.7<br>Rao.7 |

\*If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 16. Praseodymium(IV) reactions

| Reaction                                                                               | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ *         | $I$                                      | $t/^\circ\text{C}$ | pH        | Method | Comments                                                                                                                                                     | Ref.         |
|----------------------------------------------------------------------------------------|-----------------------------------------------------------|------------------------------------------|--------------------|-----------|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| $\text{Pr}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{PrOH}^{3+} + \text{H}^+$ | $K = (7 \pm 1) \times 10^{-4}$<br>or $pK_a = 3.1 \pm 0.1$ | var                                      | RT                 | 1.95–5.87 | pr     | Measured from effect of pH on absorption of $\text{Pr(IV)}$ .                                                                                                | Fara.72-0066 |
| $\text{Pr}^{IV} + \text{Br}^-$ (et or af)                                              | $(1.2 \pm 0.4) \times 10^{10}$                            | 0.75<br>[ $\text{Pr}_2(\text{SO}_4)_6$ ] | RT                 | nat       | pr     | —                                                                                                                                                            | Fara.72-0066 |
| $\text{Pr}^{IV} + \text{H}_2\text{O}_2$ (H at ?)                                       | $(8 \pm 1) \times 10^8$                                   | 0.75<br>[ $\text{Pr}_2(\text{SO}_4)_6$ ] | RT                 | nat       | pr     | —                                                                                                                                                            | Fara.72-0066 |
| $\text{Pr}^{IV} + \text{HSO}_4^-$<br>(et or H at)                                      | $(2.0 \pm 0.3) \times 10^8$                               | —                                        | RT                 | 2–3.8     | pr     | —                                                                                                                                                            | Fara.72-0066 |
| $\text{Pr}^{IV} + \text{NO}_2^-$ (et?)                                                 | $(3 \pm 1) \times 10^7$                                   | 0.75<br>[ $\text{Pr}_2(\text{SO}_4)_6$ ] | RT                 | nat       | pr     | —                                                                                                                                                            | Fara.72-0066 |
| $\text{Pr}^{IV} + \text{Pr}^{IV}$<br>(see comments)                                    | $2k = (1.6 \pm 0.8) \times 10^8$                          | —                                        | RT                 | 5.8       | pr     | Stable products of reaction suggested to be $\text{Pr}^{III}$ and $\text{O}_2$ . Initial product possibly an oxo or hydroxo bridged diprasedodymium species. | Fara.72-0066 |

data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 17. Platinum(I) and platinum(III) reactions

| No.                                                  | Reaction                                                                                                                                                                                  | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} *$ | $I$                | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                                                                                             | Ref.       |
|------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|--------------------|--------------------|-----|--------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <b><math>\text{Pt}^{\text{I}}</math> Reactions</b>   |                                                                                                                                                                                           |                                                   |                    |                    |     |        |                                                                                                                                                                                                                                                                                                      |            |
| 17.1                                                 | $\text{Pt}^{\text{I}}$ from $\text{PtCl}_4^{2-} + e_{\text{aq}}^-$                                                                                                                        | $< 4 \times 10^6$                                 | —                  | RT                 | nat | pr     | —                                                                                                                                                                                                                                                                                                    | Ghos.65    |
| 17.2                                                 | $\text{Pt}^{\text{I}} + \text{NaO}$ (et or O at)                                                                                                                                          | $< 2 \times 10^7$                                 | —                  | RT                 | nat | pr     | —                                                                                                                                                                                                                                                                                                    | Ghos.65    |
| 17.3                                                 | $\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}} \rightarrow \text{Pt}^{\text{II}} + \text{Pt}^{\text{III}}$                                                                                  | $k' = (4.1 \pm 0.5) \times 10^6$                  | 0.003              | RT                 | nat | pr     | Unclear whether rate constants refer to $k$ or $2k$ . Measured in the presence of 0.1 mol $\text{dm}^{-3}$ KCl.                                                                                                                                                                                      | Ghos.65    |
|                                                      |                                                                                                                                                                                           | $k' = (3.15 \pm 0.15) \times 10^6$                | 0.013              | RT                 | nat | pr     | Products identified in $\gamma$ -radiolysis experiments (see ref. 62-0164).                                                                                                                                                                                                                          | Ghos.65    |
|                                                      |                                                                                                                                                                                           | $k' = \text{ca. } 2.5 \times 10^6$                | 0.018              | RT                 | 2   | pr     | —                                                                                                                                                                                                                                                                                                    | Ghos.65    |
| 17.4                                                 | $\text{Pt}^{\text{I}}$ from $\text{Pt}(\text{CN})_4^{2-} + e_{\text{aq}}^-$                                                                                                               | $(1.8 \pm 0.25) \times 10^7$                      | —                  | RT                 | nat | pr     | —                                                                                                                                                                                                                                                                                                    | Ghos.65    |
| 17.5                                                 | $\text{Pt}^{\text{I}} + \text{O}_2$ (et or af)                                                                                                                                            | $(3.5 \pm 0.5) \times 10^6$                       | —                  | RT                 | nat | pr     | —                                                                                                                                                                                                                                                                                                    | Ghos.65    |
| 17.6                                                 | $\text{Pt}^{\text{I}}$ from $\text{PtCl}_4^{2-} + e_{\text{aq}}^-$ ( $L = \text{diethylenetriamine}$ ).<br>$\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}}$ (? see comments)                 | $2k = (4.6 \pm 2.0) \times 10^6$                  | $2 \times 10^{-4}$ | ca. 25             | nat | pr     | Rate constant represents decay of second transient produced from $\text{Pt}^{\text{II}} + e_{\text{aq}}^-$ . First transient decays by a first order reaction with $(2.3 \pm 1.3) \times 10^6 \text{ s}^{-1}$ , probably associated with the substitution of $\text{Cl}^-$ by $\text{H}_2\text{O}$ . | Stor...75- |
| 17.7                                                 | $\text{Pt}^{\text{I}}$ from $\text{PtCl}_4^{2-} + \text{H}$ ( $L = \text{diethylenetriamine}$ ).<br>$\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}}$ (dis?)                                  | $2k = (6.8 \pm 0.8) \times 10^6$                  | —                  | ca. 25             | 2-3 | pr     | —                                                                                                                                                                                                                                                                                                    | Stor...75- |
| 17.8                                                 | $\text{Pt}^{\text{I}}$ from $\text{Pt}(\text{en})_2^{2+} + e_{\text{aq}}^-$<br>$\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}}$ (dis?)                                                       | $2k = (0.0 \pm 0.9) \times 10^6$                  | $4 \times 10^{-4}$ | ca. 25             | nat | pr     | —                                                                                                                                                                                                                                                                                                    | Stor...75- |
| 17.9                                                 | $\text{Pt}^{\text{I}}$ from $\text{Pt}(\text{en})_2^{2+} + \text{H}$<br>$\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}}$ (dis?)                                                              | $2k = (2.8 \pm 0.6) \times 10^6$                  | —                  | ca. 25             | 2-3 | pr     | —                                                                                                                                                                                                                                                                                                    | Stor...75- |
| 17.10                                                | $\text{Pt}^{\text{I}}$ from $\text{PtCl}_4^{2-} + \text{H}$ ( $L = \text{tetraethyldiethylenetriamine}$ ).<br>$\text{Pt}^{\text{I}} + \text{Pt}^{\text{I}}$ (dis?)                        | $2k = (1.3 \pm 0.6) \times 10^{11}$ (!)           | —                  | ca.                | 2-3 | pr     | —                                                                                                                                                                                                                                                                                                    | Stor...75- |
| <b><math>\text{Pt}^{\text{III}}</math> Reactions</b> |                                                                                                                                                                                           |                                                   |                    |                    |     |        |                                                                                                                                                                                                                                                                                                      |            |
| 17.11                                                | $\text{Pt}^{\text{III}}$ from $\text{PtCl}_4^{2-} + \text{Cl}_2^-$<br>$(\text{Pt}^{\text{III}})^{\text{I}} \rightarrow (\text{Pt}^{\text{III}})^{\text{II}}$ (see comments for mechanism) | $(3 \pm 1) \times 10^6 \text{ s}^{-1}$            | —                  | ca. 25             | 0.3 | pr     | Reaction probably associated with change in number of chloride ligands and/or substitution of $\text{Cl}^-$ by $\text{H}_2\text{O}$ . Measured in the presence of 0.5 mol $\text{dm}^{-3}$ HCl.                                                                                                      | Stor...75- |
| 17.12                                                | $\text{Pt}^{\text{III}} + \text{Cu}^{\text{II}}$ (et)                                                                                                                                     | $(1.5 \pm 0.2) \times 10^6$                       | 0.5 (HCl)          | ca. 25             | 0.3 | pr     | Measured in the presence of 0.5 mol $\text{dm}^{-3}$ HCl. $\text{Cu}^{\text{II}}$ in the form of chloro complex.                                                                                                                                                                                     | Stor...75- |

TABLE 17. Platinum(I) and platinum(III) reactions — Continued

| Reaction                                                                                                                                                                             | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^a$ | $I$                | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Ref.           |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|--------------------|--------------------|-----|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| $\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}} (\text{dis})$                                                                                                                       | $2k = \text{ca. } 2 \times 10^9$                           | 0.5<br>(HCl)       | ca.<br>25          | 0.3 | pr     | Rate constant is for the decay of the second transient $\text{Pt}^{\text{III}}$ species, $(\text{Pt}^{\text{III}})^{\ddagger}$ in entry 17.11. Measured in the presence of $0.5 \text{ mol dm}^{-3} \text{ HCl}$ .                                                                                                                                                                                                                                                  | Stor...75-1188 |
| $\text{Pt}^{\text{III}}$ from $\text{PtCl}_6^{2-} + h\nu$<br>$\text{Pt}^{\text{III}} + \text{Fe}^{2+} (\text{et})$                                                                   | $(2.8 \pm 0.3) \times 10^8$                                | $2 \times 10^{-3}$ | —                  | —   | f.ph.  | From dependence of rate constant for this reaction on ionic strength charge on $\text{Pt}^{\text{III}}$ is $-1$ , and identified therefore as $\text{PtCl}_5^-$ . Broszkiewicz and Grodkowski (ref. 76-1055) suggest however that the reaction observed under the conditions employed was $\text{Cl}_2 + \text{Fe}^{2+}$ . Other experiments give $k = (4.0 \pm 0.6) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $\text{Cl}_2 + \text{Fe}^{2+}$ . | Wrig.72-7088   |
| $\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}} (\text{dis})$                                                                                                                       | $2k = (4.6 \pm 0.4) \times 10^8$                           | $10^{-3}$          | ca.<br>20          | 5.8 | f.ph.  | Rate constant calculated taking $\epsilon_{450} = 3.7 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .                                                                                                                                                                                                                                                                                                                                                  | Wrig.72-7088   |
| $\text{Pt}^{\text{III}}$ from $\text{PtCl}_6^{2-} + \text{OH}^-$                                                                                                                     | $1.8 \times 10^8 \text{ s}^{-1}$                           | —                  | RT                 | nat | pr     | Rate constant measured from decay of reactant at 450 nm.                                                                                                                                                                                                                                                                                                                                                                                                            | Adam..68-0169  |
|                                                                                                     | $2.0 \times 10^8 \text{ s}^{-1}$                           | —                  | RT                 | nat | pr     | Rate constant measured from decay of reactant at 450 nm.                                                                                                                                                                                                                                                                                                                                                                                                            | Ghos.69-0144   |
|                                                                                                                                                                                      | $2.0 \times 10^8 \text{ s}^{-1}$                           | —                  | RT                 | nat | pr     | Rate constant measured from build-up of product at 400 nm. Ligand reorganization mechanism implied from similarity of products of $\text{PtCl}_6^{2-} + \text{OH}^-$ and $\text{PtCl}_6^{2-} + \text{e}_{\text{aq}}^-$ (ref. 68-0169).                                                                                                                                                                                                                              | Adam..68-0169  |
| $\text{Pt}^{\text{III}}$ from $\text{Pt}(\text{en})_2^{2+} + \text{Cl}_2^-$<br>$(\text{Pt}^{\text{III}})^{\ddagger} \rightarrow (\text{Pt}^{\text{III}})^{\ddagger} + \text{Cl}_2^-$ | $(1.3 \pm 0.1) \times 10^8 \text{ s}^{-1}$                 | —                  | ca.<br>25          | 0.3 | pr     | Decay approximates to two consecutive first order processes (see also 17.18). Measured in the presence of $0.5 \text{ mol dm}^{-3} \text{ HCl}$ .                                                                                                                                                                                                                                                                                                                   | Stor...75-1188 |

TABLE 17. Platinum(II) and platinum(III) reactions — Continued

| No.   | Reaction                                                                                                                  | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$                                            | $I$          | $t/^\circ\text{C}$ | pH      | Method | Comments                                                                                                                                                                                                                                                                                                 | Ref.      |
|-------|---------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|--------------|--------------------|---------|--------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 17.18 | $(\text{Pt}^{\text{III}})^{\text{II}} \rightarrow (\text{Pt}^{\text{III}})^{\text{III}}$                                  | $7.7 \pm 0.8 \text{ s}^{-1}$                                                             | —            | ca.<br>25          | 0.3     | pr     | Measured in the presence of 0.5 mol dm <sup>-3</sup> HCl. See also comments under 17.17.                                                                                                                                                                                                                 | Stor...75 |
| 17.19 | $\text{Pt}^{\text{III}} + \text{Cu}^{\text{II}} (\text{et})$                                                              | $(3.2 \pm 0.7) \times 10^6$                                                              | 0.5<br>(HCl) | ca.<br>25          | 0.3     | pr     | Measured in the presence of 0.5 mol dm <sup>-3</sup> HCl.                                                                                                                                                                                                                                                | Stor...75 |
| 17.20 | $\text{Pt}^{\text{III}} + \text{Fe}^{\text{II}} (\text{et})$                                                              | $(2.5 \pm 0.4) \times 10^6$                                                              | 0.5<br>(HCl) | ca.<br>25          | 0.3     | pr     | Measured in the presence of 0.5 mol dm <sup>-3</sup> HCl.                                                                                                                                                                                                                                                | Stor...75 |
| 17.21 | $\text{Pt}^{\text{III}} \text{ from } \text{Pt}(\text{en})_2^{2+} + \text{OH}^- + \text{H}^+$                             | $(2.5 \pm 0.2) \times 10^6 \text{ s}^{-1}$<br>$(2.4 \pm 0.3) \times 10^6 \text{ s}^{-1}$ | —            | RT                 | 4.0–7.0 | pr     | —                                                                                                                                                                                                                                                                                                        | Brod...74 |
| 17.22 | $(\text{Pt}^{\text{III}})^{\text{I}} + \text{OH}^- \rightarrow (\text{Pt}^{\text{III}})^{\text{II}} + \text{H}_2\text{O}$ | $(3.1 \pm 0.5) \times 10^{10}$                                                           | —            | RT                 | 7.0–9.6 | pr     | —                                                                                                                                                                                                                                                                                                        | Brod...74 |
| 17.23 | $(\text{Pt}^{\text{III}})^{\text{I}} + \text{H}^+ \rightarrow (\text{Pt}^{\text{III}})^{\text{II}}$                       | $(4.2 \pm 0.9) \times 10^6$                                                              | —            | RT                 | 4.0–7.0 | pr     | —                                                                                                                                                                                                                                                                                                        | Brod...74 |
| 17.24 | $(\text{Pt}^{\text{III}})^{\text{II}} + (\text{Et}^{\text{III}})^{\text{II}} (\text{dis?})$                               | $(1.5 \pm 0.4) \times 10^6$                                                              | —            | RT                 | 2.9–8.5 | pr     | Measured in the presence of (0–2) $\times 10^{-2}$ mol dm <sup>-3</sup> Cl <sup>-</sup> . Unclear whether these rate constants refer to $k$ or $2k$ .                                                                                                                                                    | Brod...74 |
|       |                                                                                                                           | $(4.3 \pm 2.8) \times 10^6$                                                              | —            | RT                 | 4.0–9.1 | f.ph.  | Measured in the presence of (0–1) $\times 10^{-2}$ mol dm <sup>-3</sup> Cl <sup>-</sup> . Unclear whether these rate constants refer to $k$ or $2k$ .                                                                                                                                                    | Brod...74 |
| 17.25 | $(\text{Pt}^{\text{III}})^{\text{II}} + \text{Cu}^{\text{II}}$                                                            | $< 10^4$                                                                                 | —            | RT                 | 6.3–6.6 | pr     | —                                                                                                                                                                                                                                                                                                        | Brod...74 |
| 17.26 | $(\text{Pt}^{\text{III}})^{\text{II}} + \text{Fe}(\text{CN})_6^{4-} (\text{et})$                                          | $(2.3 \pm 0.2) \times 10^6$                                                              | —            | RT                 | 6.3–6.6 | pr     | —                                                                                                                                                                                                                                                                                                        | Brod...74 |
| 17.27 | $(\text{Pt}^{\text{III}})^{\text{II}} + \text{O}_2$                                                                       | $< 10^6$                                                                                 | —            | RT                 | 6.3–6.6 | pr     | —                                                                                                                                                                                                                                                                                                        | Brod...74 |
| 17.28 | $(\text{Pt}^{\text{III}})^{\text{I}} \rightarrow (\text{Pt}^{\text{III}})^{\text{II}} + \text{H}^+$                       | $(6.6 \pm 1.8) \times 10^6$<br>or $pK_a = 6.8 \pm 0.2$<br>$25 \pm 0 \text{ s}^{-1}$      | —            | RT                 | 2.8–4.3 | pr     | Cf. entry 17.23                                                                                                                                                                                                                                                                                          | Brod...74 |
| 17.29 | $(\text{Pt}^{\text{III}})^{\text{II}} \rightarrow ?$                                                                      | —                                                                                        | —            | RT                 | 2.8–4.3 | pr     | Reaction may be second order.                                                                                                                                                                                                                                                                            | Brod...74 |
| 17.30 | $(\text{Pt}^{\text{III}})^{\text{II}} + \text{Cl}^- \rightarrow (\text{Pt}^{\text{III}})^{\text{IV}}$                     | $(1.11 \pm 0.09) \times 10^6$                                                            | —            | RT                 | 3–4.5.1 | pr     | —                                                                                                                                                                                                                                                                                                        | Brod...74 |
| 17.31 | $(\text{Pt}^{\text{III}})^{\text{IV}} + \text{Cu}^{\text{II}} (\text{et?})$                                               | $(2.7 \pm 1.0) \times 10^6$                                                              | —            | RT                 | 2.1     | pr     | Measured in the presence of 5 $\times 10^{-2}$ mol dm <sup>-3</sup> Cl <sup>-</sup> . Measured in the presence of 0–0.5 mol dm <sup>-3</sup> 2-methyl-2-propanol. Mechanism of reaction may be complex as the rate constants were appreciably higher (25–50%) at the lower [Cu <sup>II</sup> ] employed. | Brod...74 |
|       |                                                                                                                           | $(3.2 \pm 1.1) \times 10^6$                                                              | —            | RT                 | 2.0     | f.ph.  | Measured in the presence of 10 <sup>-2</sup> mol dm <sup>-3</sup> Cl <sup>-</sup> . Rate constant calculated taking $k_{\text{iso}}(\text{Pt}^{\text{III}})^{\text{IV}} = 0.070 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ .                                                                           | Brod...74 |
| 17.32 | $(\text{Pt}^{\text{III}})^{\text{IV}} + (\text{Pt}^{\text{III}})^{\text{IV}} (\text{dis?})$                               | $k' = (5.7 \pm 1.0) \times 10^7$                                                         | —            | RT                 | 3.4     | pr     | Measured in the presence of 10 <sup>-2</sup> mol dm <sup>-3</sup> Cl <sup>-</sup> . Rate constant calculated taking $k_{\text{iso}}(\text{Pt}^{\text{III}})^{\text{IV}} = 0.070 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ .                                                                           | Brod...74 |

TABLE 17. Platinum(I) and platinum(III) reactions — Continued

| Reaction                                                                                                                                                                                              | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $I$ | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                                                                                                                                                | Ref.           |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|-----|--------------------|-----|--------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| Cont.                                                                                                                                                                                                 | $k' = (4.9 \pm 1.9) \times 10^7$                | —   | RT                 | 2.0 | f.ph.  | Measured in the presence of $(0-1) \times 10^{-2} \text{ mol dm}^{-3} \text{ Cl}^-$ and $0-0.5 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. Rate constant calculated taking $\epsilon_{\text{HCl}}(\text{Pt}^{\text{III}})^{\text{IV}} = 9490 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Unclear whether these rate constants refer to $k$ or $2k$ . | Brod...76-1093 |
| $\text{Pt}^{\text{III}}$ from $\text{trans-Pt(en)}_2\text{Cl}_2^{2+} + e_{\text{aq}}^-$ or $\text{CH}_3\text{COHCH}_3$<br>$\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}}$ (dia)                     | $2k = (5.8 \pm 1.0) \times 10^7$                | —   | ca. 25             | —   | pr     | Measured in the presence of $2.6 \text{ mol dm}^{-3}$ 2-propanol.                                                                                                                                                                                                                                                                                       | Stor...75-1188 |
| $\text{Pt}^{\text{III}}$ from $\text{trans-Pt(en)}_2\text{Cl}_2^{2+} + \text{H}$<br>$\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}}$ (dia)                                                           | $2k = (8.8 \pm 1.0) \times 10^7$                | —   | ca. 25             | 2   | pr     | Measured in the presence of $0.11-2 \text{ mol dm}^{-3}$ 2-methyl-2-propanol.                                                                                                                                                                                                                                                                           | Stor...75-1188 |
| $\text{Pt}^{\text{III}}$ from $\text{trans-Pt(en)}_2\text{Cl}_2^{2+} + \cdot\text{CH}_2\text{OH}$<br>$\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}}$ (dia)                                          | $2k = (1.04 \pm 0.38) \times 10^8$              | —   | ca. 25             | —   | pr     | Measured in the presence of $2-4 \text{ mol dm}^{-3}$ methanol.                                                                                                                                                                                                                                                                                         | Stor...75-1188 |
| $\text{Pt}^{\text{III}}$ from $\text{Pt(dien)Cl}^+ + \text{Cl}_2^-$<br>$\text{Pt}^{\text{III}} + \text{Cu}^{\text{II}}$ (et)                                                                          | $(3.2 \pm 0.7) \times 10^8$                     | —   | ca. 25             | 0.3 | pr     | Measured in the presence of $0.5 \text{ mol dm}^{-3} \text{ HCl}$ .                                                                                                                                                                                                                                                                                     | Stor...75-1188 |
| $\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}}$ (dia)                                                                                                                                               | $2k = (6.8 \pm 1.6) \times 10^8$                | —   | ca. 25             | 0.3 | pr     | Measured in the presence of $0.5 \text{ mol dm}^{-3} \text{ HCl}$ .                                                                                                                                                                                                                                                                                     | Stor...75-1188 |
| $\text{Pt}^{\text{III}}$ from $\text{Pt(dien)Cl}^+ + \text{OH}^-$<br>$(\text{Pt}^{\text{III}})^{\text{I}} \rightarrow (\text{Pt}^{\text{III}})^{\text{II}}$                                           | $(4.8 \pm 0.8) \times 10^8$                     | —   | RT                 | nat | pr     | Rate constant for initial decay of $\text{Pt}^{\text{III}}$ transient. This process is followed by (i) an intermediate process exhibiting mixed order kinetics, and (ii) a slow second order decay with $2k = (7.6 \pm 0.6) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .                                                                 | Brod...76-1093 |
| $\text{Pt}^{\text{III}}$ from $\text{PtLCl}^+ + \text{Cl}_2^-$ ( $L = \text{tetraethyldiethylenetriamine}$ ).<br>$\text{Pt}^{\text{III}} + \text{Cu}^{\text{II}}$                                     | $(1.5 \pm 0.4) \times 10^7$                     | —   | ca. 25             | 0.3 | pr     | Measured in the presence of $0.5 \text{ mol dm}^{-3} \text{ HCl}$ .                                                                                                                                                                                                                                                                                     | Stor...75-1188 |
| $\text{Pt}^{\text{III}} + \text{Pt}^{\text{III}}$                                                                                                                                                     | $2k = \text{ca. } 8 \times 10^8$                | —   | ca. 25             | 0.3 | pr     | Measured in the presence of $0.5 \text{ mol dm}^{-3} \text{ HCl}$ .                                                                                                                                                                                                                                                                                     | Stor...75-1188 |
| $\text{Pt}^{\text{III}}$ from $\text{PtLCl}^+ + \text{OH}^-$ ( $L = \text{tetraethyldiethylenetriamine}$ ).<br>$(\text{Pt}^{\text{III}})^{\text{I}} \rightarrow (\text{Pt}^{\text{III}})^{\text{II}}$ | $1.8 \pm 0.6 \text{ s}^{-1}$                    | —   | ca. 25             | nat | pr     | —                                                                                                                                                                                                                                                                                                                                                       | Brod...76-1093 |

ata source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 18. Rhodium(II) reactions

| No.  | Reaction                                                                                                                                                                                     | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ * | $I$ | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                      | Ref      |
|------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------|-----|--------------------|-----|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| 18.1 | $\text{Rh}(\text{NH}_3)_4^{2+}$ and related complexes<br>$\text{Rh}(\text{NH}_3)_4^{2+} + \text{H}_2\text{O} \rightarrow$<br>$\text{Rh}(\text{NH}_3)_3\text{H}_2\text{O}^{2+} + \text{NH}_3$ | $3.5 \times 10^8 \text{ s}^{-1}$                  | —   | RT                 | 4.0 | pr     | Rate constant measured by change in conductivity resulting from $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$ . Solutions contained also 0.5 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. | Lili.,75 |
| 18.2 | $\text{Rh}(\text{NH}_3)_3\text{H}_2\text{O}^{2+} + \text{H}_2\text{O} \rightarrow$<br>$\text{Rh}(\text{NH}_3)_2(\text{H}_2\text{O})_2^{2+} + \text{NH}_3$                                    | $40 \text{ s}^{-1}$                               | —   | RT                 | 4.0 | pr     | Rate constant measured by change in conductivity resulting from $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$ . Solutions contained also 0.5 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. | Lili.,75 |
| 18.3 | $\text{Rh}(\text{NH}_3)_4^{2+} + \text{O}_2 \rightarrow$<br>$\text{O}_2\text{Rh}(\text{NH}_3)_4^{2+}$                                                                                        | $3.1 \times 10^6$                                 | —   | RT                 | 4.0 | pr     | Product characterised by conductivity measurements. Measured in the presence of 0.5 mol $\text{dm}^{-3}$ 2-methyl-2-propanol.                                                                 | Lili.,75 |
| 18.4 | $\text{Rh}(\text{NH}_3)_4^{2+} +$<br>$\text{Rh}(\text{NH}_3)_3^{2+}$ (dis?)                                                                                                                  | $2k = \text{ca. } 1.2 \times 10^7$                | —   | RT                 | 4.0 | pr     | Estimated from dependence of chain length in the $\text{Rh}(\text{NH}_3)_4^{2+} + \text{Rh}(\text{NH}_3)_3^{2+}$ reaction on dose rate.                                                       | Lili.,75 |
| 18.5 | $\text{Rh}(\text{NH}_3)_4^{2+} +$<br>$\text{Rh}(\text{NH}_3)_4\text{Br}_2^{2+} \rightarrow$<br>$\text{Rh}(\text{NH}_3)_3^{2+} + \text{Rh}(\text{NH}_3)_4\text{Br}_2$                         | $\text{ca. } 1.4 \times 10^6$                     | —   | RT                 | 4.0 | pr     | Estimated from initial conductivity change. Measured in the presence of 0.5 mol $\text{dm}^{-3}$ 2-methyl-2-propanol. Products inferred from chain reaction which ensues.                     | Lili.,75 |

\*If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 19. Ruthenium(I), (II), (III) and (IV) reactions

| Reaction                                                                                                                                                                                     | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$                  | $t/^\circ\text{C}$ | pH       | Method | Comments                                                                                                                                                                                                                                                                            | Ref.          |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|----------------------|--------------------|----------|--------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------|
| $\text{Ru}^{\text{I}}$<br>$\text{Ru}(\text{NH}_3)_6\text{N}_2^{+}$<br>$\text{Ru}(\text{NH}_3)_6\text{N}_2^{+} + \text{Ru}(\text{NH}_3)_6\text{N}_2^{+} \text{ (dia)}$                        | $2k = 2.7 \times 10^9$                                       | $< 6 \times 10^{-4}$ | $20 \pm 2$         | nat      | pr     | Deposit of metallic ruthenium and molecular nitrogen ( $G(\text{N}_2) = 1.25$ ) formed as stable products. Immediate products of reaction unknown.                                                                                                                                  | Baxe.71-0234  |
| $\text{Ru}^{\text{II}}$<br>$\text{Ru}(\text{NH}_3)_6\text{Cl}^+ + \text{H}_2\text{O} \rightarrow \text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{2+} + \text{Cl}^-$                              | $4.7 \pm 0.4 \text{ s}^{-1}$                                 | —                    | 20                 | nat      | pr     | Product characterised by its absorption spectrum.                                                                                                                                                                                                                                   | Baxe..70-0178 |
| $\text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Cl}^{2+} \rightarrow \text{Ru}(\text{NH}_3)_6\text{Cl}^+ + \text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{2+}$ | $1.0 \times 10^9$                                            | $3 \times 10^{-4}$   | 20                 | nat      | pr     | Products inferred from fact that radiation brings about complete aquation of $\text{Ru}(\text{NH}_3)_6\text{Cl}^{2+}$ .                                                                                                                                                             | Baxe..70-0178 |
| $\text{Ru}(\text{NH}_3)_6\text{NO}^{2+} + \text{O}_2$<br>(or or at)                                                                                                                          | $7.6 \times 10^9$                                            | —                    | RT                 | —        | pr     | —                                                                                                                                                                                                                                                                                   | Armo.75-1049  |
| $\text{Ru}(\text{NH}_3)_6\text{NO}^{2+} + \text{H}_5\text{CC}(\text{CH}_3)_2\text{OH} \rightarrow \text{Ru}(\text{NH}_3)_6\text{NO} \cdot \text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}^{2+}$  | $3.7 \times 10^9$                                            | —                    | RT                 | 1.0-10.3 | pr     | Measured in the presence of 0.1 - 2.0 mol dm <sup>-3</sup> 2-methyl-2-propanol. Product characterised by elemental microanalysis, ion exchange chromatography, and uv-visible, ir and nmr spectroscopy.                                                                             | Armo..75-1077 |
| $\text{Ru}(\text{NH}_3)_6\text{NO}^{2+} + \text{O}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$<br>(af or et)                                                                               | $3 \times 10^9$                                              | —                    | RT                 | nat      | pr     | Measured in the presence of 1 mol dm <sup>-3</sup> 2-methyl-2-propanol.                                                                                                                                                                                                             | Armo..75-1077 |
| $\text{Ru}^{\text{III}}$<br>$\text{Ru}(\text{NH}_3)_6\text{N}_2^{3+} + \text{H}_2\text{O} \rightarrow \text{Ru}(\text{NH}_3)_6\text{OH}^{2+} + \text{H}^+ + \text{N}_2$                      | $250 \pm 20 \text{ s}^{-1}$                                  | —                    | $20 \pm 2$         | nat      | pr     | Measured from decay of $\text{Ru}(\text{NH}_3)_6\text{N}_2^{3+}$ absorption.                                                                                                                                                                                                        | Baxe.71-0234  |
|                                                                                                                                                                                              | $270 \pm 20 \text{ s}^{-1}$                                  | —                    | $20 \pm 2$         | nat      | pr     | Measured from the formation of $\text{Ru}(\text{NH}_3)_6\text{OH}^{2+}$ . Ru product characterised by its absorption spectrum $G(\text{N}_2) = 0.7 (= 2 G_{\text{ea}} + G_{\text{on}})$ measured in $\gamma$ -radiolysis experiments with $\text{N}_2\text{O}$ saturated solutions. | Baxe.71-0234  |

TABLE 19. Ruthenium(I), (II), (III) and (IV) reactions — Continued

| No.  | Reaction                                                                                                                                                                                                                                      | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ }^a$ | $I$                | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                                                                                                                                      | Ref.      |
|------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|--------------------|--------------------|-----|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 19.8 | $\text{Ru}^{\text{IV}}$ (The precise nature of these complexes is uncertain; all were formed by OH oxidation of the corresponding $\text{Ru}^{\text{III}}$ complex).<br>$\text{Ru}(\text{NH}_3)_6^{4+} + \text{Ru}(\text{NH}_3)_6^{4+}$ (dia) | $4.5 \times 10^8$                                          | $3 \times 10^{-2}$ | 20                 | nat | pr     | Unclear whether rate constant refers to $k$ or $2k$ . A product of this reaction (possibly $\text{Ru}(\text{NH}_3)_6^{3+}$ ) decays by a first order process with $k = 0.75 \text{ s}^{-1}$ . Further, slower reactions ensue before the formation of the stable products, and these presumably are due to aquation and hydrolysis reactions. | Baxe..70- |
| 19.9 | $\text{Ru}(\text{NH}_3)_5\text{Cl}^{3+} \rightarrow$<br>products                                                                                                                                                                              | $2.5 \times 10^8 \text{ s}^{-1}$                           | $3 \times 10^{-2}$ | 20                 | nat | pr     | The product of this reaction undergoes two further unimolecular reactions with rate constants of 44 and $0.45 \text{ s}^{-1}$ . These are probably associated with aquation and hydrolysis reactions.                                                                                                                                         | Baxe..70- |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 20. Samarium(II) reactions

| No.   | Reaction                                                                       | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>  | $I$                                                             | $t/^\circ\text{C}$ | pH          | Method         | Comments    | Ref.                                         |
|-------|--------------------------------------------------------------------------------|-------------------------------------------------------------|-----------------------------------------------------------------|--------------------|-------------|----------------|-------------|----------------------------------------------|
| 20.1  | $\text{Sm}^{2+}_{\text{aq}} + \text{BrO}_3^- (\text{et})$                      | $7.1 \times 10^6$<br>$(7.0 \pm 0.5) \times 10^7$            | 0.015<br>0.0375                                                 | RT<br>RT           | nat<br>6    | pr<br>pr       | -<br>-      | Fara.72-0065<br>Pika.73-1084                 |
| 20.2  | $\text{Sm}^{2+} + \text{Co}(\text{en})_3^{3+}$                                 | $< 1 \times 10^6$                                           | 0.06-<br>1.0                                                    | RT                 | 6           | pr             | -           | Fara.73-0107                                 |
| 20.3  | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{Br}^{2+} (\text{et})$          | $3.5 \times 10^7$<br>$1.6 \times 10^8$<br>$2.5 \times 10^8$ | 0.06<br>1.0<br>( $\text{NaClO}_4$ )<br>1.0<br>( $\text{NaCl}$ ) | RT<br>RT<br>RT     | 6<br>6<br>6 | pr<br>pr<br>pr | -<br>-<br>- | Fara.73-0107<br>Fara.73-0107<br>Fara.73-0107 |
| 20.4  | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{Cl}^{2+} (\text{et})$          | $3.8 \times 10^7$<br>$1.7 \times 10^8$<br>$2.3 \times 10^8$ | 0.06<br>1.0<br>( $\text{NaClO}_4$ )<br>1.0<br>( $\text{NaCl}$ ) | RT<br>RT<br>RT     | 6<br>6<br>6 | pr<br>pr<br>pr | -<br>-<br>- | Fara.73-0107<br>Fara.73-0107<br>Fara.73-0107 |
| 20.5  | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{CN}^{2+}$                      | $< 3.0 \times 10^6$                                         | 0.06                                                            | RT                 | 6           | pr             | -           | Fara.73-0107                                 |
| 20.6  | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{F}^{2+} (\text{et})$           | $2.5 \times 10^7$<br>$1.1 \times 10^8$<br>$1.8 \times 10^8$ | 0.06<br>1.0<br>( $\text{NaClO}_4$ )<br>1.0<br>( $\text{NaCl}$ ) | RT<br>RT<br>RT     | 6<br>6<br>6 | pr<br>pr<br>pr | -<br>-<br>- | Fara.73-0107<br>Fara.73-0107<br>Fara.73-0107 |
| 20.7  | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{2+} (\text{et})$ | $6.0 \times 10^6$<br>$8.8 \times 10^6$<br>$2.6 \times 10^7$ | 0.3<br>1.0<br>( $\text{NaClO}_4$ )<br>1.0<br>( $\text{NaCl}$ )  | RT<br>RT<br>RT     | -<br>-<br>- | pr<br>pr<br>pr | -<br>-<br>- | Fara.73-0107<br>Fara.73-0107<br>Fara.73-0107 |
| 20.8  | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{I}^{2+} (\text{et})$           | $5.8 \times 10^7$                                           | 0.06                                                            | RT                 | 6           | pr             | -           | Fara.73-0107                                 |
| 20.9  | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{N}_3^{2+} (\text{et})$         | $7.8 \times 10^7$<br>$2.5 \times 10^8$                      | 0.06<br>0.5<br>( $\text{NaClO}_4$ )                             | RT<br>RT           | 6<br>6      | pr<br>pr       | -<br>-      | Fara.73-0107<br>Fara.73-0107                 |
| 20.10 | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$                     | $< 1.0 \times 10^6$<br>$< 1.0 \times 10^6$                  | 0.06<br>0.5<br>( $\text{NaClO}_4$ )                             | RT<br>RT           | 6<br>6      | pr<br>pr       | -<br>-      | Fara.73-0107<br>Fara.73-0107                 |
| 20.11 | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_6^{3+} (\text{et})$                   | $< 1.0 \times 10^6$<br>$5.0 \times 10^6$                    | 0.06<br>1.0<br>( $\text{NaCl}$ )                                | RT<br>RT           | 6<br>6      | pr<br>pr       | -<br>-      | Fara.73-0107<br>Fara.73-0107                 |
| 20.12 | $\text{Sm}^{2+} + \text{Co}(\text{NH}_3)_6\text{OH}^{2+} (\text{et})$          | $1.5 \times 10^7$<br>$5.0 \times 10^7$<br>$5.0 \times 10^7$ | 0.3<br>1.0<br>( $\text{NaClO}_4$ )<br>1.0<br>( $\text{NaCl}$ )  | RT<br>RT<br>RT     | -<br>-<br>- | pr<br>pr<br>pr | -<br>-<br>- | Fara.73-0107<br>Fara.73-0107<br>Fara.73-0107 |
| 20.13 | $\text{Sm}^{2+} + \text{CrO}_4^{2-} (\text{et})$                               | $(4.0 \pm 0.5) \times 10^6$                                 | 0.375                                                           | RT                 | 6           | pr             | -           | Pika.73-1084                                 |
| 20.14 | $\text{Sm}^{2+} + \text{Cu}^{2+} (\text{et})$                                  | $8.3 \times 10^7$                                           | 0.015                                                           | RT                 | nat         | pr             | -           | Fara.72-0065                                 |
| 20.15 | $\text{Sm}^{2+} + \text{H}_2\text{O}_2 (\text{et})$                            | $3.5 \times 10^7$<br>$(6.7 \pm 0.3) \times 10^7$            | 0.015<br>0.375                                                  | RT<br>RT           | nat<br>6    | pr<br>pr       | -<br>-      | Fara.72-0065<br>Pika.73-1084                 |
| 20.16 | $\text{Sm}^{2+} + \text{Eu}^{3+} (\text{et})$                                  | $7.5 \times 10^6$                                           | 0.015                                                           | RT                 | nat         | pr             | -           | Fara.72-0065                                 |
| 20.17 | $\text{Sm}^{2+} + \text{IO}_3^- (\text{et})$                                   | $4.9 \times 10^7$                                           | 0.015                                                           | RT                 | nat         | pr             | -           | Fara.72-0065                                 |
| 20.18 | $\text{Sm}^{2+} + \text{MnO}_4^- (\text{et})$                                  | $(4.7 \pm 0.5) \times 10^6$<br>$6.5 \times 10^6$            | 0.375<br>0.015                                                  | RT<br>RT           | 6<br>nat    | pr<br>pr       | -<br>-      | Pika.73-1084<br>Fara.72-0065                 |
| 20.19 | $\text{Sm}^{2+} + \text{NO}_2^- (\text{et})$                                   | $1.1 \times 10^8$<br>$(1.3 \pm 0.2) \times 10^8$            | $\rightarrow 0$<br>0.375                                        | RT<br>RT           | nat<br>6    | pr<br>pr       | -<br>-      | Fara.72-0065<br>Pika.73-1084                 |
| 20.20 | $\text{Sm}^{2+} + \text{NO}_3^- (\text{et})$                                   | $(1.5 \pm 0.2) \times 10^8$<br>$2.0 \times 10^8$            | 0.375<br>0.015                                                  | RT<br>RT           | 6<br>nat    | pr<br>pr       | -<br>-      | Pika.73-1084<br>Fara.72-0065                 |
| 20.21 | $\text{Sm}^{2+} + \text{N}_2\text{O} (\text{et}?)$                             | $2.0 \times 10^8$                                           | 0.015                                                           | RT                 | nat         | pr             | -           | Fara.72-0065                                 |

TABLE 20. Samarium(II) reactions — Continued

| No.   | Reaction                                                                   | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$                         | $t/^\circ\text{C}$ | pH  | Method | Comments | Ref.         |
|-------|----------------------------------------------------------------------------|--------------------------------------------------------------|-----------------------------|--------------------|-----|--------|----------|--------------|
| 20.22 | $\text{Sm}^{2+} + \text{O}_2$ (af or et)                                   | $3.9 \times 10^8$                                            | 0.015                       | RT                 | nat | pr     | —        | Fara.72-0065 |
|       |                                                                            | $(4.2 \pm 0.5) \times 10^8$                                  | 0.375                       | RT                 | 3-6 | pr     | —        | Pika.73-1084 |
| 20.23 | $\text{Sm}^{2+} + \text{OH}$ (et)                                          | $6 \times 10^9$                                              | —                           | RT                 | nat | pr     | —        | Fara.72-0065 |
|       |                                                                            | $(6.2 \pm 0.8) \times 10^9$                                  | 0.375                       | RT                 | 3-6 | pr     | —        | Pika.73-1084 |
| 20.24 | $\text{Sm}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Br}^{2+}$<br>(et)          | $1.5 \times 10^8$                                            | 0.06                        | RT                 | 6   | pr     | —        | Fara.73-0107 |
| 20.25 | $\text{Sm}^{2+} + \text{Ru}(\text{NH}_3)_6\text{Cl}^{2+}$<br>(et)          | $1.5 \times 10^8$                                            | 0.06                        | RT                 | 6   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $4.3 \times 10^8$                                            | 1.0<br>( $\text{NaClO}_4$ ) | RT                 | 6   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $6.5 \times 10^8$                                            | 1.0<br>( $\text{NaCl}$ )    | RT                 | 6   | pr     | —        | Fara.73-0107 |
| 20.26 | $\text{Sm}^{2+} + \text{Ru}(\text{NH}_3)_6\text{H}_2\text{O}^{3+}$<br>(et) | $6.5 \times 10^7$                                            | 0.3                         | RT                 | 2   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $1.8 \times 10^8$                                            | 1.0<br>( $\text{NaClO}_4$ ) | RT                 | 2   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $1.3 \times 10^9$                                            | 1.0<br>( $\text{NaCl}$ )    | RT                 | 2   | pr     | —        | Fara.73-0107 |
| 20.27 | $\text{Sm}^{2+} + \text{Ru}(\text{NH}_3)_6\text{I}^{2+}$<br>(et)           | $ca. 10^8$                                                   | 0.06                        | RT                 | 6   | pr     | —        | Fara.73-0107 |
| 20.28 | $\text{Sm}^{2+} + \text{Ru}(\text{NH}_3)_6\text{OH}^{2+}$<br>(et)          | $4.0 \times 10^7$                                            | 0.06                        | RT                 | 6   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $2.2 \times 10^8$                                            | 1.0<br>( $\text{NaClO}_4$ ) | RT                 | 6   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $6.0 \times 10^8$                                            | 1.0<br>( $\text{NaCl}$ )    | RT                 | 6   | pr     | —        | Fara.73-0107 |
| 20.29 | $\text{Sm}^{2+} + \text{Ru}(\text{NH}_3)_6\text{S}^{3+}$<br>(et)           | $2.5 \times 10^7$                                            | 0.06                        | RT                 | 6   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $2.0 \times 10^8$                                            | 1.0<br>( $\text{NaClO}_4$ ) | RT                 | 6   | pr     | —        | Fara.73-0107 |
|       |                                                                            | $8.0 \times 10^8$                                            | 1.0<br>( $\text{NaCl}$ )    | RT                 | 6   | pr     | —        | Fara.73-0107 |
| 20.30 | $\text{Sm}^{2+} + \text{Yb}^{3+}$ (et)                                     | $3.0 \times 10^8$                                            | 0.015                       | RT                 | nat | pr     | —        | Fara.72-0065 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 21. Thallium(0) and (II) reactions

| No.   | Reaction                                                                                                                                  | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$                       | $t/^\circ\text{C}$ | pH              | Method         | Comments                                                                                                                                                                                                                                                                                                      | Ref.                           |
|-------|-------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|---------------------------|--------------------|-----------------|----------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|
| 21.1  | $\text{Tl}^0$<br>$\text{Tl}_2\text{O}_3$<br>$\text{Tl}^0 + \text{H}_2\text{O}_2 \rightarrow$<br>$\text{Tl}^+ + \text{OH}^- + \text{OH}^-$ | $5 \times 10^6$                                            | -                         | RT                 | 0.1, 5.2        | $\gamma$       | Rate constant and products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Tl}^+$ solutions.                                                                                                                                                                       | Fara..71-0036                  |
| 21.2  | $\text{Tl}^0 + \text{HO}_2 \rightarrow$<br>$\text{Tl}^+ + \text{HO}_2^-$                                                                  | $< 10^7$<br>$1.3 \times 10^{10}$                           | -                         | RT                 | nat<br>0.1, 5.2 | pr<br>$\gamma$ | -<br>Rate constant and products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Tl}^+$ solutions.                                                                                                                                                                  | Fara..71-0036<br>Fara..71-0036 |
| 21.3  | $\text{Tl}^0 + \text{O}_2 \rightarrow$<br>$\text{Tl}^+ + \text{O}_2^-$                                                                    | $(1.0 \pm 0.2) \times 10^7$                                | -                         | RT                 | nat             | pr             | -                                                                                                                                                                                                                                                                                                             | Fara..71-0036                  |
| 21.4  | $\text{Tl}^0 + \text{O}_2^- \rightarrow$<br>$\text{Tl}^+ + \text{O}_2^{2-}$                                                               | $1.4 \times 10^9$                                          | -                         | RT                 | 5.2             | $\gamma$       | Rate constant and products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Tl}^+$ solutions.                                                                                                                                                                       | Fara..71-0036                  |
| 21.5  | $\text{Tl}^0 + \text{Tl}^+ \rightleftharpoons$<br>$\text{Tl}_2^+$                                                                         | $K = 2.3 \times 10^8 \text{M}^{-1}$<br>$k_t > 10^{10}$     | -                         | RT                 | 6.5             | pr             | Measured from the effect of $[\text{Tl}^+]$ on the absorption due to $\text{Tl}_2^+$ .                                                                                                                                                                                                                        | Cerc..66-0097                  |
| 21.6  | $\text{Tl}^0 + \text{Tl}^{\text{II}} \rightarrow$<br>$\text{Tl}^+ + \text{Tl}^{\text{I}}$                                                 | $(4.5 \pm 1) \times 10^9$                                  | -                         | RT                 | nat             | pr             | Products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Tl}^+$ solutions. No account taken of the hydrolysis of $\text{Tl}^{2+}$ (see entry 21.19). No account taken of competing reaction $\text{Tl}_2^+ + \text{Tl}^{\text{II}} \rightarrow$ (see entry 21.12). | Fara..71-0036                  |
| 21.7  | $\text{Tl}^0 (?) + 1,4\text{-benzo-quinone} \rightarrow \text{Tl}^+ + (1,4\text{-benzo-quinone})^-$<br>$\text{Tl}_2^+$                    | $2.8 \times 10^9$                                          | -                         | ca. 25             | 7.0             | pr             | Semiquinone product identified by its absorption spectrum.                                                                                                                                                                                                                                                    | Rao.75-1032                    |
| 21.8  | $\text{Tl}_2^+ + \text{H}_2\text{O}_2 \rightarrow$<br>$2\text{Tl}^+ + \text{OH}^- + \text{OH}^-$                                          | $(7 \pm 2) \times 10^6$                                    | -                         | RT                 | nat             | pr             | Products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Tl}^+$ solutions.                                                                                                                                                                                         | Fara..71-0036                  |
| 21.9  | $\text{Tl}_2^+ + \text{N}_2\text{O}$<br>(O at or et)                                                                                      | $(1.4 \pm 0.2) \times 10^7$                                | -                         | 25                 | nat             | pr             | $\gamma$ -radiolysis studies indicate that $\text{N}_2$ is one of the products of this reaction.                                                                                                                                                                                                              | Sell72-0844                    |
| 21.10 | $\text{Tl}_2^+ + \text{O}_2 \rightarrow$<br>$2\text{Tl}^+ + \text{O}_2^-$                                                                 | $(1.0 \pm 0.2) \times 10^7$<br>$1.2 \times 10^7$           | -                         | RT                 | nat<br>0.1, 5.2 | pr<br>$\gamma$ | -<br>Rate constant and products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Tl}^+$ solutions.                                                                                                                                                                  | Fara..71-0036<br>Fara..71-0036 |
| 21.11 | $\text{Tl}_2^+ \rightleftharpoons \text{Tl}^0 + \text{Tl}^+$                                                                              | see entry 21.5                                             |                           |                    |                 |                |                                                                                                                                                                                                                                                                                                               |                                |
| 21.12 | $\text{Tl}_2^+ + \text{Tl}^{\text{II}} \rightarrow$<br>$3\text{Tl}^+$                                                                     | $(4.4 \pm 0.9) \times 10^8$<br>$(4.5 \pm 1) \times 10^9$   | $\rightarrow 0$<br>0.0006 | RT                 | nat             | pr             | Products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Tl}^+$ solutions. No account taken of the hydrolysis of $\text{Tl}^+$ (see entry 21.19).                                                                                                                  | Cerc..66-0097<br>Fara..71-0036 |
|       |                                                                                                                                           | $(7.5 \pm 1) \times 10^8$                                  | 0.015                     | RT                 | nat             | pr             |                                                                                                                                                                                                                                                                                                               |                                |

TABLE 21. Thallium(0) and (II) reactions — Continued

| No.                                                                                                   | Reaction                                                                                                                                | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>                                         | $I$                  | $t/^\circ\text{C}$ | pH                | Method         | Comments                                                                                                                                                                                                               | Ref.           |
|-------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|----------------------|--------------------|-------------------|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| 21.13                                                                                                 | $\text{Ti}_2^+ + 1,4\text{-dicyano-}$<br>$\text{benzene} \rightarrow 2\text{Ti}^+ +$<br>$(1,4\text{-dicyanobenzene})^-$                 | $2.7 \times 10^9$                                                                                    | —                    | RT                 |                   | pr             | Organic product characterised by its absorption spectrum.                                                                                                                                                              | Robi.73-0121   |
| $\text{Ti}^{\text{II}}$ (Rate constants from pulse radiolysis and flash photolysis experiments only). |                                                                                                                                         |                                                                                                      |                      |                    |                   |                |                                                                                                                                                                                                                        |                |
| 21.14                                                                                                 | $\text{Ti}_2^{3+} \text{ and } \text{TiOH}^+$<br>$\text{Ti}^{2+} + \text{Co}^{3+} \rightleftharpoons$<br>$\text{Ti}^+ + \text{Co}^{2+}$ | $k_t = (6.2 \pm 0.5) \times 10^8$                                                                    | 0.75                 | 25                 | 0.6               | f.ph.          | Evidence for products and equilibrium from conventional kinetic studies.                                                                                                                                               | Falc..74-7625  |
| 21.15                                                                                                 | $\text{Ti}^{2+} + \text{Co}^{3+} \rightarrow$<br>$\text{Ti}^{3+} + \text{Co}^{2+}$                                                      | $(9.5 \pm 0.5) \times 10^6$                                                                          | 0.55                 | $22 \pm 2$         | 0.3               | f.ph.          | Evidence for products from conventional kinetic studies.                                                                                                                                                               | Falc..75-7093  |
| 21.16                                                                                                 | $\text{Ti}^{2+} + \text{Fe}^{3+} \rightarrow$<br>$\text{Ti}^+ + \text{Fe}^{2+}$                                                         | $(2.42 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 14.7               | 0.6               | f.ph.          | Evidence for products from conventional kinetic studies.                                                                                                                                                               | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(2.50 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 18.3               | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(2.53 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 20.7               | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(2.60 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 24.8               | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(2.70 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 29.0               | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(2.73 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 33.9               | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(2.81 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 36.0               | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(2.91 \pm 0.1) \times 10^6$                                                                         | 0.30                 | 39.6               | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $E_a = 48 \pm 2 \text{ kJ mol}^{-1}$                                                                 | 0.30                 | 14-40              | 0.6               | f.ph.          |                                                                                                                                                                                                                        | Falc..75-7093  |
|                                                                                                       |                                                                                                                                         | $(6.7 \pm 0.7) \times 10^6$                                                                          | 1                    | 23                 | 0                 | pr             |                                                                                                                                                                                                                        | Schw...74-1017 |
|                                                                                                       |                                                                                                                                         |                                                                                                      | (HClO <sub>4</sub> ) |                    |                   |                |                                                                                                                                                                                                                        |                |
| 21.17                                                                                                 | $\text{Ti}^{2+} + \text{Fe}^{3+} \rightleftharpoons$<br>$\text{Ti}^{3+} + \text{Fe}^{2+}$                                               | $(1.1 \pm 0.15) \times 10^6$                                                                         | 0.30                 | 25                 | 0.6               | f.ph.          | Evidence for products and equilibrium from conventional kinetic studies.                                                                                                                                               | Falc..74-7625  |
| 21.18                                                                                                 | $\text{Ti}^{2+} + \text{HO}_2 \rightarrow$<br>$\text{Ti}^+ + \text{H}^+ + \text{O}_2$                                                   | $(2.5 \pm 1) \times 10^9$                                                                            | —                    | RT                 | 1                 | pr             | Estimated from initial decay of $\text{Ti}^{\text{II}}$ in aerated solutions.                                                                                                                                          | Cerc..66-0097  |
| 21.19                                                                                                 | $\text{Ti}^{2+} + \text{H}_2\text{O} \rightleftharpoons$<br>$\text{TiOH}^+ + \text{H}^+$                                                | $pK = 4.6 \pm 0.2$<br>$k_t = 3.5 \times 10^8 \text{ s}^{-1}$<br>$k_r = (1.4 \pm 0.5) \times 10^{10}$ | var<br>var<br>var    | 21<br>21<br>21     | 2-7<br>2-7<br>2-7 | pr<br>pr<br>pr | Evidence for equilibrium from optical and conductivity measurements.                                                                                                                                                   | O'Ne.75-1130   |
| 21.20                                                                                                 | $\text{Ti}^{2+} + \text{H}_2\text{O}_2 \rightarrow$<br>$\text{Ti}^+ + \text{HO}_2 + \text{H}^+$                                         | $(2.8 \pm 0.8) \times 10^7$                                                                          | —                    | RT                 | 1                 | pr             | Evidence for products from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Ti}^{\text{I}}$ solutions. (see ref. 71-0036).                                                                | Cerc..66-0097  |
| 21.21                                                                                                 | $\text{Ti}^{2+} + \text{Mn}^{3+} \rightarrow$<br>$\text{Ti}^+ + \text{Mn}^{2+}$                                                         | $(1.9 \pm 0.2) \times 10^4$                                                                          | 0.75                 | $22 \pm 3$         | 0.3               | f.ph.          | Evidence for products from conventional kinetic studies etc. (see ref. 75-7093).                                                                                                                                       | Falc..75-7093  |
| 21.22                                                                                                 | $\text{Ti}^{\text{II}} + \text{O}_2^- \rightarrow$<br>$\text{Ti}^{\text{I}} + \text{O}_2$                                               | $2 \times 10^{10}$                                                                                   | —                    | RT                 | 5.2               | $\gamma$       | Rate constant and products deduced from $\text{H}_2\text{O}_2$ and $\text{H}_2$ yields in $\gamma$ -irradiated $\text{Ti}^{\text{I}}$ solutions. No account taken of hydrolysis of $\text{Ti}^{2+}$ (see entry 21.19). | Fara..71-0036  |
| 21.23                                                                                                 | $\text{Ti}^{\text{II}} + \text{Ti}^0$                                                                                                   | see entry 21.6                                                                                       |                      |                    |                   |                |                                                                                                                                                                                                                        |                |
| 21.24                                                                                                 | $\text{Ti}^{\text{II}} + \text{Ti}_2^+$                                                                                                 | see entry 21.12                                                                                      |                      |                    |                   |                |                                                                                                                                                                                                                        |                |

TABLE 21. Thallium(0) and (II) reactions — Continued

| No.   | Reaction                                                   | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>      | $I$                      | $t/^\circ\text{C}$ | pH    | Method   | Comments                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Ref.           |
|-------|------------------------------------------------------------|-------------------------------------------------------------------|--------------------------|--------------------|-------|----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------|
| 21.25 | $\text{Tl}^{2+} + \text{Tl}^{2+}$ (dis)                    | $2k = (3.8 \pm 0.6) \times 10^8$                                  | 1<br>( $\text{HClO}_4$ ) | 23                 | 0     | pr       | Measured from decay of $\text{Tl}^{2+}$ monitored at 280 nm. Value of $\epsilon_{280}$ used to calculate rate constant not given, but is ca. $3200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .                                                                                                                                                                                                                                                                                                                                        | Schw...74-1017 |
|       |                                                            | $2k = (5.2 \pm 0.5) \times 10^8$                                  | 0.25                     | 25                 | 1     | f.ph.    | Measured from decay of $\text{Tl}^{2+}$ monitored at 270 nm. Rate constant calculated taking $\epsilon_{270} = 5500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . This value was obtained by interpolation from the measured spectrum of $\text{Tl}^{2+}$ and the value of $\epsilon_{280} = 5400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ measured by Cercek <i>et al</i> (ref. 66-0097). Note however that this latter value was measured in solutions at pH ca. 6.5 and refers therefore to $\text{TlOH}^+$ (see entry 21.19). | Falc...74-7625 |
|       |                                                            | $2k = (5.5 \pm 0.5) \times 10^8$                                  | 0.25                     | 25                 | 0.6   | f.ph.    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |
|       |                                                            | $2k = (9.2 \pm 0.9) \times 10^8$                                  | 0.50                     | 25                 | 0.6   | f.ph.    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |
|       |                                                            | $2k = (1.3 \pm 0.1) \times 10^9$                                  | 1.0                      | 25                 | 0.6   | f.ph.    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |
|       |                                                            | $2k = (1.2 \pm 0.1) \times 10^9$                                  | 1.0                      | 25                 | 0.3   | f.ph.    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |
|       |                                                            | $2k = (1.3 \pm 0.1) \times 10^9$                                  | 1.0                      | 25                 | 0     | f.ph.    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |
|       |                                                            | $E_a = 7.9 \pm 1.5 \text{ kJ mol}^{-1}$                           | —                        | 15-45              | —     | f.ph.    |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |
|       |                                                            | $2k/\epsilon_{270} = (6.1 \pm 0.6) \times 10^4 \text{ cm s}^{-1}$ | 1<br>( $\text{HClO}_4$ ) | $25 \pm 2$         | 0     | f.ph.    | Measured in the presence of $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ Tl}^{\text{III}}$ and $1 \times 10^{-4} \text{ mol dm}^{-3} \text{ Tl}^{\text{I}}$ .                                                                                                                                                                                                                                                                                                                                                                              | Burc.70-7309   |
|       |                                                            | $2k/\epsilon_{270} = (1.3 \pm 0.2) \times 10^6 \text{ cm s}^{-1}$ | 1<br>( $\text{HClO}_4$ ) | $25 \pm 2$         | 0     | f.ph.    | Measured in the presence of $5 \times 10^{-3} \text{ mol dm}^{-3} \text{ Tl}^{\text{III}}$ and $5 \times 10^{-2} \text{ mol dm}^{-3}$ 2-propanol.                                                                                                                                                                                                                                                                                                                                                                                          | Burc.70-7309   |
|       |                                                            |                                                                   |                          |                    |       |          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                |
| 21.26 | $\text{TlOH}^+ + \text{TlOH}^+$<br>(dis)                   | $2k = (4.6 \pm 1.6) \times 10^9$                                  | ca. 0                    | RT                 | 6.5   | pr       | Measured from decay of $\text{TlOH}^+$ monitored at 260 nm. Rate constant calculated taking $\epsilon_{260} = 5400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .                                                                                                                                                                                                                                                                                                                                                                        | Cerc..66-0097  |
|       |                                                            | $2k = 5 \times 10^9$                                              | —                        | RT                 | > 5.5 | pr       | Extinction coefficient used to calculate rate constant not given.                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | O'Ne.75-1130   |
| 21.27 | $\text{Tl}^{2+} + \cdot\text{CH}_2\text{OH}$<br>(et or af) | $(1.2 \pm 0.3) \times 10^4$                                       | —                        | $23 \pm 2$         | 0.43  | $\gamma$ | Estimated from the $\gamma$ -ray induced chain reaction in $\text{Tl}^{\text{II}} + \text{methanol}$ solutions, taking $k(\text{Tl}^{\text{II}} + \text{Tl}^{\text{II}}) = 5.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see entry 21.25).                                                                                                                                                                                                                                                                                | Burc.70-0336   |
| 21.28 | $\text{Tl}^{2+} + \text{CH}_3\text{C HOH}$<br>(et or af)   | $(1.5 \pm 0.4) \times 10^4$                                       | —                        | $23 \pm 2$         | 0.43  | $\gamma$ | Estimated from the $\gamma$ -ray induced chain reaction in $\text{Tl}^{\text{II}} + \text{ethanol}$ solutions, taking $k(\text{Tl}^{\text{II}} + \text{Tl}^{\text{II}}) = 5.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see entry 21.25).                                                                                                                                                                                                                                                                                 | Burc.70-0336   |

TABLE 21. Thallium(0) and (II) reactions — Continued

| No.   | Reaction                                                                                                              | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | <i>I</i> | <i>t</i> /°C | pH      | Method   | Comments                                                                                                                                                                                                                                              | Ref.                           |
|-------|-----------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|----------|--------------|---------|----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|
| 21.29 | $\text{Tl}^{2+} + \text{CH}_3\text{COHCH}_3$<br>(et or af)                                                            | $(9.4 \pm 2.3) \times 10^8$                                | —        | $23 \pm 2$   | 0.43    | $\gamma$ | Estimated from the $\gamma$ -ray induced chain reaction in $\text{Tl}^{\text{II}} + 2$ -propanol solutions, taking $k(\text{Tl}^{\text{II}} + \text{Tl}^{\text{II}}) = 5.5 \times 10^8 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (see entry 21.25). | Burc.70-0336                   |
| 21.30 | $\text{Tl}^{2+} + \text{anisole} \rightarrow \text{Tl}^+ + (\text{anisole})^+$                                        | $(5.0 \pm 0.5) \times 10^8$                                | —        | $20 \pm 2$   | 4       | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1171                  |
| 21.31 | $\text{Tl}^{2+} + 1,2\text{-dimethoxybenzene} \rightarrow \text{Tl}^+ + (1,2\text{-dimethoxybenzene})^+$              | $(6.0 \pm 0.6) \times 10^8$                                | —        | $20 \pm 2$   | 4       | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1171<br>O'Ne..75-1086 |
| 21.32 | $\text{TlOH}^+ + 1,2\text{-dimethoxybenzene} \rightarrow \text{Tl}^+ + \text{OH}^- + (1,2\text{-dimethoxybenzene})^+$ | $1.2 \times 10^9$                                          | —        | RT           | $> 4.7$ | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1086                  |
| 21.33 | $\text{Tl}^{2+} + 1,3\text{-dimethoxybenzene} \rightarrow \text{Tl}^+ + (1,3\text{-dimethoxybenzene})^+$              | $(8.0 \pm 0.8) \times 10^8$                                | —        | $20 \pm 2$   | 4       | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1171                  |
| 21.34 | $\text{Tl}^{2+} + 1,4\text{-dimethoxybenzene} \rightarrow \text{Tl}^+ + (1,4\text{-dimethoxybenzene})^+$              | $(6.5 \pm 0.7) \times 10^8$                                | —        | $20 \pm 2$   | 4       | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1086<br>O'Ne..75-1171 |
| 21.35 | $\text{TlOH}^+ + 1,4\text{-dimethoxybenzene} \rightarrow \text{Tl}^+ + \text{OH}^- + (1,4\text{-dimethoxybenzene})^+$ | $4.5 \times 10^8$                                          | —        | RT           | $> 4.7$ | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1086                  |
| 21.36 | $\text{TlOH}^+ + \text{menaquinone}$                                                                                  | slow                                                       | —        | RT           | 6.8     | pr       | —                                                                                                                                                                                                                                                     | Rao.73-1047                    |
| 21.37 | $\text{Tl}^{2+} + 1,2,3\text{-trimethoxybenzene} \rightarrow \text{Tl}^+ + (1,2,3\text{-trimethoxybenzene})^+$        | $(3.2 \pm 0.3) \times 10^8$                                | —        | $20 \pm 2$   | 4       | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1171                  |
| 21.38 | $\text{Tl}^{2+} + 1,2,4\text{-trimethoxybenzene} \rightarrow \text{Tl}^+ + (1,2,4\text{-trimethoxybenzene})^+$        | $(6.8 \pm 0.7) \times 10^8$                                | —        | $20 \pm 2$   | 4       | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1171                  |
| 21.39 | $\text{Tl}^{2+} + 1,3,5\text{-trimethoxybenzene} \rightarrow \text{Tl}^+ + (1,3,5\text{-trimethoxybenzene})^+$        | $(7.0 \pm 0.7) \times 10^8$                                | —        | $20 \pm 2$   | 4       | pr       | Radical cation product characterised by its absorption and esr spectra.                                                                                                                                                                               | O'Ne..75-1171                  |

TABLE 21. Thallium(0) and (II) reactions — Continued

| No.                                                | Reaction                                                           | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>   | $I$                       | $t/^\circ\text{C}$ | pH | Method | Comments                                                                                | Ref.         |
|----------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------|---------------------------|--------------------|----|--------|-----------------------------------------------------------------------------------------|--------------|
| <i>Tl<sup>II</sup> chloro-complexes</i>            |                                                                    |                                                              |                           |                    |    |        |                                                                                         |              |
| 21.40                                              | $\text{Tl}^{3+} + \text{Cl}^- \rightleftharpoons \text{TlCl}^+$    | $K = (6.2 \pm 0.7) \times 10^4 \text{ dm}^3 \text{mol}^{-1}$ | 1<br>(HClO <sub>4</sub> ) | 23                 | 0  | pr     | Measured from effect of [Cl <sup>-</sup> ] on absorption spectrum of Tl <sup>II</sup> . | Dods.74-1038 |
|                                                    |                                                                    | $k_t = 9 \times 10^9$                                        | 1<br>(HClO <sub>4</sub> ) | 23                 | 0  | pr     | Measured from rate of attainment of equilibrium.                                        | Dods.74-1038 |
|                                                    |                                                                    | $k_r = 1.4 \times 10^{10} \text{ s}^{-1}$                    | 1<br>(HClO <sub>4</sub> ) | 23                 | 0  | pr     |                                                                                         |              |
| 21.41                                              | $\text{TlCl}^+ + \text{Cl}^- \rightleftharpoons \text{TlCl}_2^+$   | $K = (1.9 \pm 0.4) \times 10^3 \text{ dm}^3 \text{mol}^{-1}$ | 1<br>(HClO <sub>4</sub> ) | 23                 | 0  | pr     | Measured from effect of [Cl <sup>-</sup> ] on absorption spectrum of Tl <sup>II</sup> . | Dods.74-1038 |
| 21.42                                              | $\text{TlCl}_2^+ + \text{Cl}^- \rightleftharpoons \text{TlCl}_3^+$ | $K = 13 \pm 3 \text{ dm}^3 \text{mol}^{-1}$                  | 1<br>(HClO <sub>4</sub> ) | 23                 | 0  | pr     | Measured from effect of [Cl <sup>-</sup> ] on absorption spectrum of Tl <sup>II</sup> . | Dods.74-1038 |
| 21.43                                              | $\text{Tl}^{\text{II}} + \text{Tl}^{\text{II}} (\text{dis})$       | $2k = 5.38 \times 10^9$                                      | 1                         | 23                 | 0  | pr     | [Cl <sup>-</sup> ] = $1 \times 10^{-3} \text{ mol dm}^{-3}$                             | Dods.74-1038 |
|                                                    |                                                                    | $2k = 5.58 \times 10^9$                                      | 1                         | 23                 | 0  | pr     | [Cl <sup>-</sup> ] = $9.7 \times 10^{-3} \text{ mol dm}^{-3}$                           | Dods.74-1038 |
|                                                    |                                                                    | $2k = 4.74 \times 10^9$                                      | 1                         | 23                 | 0  | pr     | [Cl <sup>-</sup> ] = 0.1 mol dm <sup>-3</sup>                                           | Dods.74-1038 |
|                                                    |                                                                    | $2k = 3.70 \times 10^9$                                      | 1                         | 23                 | 0  | pr     | [Cl <sup>-</sup> ] = 0.98 mol dm <sup>-3</sup>                                          | Dods.74-1038 |
| Plus data at intermediate chloride concentrations. |                                                                    |                                                              |                           |                    |    |        |                                                                                         |              |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 22. Thulium(II) reactions

| No.  | Reaction                                        | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$ | $t/^\circ\text{C}$ | pH  | Method | Comments | Ref.         |
|------|-------------------------------------------------|------------------------------------------------------------|-----|--------------------|-----|--------|----------|--------------|
| 22.1 | $\text{Tm}^{\text{II}} + \text{OH} (\text{et})$ | $(7 \pm 1) \times 10^9$                                    | —   | RT                 | 3-6 | pr     | —        | Pika.73-1084 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 23. Ytterbium(II) reactions

| No.                                                                   | Reaction                                                                        | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup> | $I$                  | $t/^\circ\text{C}$ | pH  | Method | Comments | Ref.         |
|-----------------------------------------------------------------------|---------------------------------------------------------------------------------|------------------------------------------------------------|----------------------|--------------------|-----|--------|----------|--------------|
| $\text{Yb}^{2+}$ (Rate constants from pulse radiolysis studies only). |                                                                                 |                                                            |                      |                    |     |        |          |              |
| 23.1                                                                  | $\text{Yb}^{2+} + \text{BrO}_3^-$                                               | $< 10^8$                                                   | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.2                                                                  | $\text{Yb}^{2+} + \text{Co(en)}_3^{3+}$                                         | $< 5 \times 10^8$                                          | 0.06-1.0             | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.3                                                                  | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{Br}^{2+} \text{ (et)}$          | $3.0 \times 10^8$                                          | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 | $1.4 \times 10^7$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.4                                                                  | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{Cl}^{2+} \text{ (et)}$          |                                                            | ( $\text{NaClO}_4$ ) |                    |     |        |          |              |
|                                                                       |                                                                                 | $2.5 \times 10^7$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 |                                                            | ( $\text{NaCl}$ )    |                    |     |        |          |              |
|                                                                       |                                                                                 | $4.3 \times 10^8$                                          | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.5                                                                  | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{CN}^{2+} \text{ (et)}$          | $1.9 \times 10^7$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 | $2.3 \times 10^7$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.6                                                                  | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{F}^{2+} \text{ (et)}$           |                                                            | ( $\text{NaClO}_4$ ) |                    |     |        |          |              |
|                                                                       |                                                                                 | $3.0 \times 10^8$                                          | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.7                                                                  | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} \text{ (et)}$ | $1.1 \times 10^7$                                          | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 | $6.0 \times 10^7$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.8                                                                  | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{N}_5^{2+} \text{ (et)}$         |                                                            | ( $\text{NaClO}_4$ ) |                    |     |        |          |              |
|                                                                       |                                                                                 | $1.0 \times 10^8$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 |                                                            | ( $\text{NaCl}$ )    |                    |     |        |          |              |
|                                                                       |                                                                                 | $2.2 \times 10^8$                                          | 0.3                  | RT                 | 2   | pr     | -        | Fara.73-0107 |
| 23.9                                                                  | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$                      | $6.4 \times 10^8$                                          | 1.0                  | RT                 | 2   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 | $1.6 \times 10^7$                                          | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.10                                                                 | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{OH}^{2+} \text{ (et)}$          | $2.6 \times 10^7$                                          | 0.5                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 |                                                            | ( $\text{NaClO}_4$ ) |                    |     |        |          |              |
| 23.11                                                                 | $\text{Yb}^{2+} + \text{Co}(\text{NH}_3)_5\text{OH}^{2+} \text{ (et)}$          | $< 5.0 \times 10^4$                                        | 0.5                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 |                                                            | ( $\text{NaClO}_4$ ) |                    |     |        |          |              |
| 23.12                                                                 | $\text{Yb}^{2+} + \text{Cu}^{2+} \text{ (et)}$                                  | $< 5.0 \times 10^4$                                        | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 | $7.7 \times 10^8$                                          | 0.3                  | RT                 | 5.5 | pr     | -        | Fara.73-0107 |
| 23.13                                                                 | $\text{Yb}^{2+} + \text{H}_2\text{O}_2 \text{ (et)}$                            | $1.9 \times 10^7$                                          | 1.0                  | RT                 | 5.5 | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 | $2.9 \times 10^7$                                          | 1.0                  | RT                 | 5.5 | pr     | -        | Fara.73-0107 |
| 23.14                                                                 | $\text{Yb}^{2+} + \text{IO}_3^- \text{ (et)}$                                   |                                                            | ( $\text{NaClO}_4$ ) |                    |     |        |          |              |
|                                                                       |                                                                                 | $1.2 \times 10^7$                                          | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.15                                                                 | $\text{Yb}^{2+} + \text{MnO}_4^- \text{ (et)}$                                  | $9.1 \times 10^8$                                          | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.16                                                                 | $\text{Yb}^{2+} + \text{NO}_2^- \text{ (et)}$                                   | $2.1 \times 10^8$                                          | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.17                                                                 | $\text{Yb}^{2+} + \text{NO}_3^- \text{ (et)}$                                   | $8.3 \times 10^7$                                          | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.18                                                                 | $\text{Yb}^{2+} + \text{N}_2\text{O} \text{ (et?)}$                             | $4.7 \times 10^7$                                          | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.19                                                                 | $\text{Yb}^{2+} + \text{O}_2 \text{ (et or af)}$                                | $3.6 \times 10^8$                                          | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.20                                                                 | $\text{Yb}^{2+} + \text{OH}^- \text{ (et)}$                                     | $ca. 10^4$                                                 | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
|                                                                       |                                                                                 | $(6.3 \pm 1) \times 10^7$                                  | 0.375                | RT                 | 2   | pr     | -        | Pika.73-1084 |
| 23.21                                                                 | $\text{Yb}^{2+} + \text{Ru}(\text{NH}_3)_5\text{Br}^{2+} \text{ (et)}$          | $6.5 \times 10^7$                                          | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
|                                                                       |                                                                                 | $3 \times 10^9$                                            | 0.015                | RT                 | nat | pr     | -        | Fara.72-0065 |
| 23.22                                                                 | $\text{Yb}^{2+} + \text{Ru}(\text{NH}_3)_5\text{Cl}^{2+} \text{ (et)}$          | $(3.2 \pm 0.3) \times 10^8$                                | 0.375                | RT                 | 2   | pr     | -        | Pika.73-1084 |
|                                                                       |                                                                                 | $3.3 \times 10^7$                                          | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.23                                                                 | $\text{Yb}^{2+} + \text{Ru}(\text{NH}_3)_5\text{Cl}^{2+} \text{ (et)}$          | $1.5 \times 10^7$                                          | 0.06                 | RT                 | 6   | pr     | -        | Fara.73-0107 |
|                                                                       |                                                                                 | $1.8 \times 10^8$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.24                                                                 | $\text{Yb}^{2+} + \text{Ru}(\text{NH}_3)_5\text{Cl}^{2+} \text{ (et)}$          |                                                            | ( $\text{NaClO}_4$ ) |                    |     |        |          |              |
|                                                                       |                                                                                 | $2.8 \times 10^8$                                          | 1.0                  | RT                 | 6   | pr     | -        | Fara.73-0107 |
| 23.25                                                                 | $\text{Yb}^{2+} + \text{Ru}(\text{NH}_3)_5\text{Cl}^{2+} \text{ (et)}$          |                                                            | ( $\text{NaCl}$ )    |                    |     |        |          |              |
|                                                                       |                                                                                 |                                                            |                      |                    |     |        |          |              |

TABLE 23. Ytterbium(II) reactions — Continued

| No.   | Reaction                                                                   | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$                                              | $t/^\circ\text{C}$ | pH | Method | Comments | Ref.         |
|-------|----------------------------------------------------------------------------|--------------------------------------------------------------|--------------------------------------------------|--------------------|----|--------|----------|--------------|
| 23.23 | $\text{Yb}^{3+} + \text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$<br>(et) | $1.0 \times 10^7$                                            | 0.3                                              | RT                 | 2  | pr     | —        | Fara.73-0107 |
|       |                                                                            | $2.9 \times 10^7$                                            | 1.0                                              | RT                 | 2  | pr     | —        | Fara.73-0107 |
|       |                                                                            | $3.2 \times 10^8$                                            | 1.0<br>( $\text{NaClO}_4$ )<br>( $\text{NaCl}$ ) | RT                 | 2  | pr     | —        | Fara.73-0107 |
| 23.24 | $\text{Yb}^{3+} + \text{Ru}(\text{NH}_3)_5\text{I}^{2+}$ (et)              | $\text{ca. } 10^8$                                           | 0.06                                             | RT                 | 6  | pr     | —        | Fara.73-0107 |
| 23.25 | $\text{Yb}^{3+} + \text{Ru}(\text{NH}_3)_6^{3+}$ (et)                      | $5.0 \times 10^8$                                            | 0.06                                             | RT                 | 6  | pr     | —        | Fara.73-0107 |
|       |                                                                            | $4.5 \times 10^7$                                            | 1.0                                              | RT                 | 6  | pr     | —        | Fara.73-0107 |
|       |                                                                            | $3.0 \times 10^8$                                            | 1.0<br>( $\text{NaClO}_4$ )<br>( $\text{NaCl}$ ) | RT                 | 6  | pr     | —        | Fara.73-0107 |
| 23.26 | $\text{Yb}^{3+} + \text{Ru}(\text{NH}_3)_5\text{OH}^{2+}$<br>(et)          | $1.3 \times 10^7$                                            | 0.06                                             | RT                 | 6  | pr     | —        | Fara.73-0107 |
|       |                                                                            | $2.3 \times 10^7$                                            | 0.3                                              | RT                 | 6  | pr     | —        | Fara.73-0107 |
|       |                                                                            | $5.0 \times 10^7$                                            | 1.0                                              | RT                 | 6  | pr     | —        | Fara.73-0107 |
|       |                                                                            | $1.4 \times 10^8$                                            | 1.0<br>( $\text{NaClO}_4$ )<br>( $\text{NaCl}$ ) | RT                 | 6  | pr     | —        | Fara.73-0107 |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for 2  $k$ ).

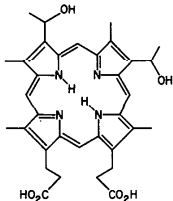
TABLE 24. Zinc(II) reactions

| No.   | Reaction                                                                                           | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ <sup>a</sup>  | $I$                                | $t/^\circ\text{C}$ | pH         | Method         | Comments                                                                                                                                                                                           | Ref.                          |
|-------|----------------------------------------------------------------------------------------------------|-------------------------------------------------------------|------------------------------------|--------------------|------------|----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|
|       | $\text{Zn}^{2+}_{\text{aq}}$                                                                       |                                                             |                                    |                    |            |                |                                                                                                                                                                                                    |                               |
| 24.1  | $\text{Zn}^{2+} + \text{BrO}_3^-$ (et)                                                             | $(2.1 \pm 0.3) \times 10^9$                                 | 0.08                               | RT                 | nat        | pr             | —                                                                                                                                                                                                  | Meye.68-0855                  |
| 24.2  | $\text{Zn}^{2+} + \text{Cd}^{2+}$ (et?)                                                            | $< 1 \times 10^7$<br>$8.3 \times 10^8$                      | 0.08<br>—                          | RT<br>RT           | nat<br>nat | pr<br>pr       | The reason for the discrepancy between these two values is not clear.                                                                                                                              | Meye.68-0855<br>Baxe..66-0848 |
| 24.3  | $\text{Zn}^{2+} + \text{ClO}_3^-$                                                                  | $< 3 \times 10^8$                                           | 0.08                               | RT                 | nat        | pr             | —                                                                                                                                                                                                  | Meye.68-0855                  |
| 24.4  | $\text{Zn}^{2+} + \text{Co}^{2+}$                                                                  | $< 3 \times 10^8$                                           | 0.08                               | RT                 | nat        | pr             | —                                                                                                                                                                                                  | Meye.68-0855                  |
| 24.5  | $\text{Zn}^{2+} + \text{Co}(\text{bpy})_3^{3+}$ (et)                                               | $2.6 \times 10^9$                                           | —                                  | RT                 | nat        | pr             | —                                                                                                                                                                                                  | Baxe..72-0381                 |
| 24.6  | $\text{Zn}^{2+} + \text{Co}(\text{en})_3^{2+}$ (et)                                                | $(2.5 \pm 0.4) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.7  | $\text{Zn}^{2+} + \text{cis-Co}(\text{en})_2\text{Cl}_2^+$ (et)                                    | $(1.91 \pm 0.3) \times 10^8$                                | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.8  | $\text{Zn}^{2+} + \text{trans-Co}(\text{en})_2\text{Cl}_2^+$ (et)                                  | $(2.3 \pm 0.3) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.9  | $\text{Zn}^{2+} + \text{Co}(\text{en})_2\text{CO}_3^+$ (et)                                        | $(4.7 \pm 0.7) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.10 | $\text{Zn}^{2+} + \text{cis-Co}(\text{en})_2\text{F}_2^+$ (et)                                     | $(5.4 \pm 0.8) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.11 | $\text{Zn}^{2+} + \text{Co}(\text{en})_2\text{FH}_2\text{O}^{2+}$ (et)                             | $(4.7 \pm 0.7) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.12 | $\text{Zn}^{2+} + \text{cis-Co}(\text{en})_2\text{NH}_3\text{Cl}^{2+}$ (et)                        | $(1.47 \pm 0.2) \times 10^9$                                | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.13 | $\text{Zn}^{2+} + \text{cis-Co}(\text{en})_2\text{NH}_3\text{NO}_2^{2+}$ (et)                      | $(2.7 \pm 0.7) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.14 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5^{3+}$ (et)                                              | $(8.4 \pm 1.3) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.15 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (et)                                     | $(2.6 \pm 0.4) \times 10^9$                                 | 0.08                               | RT                 | 4.0        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.16 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (et)                                     | $(2.2 \pm 0.3) \times 10^9$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.17 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{CN}^{2+}$ (et)                                     | $(1.30 \pm 0.2) \times 10^9$                                | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.18 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{F}^{2+}$ (et)                                      | $(8.2 \pm 1.2) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.19 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{fumarate}^+$ (et)                                  | $(1.2 \pm 0.3) \times 10^9$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.20 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ (et)                            | $(1.56 \pm 0.2) \times 10^9$                                | 0.08                               | RT                 | 4.0        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.21 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{OH}^{2+}$ (et)                                     | $(1.10 \pm 0.2) \times 10^9$                                | 0.08                               | RT                 | 6.6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.22 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{N}_3^{2+}$ (et)                                    | $(1.49 \pm 0.2) \times 10^9$                                | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.23 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{NCS}^{2+}$ (et)                                    | $(1.65 \pm 0.2) \times 10^9$                                | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.24 | $\text{Zn}^{2+} + \text{Co}(\text{NH}_3)_5\text{OOCCH}_3^{2+}$ (et)                                | $(5.0 \pm 0.8) \times 10^8$                                 | 0.08                               | RT                 | 5-6        | pr             | —                                                                                                                                                                                                  | Meye.69-0428                  |
| 24.25 | $\text{Zn}^{2+} + \text{Cr}^{3+}$                                                                  | $< 10^7$                                                    | —                                  | RT                 | nat        | pr             | —                                                                                                                                                                                                  | Baxe..66-0848                 |
| 24.26 | $\text{Zn}^{2+} + \text{Cr}_2\text{O}_7^{2-}$ (et)                                                 | $(1.6 \pm 0.2) \times 10^{10}$                              | 0.020*                             | 25±2               | nat        | pr             | —                                                                                                                                                                                                  | Buxt..76-1072                 |
| 24.27 | $\text{Zn}^{2+} + \text{Cu}^{2+}$ (et)                                                             | $(2.5 \pm 0.4) \times 10^8$<br>$(9.5 \pm 2.0) \times 10^9$  | 0.08<br>0.4<br>( $\text{ZnSO}_4$ ) | RT<br>RT           | nat<br>5-8 | pr<br>$\gamma$ | Measured by competition with $\text{NO}_3^-$ . Rate constant calculated taking $k(\text{Zn}^{2+} + \text{NO}_3^-) = 2.1 \times 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ (see entry 24.33). | Meye.68-0855<br>Fiti70-0117   |
| 24.28 | $\text{Zn}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Zn}^{2+} + \text{OH}^- + \text{OH}^\cdot$ | $(1.80 \pm 0.3) \times 10^9$<br>$(2.3 \pm 0.2) \times 10^9$ | —<br>—                             | RT<br>25±2         | nat<br>nat | pr<br>pr       | Products inferred from $\gamma$ -radiolysis experiments (see ref. 73-0039).                                                                                                                        | Meye.68-0855<br>Buxt..76-1072 |
|       |                                                                                                    | $E_a = 10.5 \pm 1.0 \text{ kJ mol}^{-1}$                    | —                                  | —                  | nat        | pr             | —                                                                                                                                                                                                  | Buxt..76-1072                 |

TABLE 24. Zinc(I) reactions — Continued

| No.   | Reaction                                                                                                     | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup>                                   | $I$                 | $t/^\circ\text{C}$       | pH                | Method         | Comments                                                                                                                                                                                                                                                                                        | Ref.                         |
|-------|--------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|---------------------|--------------------------|-------------------|----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| 24.29 | $\text{Zn}^+ + \text{H}_2\text{O}^+$                                                                         | $< 10^8$                                                                                       | 0.08                | RT                       | —                 | pr             | —                                                                                                                                                                                                                                                                                               | Meye.68-0855                 |
| 24.30 | $\text{Zn}^+ + \text{IO}_3^-$ (et)                                                                           | $(3.6 \pm 0.5) \times 10^9$<br>$(1.7 \pm 0.3) \times 10^{10}$                                  | 0.08<br>0.4         | RT<br>RT                 | nat<br>5-8        | pr<br>$\gamma$ | Measured by competition with $\text{NO}_3^-$ . Rate constant calculated taking $k(\text{Zn}^+ + \text{NO}_3^-) = 2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see entry 24.33).                                                                                               | Meye.68-0855<br>Fiti70-0117  |
|       |                                                                                                              |                                                                                                | ( $\text{ZnSO}_4$ ) |                          |                   |                |                                                                                                                                                                                                                                                                                                 |                              |
| 24.31 | $\text{Zn}^+ + \text{Ni}^{2+}$ (et)                                                                          | $< 5 \times 10^8$<br>$5 \times 10^7$                                                           | 0.08<br>—           | RT<br>RT                 | nat<br>nat        | pr<br>pr       | —<br>—                                                                                                                                                                                                                                                                                          | Meye.68-0855<br>Baxe.66-0848 |
| 24.32 | $\text{Zn}^+ + \text{NO}_3^-$ (et)                                                                           | $(2.2 \pm 0.3) \times 10^9$                                                                    | 0.08                | RT                       | nat               | pr             | —                                                                                                                                                                                                                                                                                               | Meye.68-0855                 |
| 24.33 | $\text{Zn}^+ + \text{NO}_3^-$ (et)                                                                           | $(2.1 \pm 0.3) \times 10^9$                                                                    | 0.08                | RT                       | nat               | pr             | —                                                                                                                                                                                                                                                                                               | Meye.68-0855                 |
| 24.34 | $\text{Zn}^+ + \text{N}_2\text{O} \rightarrow$<br>$\text{ZnO}^+ + \text{N}_2$                                | $< 1.3 \times 10^7$<br>$(3.7 \pm 0.4) \times 10^7$<br>$E_a = 35.5 \pm 1.4 \text{ kJ mol}^{-1}$ | —<br>—<br>—         | RT<br>$25 \pm 2$<br>1-30 | nat<br>nat<br>nat | pr<br>pr<br>pr | Products characterized by their absorption spectrum (see ref. 76-1072) and in $\gamma$ -radiolysis experiments (see ref. 73-0039).                                                                                                                                                              | Meye.68-0855<br>Buxt.76-1072 |
| 24.35 | $\text{Zn}^+ + \text{O}_2 \rightarrow$<br>$\text{Zn}^{2+} + \text{O}_2^-$                                    | $(2.4 \pm 0.4) \times 10^9$<br>$3.3 \times 10^9$                                               | —<br>—              | RT<br>RT                 | nat<br>nat        | pr<br>pr       | Products characterized by their absorption spectrum (see ref. 76-1072) and reactivity with 1,4-benzoquinone (see ref. 76-1134).                                                                                                                                                                 | Meye.68-0855<br>Baxe.66-0848 |
| 24.36 | $\text{Zn}^+ + \text{OH}$ (et)                                                                               | $5.7 \times 10^9$<br><br>$ca. 8 \times 10^9$                                                   | —<br>—              | RT<br>$25 \pm 2$         | nat<br>nat        | pr<br>pr       | No correction made for competing reaction $\text{Zn}^+ + \text{Zn}^+$ . Estimated from decay of $\text{Zn}^+$ in the absence of OH scavengers taking into account competing reactions such as $\text{Zn}^+ + \text{Zn}^+$ , $\text{Zn}^+ + \text{H}_2\text{O}_2$ , $\text{OH} + \text{OH}$ etc. | Baxe.66-0848<br>Buxt.75-1027 |
| 24.37 | $\text{Zn}^+ + \text{Pb}^{2+}$ (et)                                                                          | $4.0 \times 10^8$                                                                              | —                   | RT                       | nat               | pr             | —                                                                                                                                                                                                                                                                                               | Baxe.66-0848                 |
| 24.38 | $\text{Zn}^+ + \text{Ru}(\text{bpy})_3^{2+}$ (et)                                                            | $2.5 \times 10^9$                                                                              | —                   | RT                       | nat               | pr             | —                                                                                                                                                                                                                                                                                               | Baxe.72-0381                 |
| 24.39 | $\text{Zn}^+ + \text{Ru}(\text{NH}_3)_6^{3+}$ (et)                                                           | $(2.2 \pm 0.3) \times 10^9$                                                                    | 0.08                | RT                       | nat               | pr             | —                                                                                                                                                                                                                                                                                               | Navo.70-1229                 |
| 24.40 | $\text{Zn}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow$<br>$\text{Zn}^{2+} + \text{SO}_4^- + \text{SO}_4^{2-}$ | $(1.3 \pm 0.1) \times 10^9$                                                                    | 0.02*               | $25 \pm 2$               | nat               | pr             | —                                                                                                                                                                                                                                                                                               | Buxt.76-1072                 |
| 24.41 | $\text{Zn}^+ + \text{Zn}^+$                                                                                  | $2k < 8 \times 10^8$                                                                           | 0.4                 | $25 \pm 2$               | nat               | pr             | Estimated from rate of decay of $\text{Zn}^+$ in the presence of 2-methyl-2-propanol. Major competing reaction is $\text{Zn}^+ + \cdot\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ .                                                                                                            | Buxt.75-1027                 |
| 24.42 | $\text{Zn}^+ + \text{allyl alcohol} \rightarrow$<br>$(\text{Zn} - \text{allyl alcohol})^+$                   | $ca. 10^8$                                                                                     | —                   | $25 \pm 2$               | nat               | pr             | Product characterized by its absorption spectrum.                                                                                                                                                                                                                                               | Buxt.76-1072                 |

TABLE 24. Zinc(I) reactions — Continued

| No.                                                                                                                                                                       | Reaction                                                                                         | $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ <sup>a</sup> | $I$ | $t/^\circ\text{C}$ | pH  | Method | Comments                                                                                                                                                                                                                                                         | Ref.                     |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-----|--------------------|-----|--------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| 24.43                                                                                                                                                                     | $\text{Zn}^+ + \text{benzophenone} \rightarrow \text{Zn}^{2+} + (\text{benzophenone})^-$         | $2.5 \times 10^9$                                            | —   | RT                 | 7.0 | pr     | Measured in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. Ketyl radical product characterised by its absorption spectrum.                                                                                                              | Rao.75-1032              |
| 24.44                                                                                                                                                                     | $\text{Zn}^+ + 1,4\text{-benzoquinone} \rightarrow \text{Zn}^{2+} + (1,4\text{-benzoquinone})^-$ | $(3.0 \pm 0.6) 10^9$                                         | —   | $25 \pm 2$         | 5.7 | pr     | Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption spectrum.                                                                                                                          | Sell.76-1134             |
|                                                                                                                                                                           |                                                                                                  | $4.8 \times 10^9$                                            | —   | RT                 | 7.0 | pr     | Measured in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. Measured in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption spectrum.                           | Rao.75-1032              |
| 24.45                                                                                                                                                                     | $\text{Zn}^+ + \text{menaquinone} \rightarrow \text{Zn}^{2+} + (\text{menaquinone})^-$           | $(3.8 \pm 0.4) \times 10^9$                                  | —   | RT                 | 7.1 | pr     | Measured in the presence of <i>ca.</i> $1 \text{ mol dm}^{-3}$ 2-methyl-2-propanol. Semi-quinone product characterised by its absorption spectrum.                                                                                                               | Rao.73-1047, Rao.75-1032 |
| <b>Zn<sup>I</sup> Complexes</b>                                                                                                                                           |                                                                                                  |                                                              |     |                    |     |        |                                                                                                                                                                                                                                                                  |                          |
| $\text{ZnL}^+$ (from $\text{ZnL}^{2+} + \text{CH}_3\text{CO}^-\text{CH}_3$ ), L = hematoporphyrin (ix)<br>(no reference made to number of protons involved with complex). |                                                                                                  |                                                              |     |                    |     |        |                                                                                                                                                                                                                                                                  |                          |
|                                                                                        |                                                                                                  |                                                              |     |                    |     |        |                                                                                                                                                                                                                                                                  |                          |
| 24.46                                                                                                                                                                     | $\text{ZnL}^+ + \text{ZnL}^+ \rightarrow (\text{ZnL})_2^{2+}$                                    | $k' = (2.1 \pm 0.4) \times 10^8$                             | 0.1 | RT                 | 13  | pr     | Unclear whether $k$ or $2k$ . Measured in the presence of $1 \text{ mol dm}^{-3}$ 2-propanol. Dimerisation mechanism implied from subsequent reactions (see entry 24.47) and comparison with the products of reduction of $\text{ZnL}^{2+}$ in aprotic solvents. | Hare.74-1040             |
| 24.47                                                                                                                                                                     | $(\text{ZnL})_2^{2+} \rightarrow \text{P}$                                                       | $17 \pm 2 \text{ s}^{-1}$                                    | 0.1 | RT                 | 13  | pr     | Reaction suggested to involve internal rearrangement.                                                                                                                                                                                                            | Hare.74-1040             |
|                                                                                                                                                                           | $\text{P} \rightarrow \text{dihydroporphyrin product}$                                           | $< 0.14 \text{ s}^{-1}$                                      | 0.1 | RT                 | 13  | pr     | Reaction presumed to involve splitting of dimer.                                                                                                                                                                                                                 | Hare.74-1040             |

<sup>a</sup>If the data source gives no errors none are shown here but they should be assumed to be at least  $\pm 25\%$  (or  $\pm 50\%$  for  $2k$ ).

TABLE 25. Intramolecular electron transfer reactions for some metal complexes<sup>a</sup>

| No.                             | Reaction                                                                                            | $k/s^{-1}$ <sup>b</sup>     | $I$ | $t/^{\circ}C$ | pH  | Method | Comments                                                                                                                                                   | Ref.         |
|---------------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------|-----|---------------|-----|--------|------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------|
| <i>Electron adducts</i>         |                                                                                                     |                             |     |               |     |        |                                                                                                                                                            |              |
| 25.1                            | $(NH_3)_5Co^{III}(p-OOCC_6H_4NO_2)^- \rightarrow$<br>$(NH_3)_5Co^{II}(p-OOCC_6H_4NO_2)$             | $2.6 \times 10^3$           | -   | RT            | 7.0 | pr     | -                                                                                                                                                          | Simi.77-1027 |
| 25.2                            | $(NH_3)_5Co^{III}(m-OOCC_6H_4NO_2)^- \rightarrow$<br>$(NH_3)_5Co^{II}(m-OOCC_6H_4NO_2)$             | $1.5 \times 10^3$           | -   | RT            | 7.0 | pr     | -                                                                                                                                                          | Simi.77-1027 |
| 25.3                            | $(NH_3)_5Co^{III}(o-OOCC_6H_4NO_2)^- \rightarrow$<br>$(NH_3)_5Co^{II}(o-OOCC_6H_4NO_2)$             | $4.0 \times 10^5$           | -   | RT            | 7.0 | pr     | -                                                                                                                                                          | Simi.77-1027 |
| 25.4                            | $(NH_3)_5Co^{III}(o-OOCC_6H_4NO_2H) \rightarrow$<br>$(NH_3)_5Co^{II}(o-OOCC_6H_4NO_2) + H^+$        | $9.5 \times 10^3$           | -   | RT            | 0.8 | pr     | -                                                                                                                                                          | Simi.77-1027 |
| 25.5                            | $(NH_3)_5Co^{III}[2,4-OOCC_6H_4(NO_2)_2]^- \rightarrow$<br>$(NH_3)_5Co^{II}[2,4-OOCC_6H_4(NO_2)_2]$ | $3.5 \times 10^4$           | -   | RT            | 7.0 | pr     | -                                                                                                                                                          | Simi.77-1027 |
| 25.6                            | $(NH_3)_5Co^{III}[3,5-OOCC_6H_4(NO_2)_2]^- \rightarrow$<br>$(NH_3)_5Co^{II}[3,5-OOCC_6H_4(NO_2)_2]$ | $1.3 \times 10^3$           | -   | RT            | 7.0 | pr     | -                                                                                                                                                          | Simi.77-1027 |
| 25.7                            | $Cu^{II}(glutathione)^- \rightarrow$<br>$Cu^I(glutathione)$                                         | $(3.6 \pm 0.3) \times 10^3$ | -   | RT            | 11  | pr     | Rate constant independent of $[Cu^{II}]$ : [glutathione] ratio in range 1:2 to 1:5 and of $[Cu^{II}]$ in the range $(1-10) \times 10^{-4}$ mol $dm^{-3}$ . | Fara.76-1016 |
| 25.8                            | $Cu^{II}(gly)_2(gly)^- \rightarrow$<br>$Cu^I(gly)_3$                                                | $(1.7 \pm 0.3) \times 10^4$ | -   | RT            | 9   | pr     | Rate constant independent of $[Cu^{II}]$ : [gly] ratio in range 1:6 to 1:15 and of $[Cu^{II}]$ in the range $(1-10) \times 10^{-4}$ mol $dm^{-3}$ .        | Fara.76-1016 |
| <i>Hydroxyl radical adducts</i> |                                                                                                     |                             |     |               |     |        |                                                                                                                                                            |              |
| 25.9                            | $(NH_3)_5Co^{III}OOCC_6H_4OH \rightarrow$<br>$(NH_3)_5Co^{II}OOCC_6H_4OH + H^+$                     | $< 10^3$                    | -   | RT            | 6.0 | pr     | -                                                                                                                                                          | Cohe.71-0282 |
| <i>Hydrogen atom adducts</i>    |                                                                                                     |                             |     |               |     |        |                                                                                                                                                            |              |
| 25.10                           | $(NH_3)_5Co^{III}OOCC_6H_4H \rightarrow$<br>$(NH_3)_5Co^{II}OOCC_6H_4H + H^+$                       | $< 10^3$                    | -   | RT            | 1   | pr     | -                                                                                                                                                          | Cohe.71-0282 |

<sup>a</sup>Intramolecular electron transfer reactions of metallo-proteins and related systems *not* included..<sup>b</sup>N.B. First order rate constants.

## References

- 62-0164 Haissinsky, M., Radiolysis of compounds of the noble metals in aqueous solution. I. Action of gamma rays on the chlorides of  $Pt^{II}$  and  $Pt^{IV}$  in acid solution, *RADIATION RES.* 17(3): 274-85 (1962).
- 64-0133 Asmus, K.-D.; Henglein, A.; Ebert, M.; Keene, J.P., Pulsradiolytische Untersuchung schneller Reaktionen von hydratisierten Elektronen, freien Radikalen und Ionen mit Tetranitromethan in waessriger Loesung, *BER. BUNSENSES. PHYS. CHEM.* 68: 657-63 (1964).
- 65-0385 Baxendale, J.H.; Keene, J.P.; Stott, D.A., Determination of some fast reaction rates using the pulsed radiolysis of permanganate solutions, *Pulse Radiolysis*, Ebert, M.; Keene, J.P.; Swallow, A.J.; Baxendale, J.H. (eds.), Acad. Press, N.Y., 1965, p. 107-15.
- 65-0393 Baxendale, J.H.; Fielden, E.M.; Keene, J.P., Pulse radiolysis of  $Ag^+$  solutions, *Ibid.*, p. 207-16.
- 65-0394 Baxendale, J.H.; Fielden, E.M.; Keene, J.P., Formation of  $Cu^{III}$  in the radiolysis of  $Cu^{2+}$  solutions, *Ibid.*, p. 217-20.
- 65-0799 Cordon, S., *Ibid.*, p. 285.
- 66-0097 Cercek, B.; Ebert, M.; Swallow, A.J., Novel valence states of thallium as studied by pulse radiolysis, *J. CHEM. SOC. PT. A* (5): 612-5 (1966).
- 66-0848 Baxendale, J.H.; Keene, J.P.; Stott, D.A., Reactions and relative potentials of some metal ions in unstable valence states, *CHEM. COMMUN.* 715-16 (1966).
- 67-0019 Konstantatos, J.; Katakis, D., The radiolysis of concentrated neutral sodium perchlorate aqueous solutions, *J. PHYS. CHEM.* 71(4): 979-83 (1967).
- 67-0062 Buxton, G.V.; Dainton, F.S.; Thielens, G., Kinetics of reactions of the hydrated electron, *CHEM. COMMUN* (4): 201 (1967).
- 68-0066 Dainton, F.S.; Wiseall, B., Reactions of nitrosodimethylaniline with free radicals, *TRANS. FARADAY SOC.* 64(3): 694-705 (1968).
- 68-0169 Adams, G.E.; Broszkiewicz, R.B.; Michael, B.D., Pulse radiolysis studies on stable and transient complexes of platinum, *TRANS. FARADAY SOC.* 64(5): 1256-64 (1968).
- 68-0302 Ghosh-Mazumdar, A.S.; Hart, E.J., A pulse radiolysis study of bivalent and zerovalent gold in aqueous solutions, *ADVAN. CHEM. SER.* 81: 193-209 (1968).
- 68-0431 Pukies, J.; Roebke, W.; Henglein, A., Pulsradiolytische Untersuchung einiger Elementarprozesse der Silberreduktion, *BER. BUNSENSES. PHYS. CHEM.* 72(7): 842-7 (1968).
- 68-0435 Pukies, J.; Roebke, W., Pulsradiolytische Untersuchung der Reduktion des  $Ag^+$ -Ions in ammoniakalischer Loesung, *BER. BUNSENSES. PHYS. CHEM.* 72(9/10): 1101-5 (1968).
- 68-0855 Meyerstein, D.; Mulac, W.A., Reductions by monovalent zinc, cadmium, and nickel cations, *J. PHYS. CHEM.* 72(3): 784-8 (1968).
- 69-0144 Ghosh-Mazumdar, A.S.; Hart, E.J., Electron pulse radiolysis of aqueous tetrachloro and tetracyano complexes of  $Pt^{II}$ , *INT. J. RADIAT. PHYS. CHEM.* 1: 165-76 (1969).
- 69-0428 Meyerstein, D.; Mulac, W.A., Reduction of cobalt(III) complexes by monovalent zinc, cadmium, and nickel ions in aqueous solutions, *J. PHYS. CHEM.* 73(4): 1091-5 (1969).
- 69-0434 Jayson, G.G.; Keene, J.P.; Stirling, D.A.; Swallow, A.J., Pulse-radiolysis study of some unstable complexes of iron, *TRANS. FARADAY SOC.* 65(561): 2453-64 (1969).
- 69-0971 Taylor, R.S.; Sykes, A.G., Preparation, spectrum, and stability of indium(I) in aqueous solution, *J. CHEM. SOC. PT. A* 2419-23 (1969).
- 70-0117 Fiti, M., La cinetique de competition dans l'etude des intermediaires instables. I. Les ions  $Co^+$ ,  $Mn^+$ ,  $Zn^+$ ,  $Cd^+$  et  $Ni^+$ , *REV. ROUM. CHIM.* 15(1): 77-85 (1970).
- 70-0178 Baxendale, J.H.; Rodgers, M.A.J.; Ward, M.D., Radiolysis of aqueous solutions of ruthenium (III) hexa-ammine and chloropenta-ammine, *J. CHEM. SOC. PT. A* (8): 1246-50 (1970).
- 70-0336 Burchill, C.E.; Hickling, G.G., Radiation-induced oxidation of alcohols by  $Ti(III)$  in acid aqueous solution, *CAN. J. CHEM.* 48(16): 2466-73 (1970).
- 70-0512 Barker, G.C.; Fowles, P., Pulse radiolytic induced transient electrical conductance in liquid solutions. Part 3. Radiolysis of aqueous solutions of some inorganic systems, *TRANS. FARADAY SOC.* 66(7): 1661-9 (1970).
- 70-0580 Baxendale, J.H.; Koulkes-Pujo, A.-M., Une etude par radiolyse pulse sur l'espece transitoire  $Au II$ , *J. CHIM. PHYS.* 67(9): 1602-7 (1970).
- 70-1228 Meyerstein, D.; Mulac, W.A., The effect of ligands on the chemical properties of monovalent cadmium ions, *INORG. CHEM.* 9(7): 1762-6 (1970).
- 70-1229 Navon, G.; Meyerstein, D., The reduction of ruthenium(III) hexaammine by hydrogen atoms and monovalent zinc, cadmium, and nickel ions in aqueous solutions, *J. PHYS. CHEM.* 74(23): 4067-70 (1970).
- 70-7309 Burchill, C.E.; Wolodarsky, W.H., The photo-chemistry of aqueous solutions of  $Ti(III)$  perchlorate, *CAN. J. CHEM.* 48(19): 2955-9 (1970).
- 70-7726 Thornton, A.T.; Laurence, G.S., The rates of oxidation of  $Fe^{2+}$ ,  $Mn^{2+}$ , and  $Co^+$  by  $Br_2^-$  radical ions, *CHEM. COMMUN.* 443-4 (1970).
- 71-0036 Faraggi, M.; Zehavi, D.; Anbar, M., Effect of thalious ions on the yields of hydrogen and hydrogen peroxide in radiolyzed aqueous solutions, *TRANS. FARADAY SOC.* 67: 2057- (1971).
- 71-0097 Venerable, G.D.II; Halpern, J., Pulse radiolysis of aqueous solutions of pentacyanocobaltate(II). The detection and characterization of pentacyanocobaltate(I), *J. AMER. CHEM. SOC.* 93(9): 2176-9 (1971).
- 71-0174 Meyerstein, D., Trivalent copper. I. A pulse radiolytic study of the chemical properties of the aquo complex, *INORG. CHEM.* 10(3): 638-41 (1971).
- 71-0234 Baxendale, J.H.; Mulazzani, Q.G., A study of the oxidation and reduction of  $Ru(NH_3)_6N_2^{2+}$  by  $\gamma$ - and electron pulse radiolysis, *J. INORG. NUCL. CHEM.* 33(3): 823-30 (1971).
- 71-0282 Cohen, H.; Meyerstein, D., Oxidation of benzoatopentaamminecobalt(III) by hydroxyl radicals, *J. AMER. CHEM. SOC.* 93(17): 4179-83 (1971).
- 71-0775 Meyerstein, D., Trivalent copper. II. A pulse radiolytic study of the formation and decomposition of amino complexes, *INORG. CHEM.* 10(10): 2244-0 (1971).
- 72-0065 Faraggi, M.; Tendler, Y., Pulse radiolysis in lanthanide aqueous solutions. I. Formation spectrum and chemical properties of divalent europium, ytterbium, and samarium ions, *J. CHEM. PHYS.* 56(7): 3287-93 (1972).
- 72-0066 Faraggi, M.; Feder, A., Pulse radiolysis studies in lanthanide aqueous solutions. II. Formation, spectrum and some chemical properties of praseodymium(IV) in aqueous solution, *J. CHEM. PHYS.* 56(7): 3294-7 (1972).
- 72-0290 Faraggi, M.; Amozig, A., Pulse radiolysis of metallic ions in aqueous solutions. I. Pulse radiolysis in  $Hg^{2+}$  and  $Hg_2^{2+}$  ions in

- aqueous solutions, *INT. J. RADIAT. PHYS. CHEM.* 4(3): 353-8 (1972).
- 72-0381 Baxendale, J.H.; Fiti, M., Transient species in the reactions of some pyridyl complex ions with hydrated electrons, *J. CHEM. SOC. DALTON TRANS.* (18): 1995-8 (1972).
- 72-0460 Lati, J.; Meyerstein, D., Trivalent nickel. I. A pulse radiolytic study of the formation and decomposition of the ammoniacal complex in aqueous solution, *INORG. CHEM.* 11(10): 2393-7 (1972).
- 72-0461 Lati, J.; Meyerstein, D., Trivalent nickel. II. A pulse radiolytic study of the formation and decomposition of the ethylenediamine and glycine complexes in aqueous solution, *INORG. CHEM.* 11(10): 2397-401 (1972).
- 72-0844 Sellers, R.M., Ph.D. Thesis, Univ. of Leeds, 1972.
- 72-7088 Wright, R.C.; Laurence, G.S., Production of platinum(III) by flash photolysis of  $\text{PtCl}_6^{2-}$ , *J. CHEM. SOC., CHEM. COMMUN.* (3): 132-3 (1972).
- 73-0038 Jayson, G.G.; Parsons, B.J.; Swallow, A.J., Oxidation of ferrous ions by perhydroxyl radicals, *J. CHEM. SOC. FARADAY TRANS. 1* 69(1): 236-42 (1973).
- 73-0039 Buxton, G.V.; Dainton, F.; McCracken, D.R., Radiation chemical study of the reaction of  $\text{Ni}^+$ ,  $\text{Co}^+$  and  $\text{Cd}^+$  with  $\text{N}_2\text{O}$ . Evidence of the formation of a hyperoxidised state by oxygen atom transfer, *J. CHEM. SOC. FARADAY TRANS. 1* 69(1): 243-54 (1973).
- 73-0043 Nazhat, N.B.; Asmus, K.-D., Reduction of mercuric chloride by hydrated electrons and reducing radicals in aqueous solutions. Formation and reactions of  $\text{HgCl}$ , *J. PHYS. CHEM.* 77(5): 614-20 (1973).
- 73-0107 Faraggi, M.; Feder, A., Electron-transfer reactions of cobalt(III) and ruthenium(III) amines with europium(II), ytterbium(II), and samarium(II) in aqueous solutions, *INORG. CHEM.* 12(1): 236-41 (1973).
- 73-0121 Robinson, E.A.; Schulte-Frohlinde, D., Pulse radiolysis of 1,4-dicyanobenzene in aqueous solutions in the presence and absence of thallium(I) ions, *J. CHEM. SOC. FARADAY TRANS. 1* 69(4): 707-18 (1973).
- 73-0122 Jayson, G.G.; Parsons, B.J.; Swallow, A.J., Appearance of sulphatoferric complexes in the oxidation of ferrous sulphate solutions. A study by pulse radiolysis, *J. CHEM. SOC. FARADAY TRANS. 1* 69(6): 1079-89 (1973).
- 73-1047 Rao, P.S.; Hayon, E., One-electron redox reactions of free radicals in solution. Rate of electron transfer processes of quinones, *BIOCHIM. BIOPHYS. ACTA* 292: 516-33 (1973).
- 73-1053 Farhataziz, Mihalcea, I.; Sharp, L.J.; Hentz, R.R. Pulse radiolysis of liquids at high pressures. IV. Hydrogen-atom reactions in aqueous 0.1M  $\text{HClO}_4$  solutions, *J. CHEM. PHYS.* 59(5): 2309-15 (1973).
- 73-1057 Ellis, J.D.; Green, M.; Sykes, A.G.; Buxton, G.V.; Sellers, R.M., Pulse radiolysis of titanium(III) and other metal(III) ions in the presence of formic acid, *J. CHEM. SOC., DALTON TRANS.* (16): 1724-8 (1973).
- 73-1066 Broszkiewicz, R.K., Pulse radiolysis studies on complexes of iridium, *J. CHEM. SOC. DALTON TRANS.* (17): 1799-802 (1973).
- 73-1080 Fujita, S.; Horii, H.; Taniguchi, S., Pulse radiolysis of mercuric ion in aqueous solutions, *J. PHYS. CHEM.* 77(24): 2868-71 (1973).
- 73-1084 Pikaev, A.K.; Sibirskaia, G.K.; Spitsyn, V.I., Study of divalent samarium, europium, thulium, ytterbium, and of tetravalent praseodymium ions by pulse radiolysis in aqueous solution, *DOKL. PHYS. CHEM. (ENGL. TRANSL.)* 209(4-6): 339-42 (1973), *Transl. from DOKL. AKAD. NAUK SSSR* 209(5): 1154-7 (1973).
- 73-1104 Rao, P.S.; Hayon, E., Rate constants of electron transfer processes in solution: Dependence on the redox potential of the acceptor, *NATURE(LONDON)* 243: 344-6 (1973).
- 74-1017 Schwarz, H.A.; Comstock, D.; Yandell, J.K.; Dodson, R.W., A pulse radiolysis study of thallium(II) in aqueous perchloric acid solutions, *J. PHYS. CHEM.* 78(5): 488-93 (1974).
- 74-1037 Kelm, M.; Lilie, J.; Henglein, A.; Janata, E., Pulse radiolytic study of  $\text{Ni}^+$ . Nickel-carbon bond formation, *J. PHYS. CHEM.* 78(9): 882-7 (1974).
- 74-1038 Dodson, R.W.; Schwarz, H.A., Pulse radiolysis studies of chloride complexes of thallium(II). Absorption spectra and stability constants of  $\text{TlCl}^+$ ,  $\text{TlCl}_2$ , and  $\text{TlCl}_3$ , *J. PHYS. CHEM.* 78(9): 892-9 (1974).
- 74-1040 Harel, Y.; Meyerstein, D., On the mechanism of reduction of porphyrins. A pulse radiolytic study, *J. AMER. CHEM. SOC.* 96(9): 2720-7 (1974).
- 74-1072 Mulazzani, Q.G.; Ward, M.D.; Semeraro, G.; Emmi, S.S.; Giordani, P., Gamma and pulse radiolysis of tetracyanonickelate(II) anion in aqueous solution, *INT. J. RADIAT. PHYS. CHEM.* 6(3): 187-201 (1974).
- 74-1104 Laurence, G.S.; Thornton, A.T., Kinetics of oxidation of transition-metal ions by halogen radical anions. Part. IV. The oxidation of vanadium(II) and chromium(II) by diiodide, dibromide, and dichloride ions generated by pulse radiolysis, *J. CHEM. SOC., DALTON TRANS.* (11): 1142-8 (1974).
- 74-1142 Cohen, H.; Meyerstein, D., Ultraviolet-visible spectrum, and kinetics of formation and decomposition, of penta-aquahydrochromium(III) and chromium(II) in aqueous perchlorate solutions: A pulse-radiolysis study, *J. CHEM. SOC., DALTON TRANS.* (23): 2559-64 (1974).
- 74-1146 Cohen, H.; Meyerstein, D., Chromium-carbon bonds in aqueous solutions. A pulse radiolytic study, *INORG. CHEM.* 13(10): 2434-43 (1974).
- 74-7265 Falcinella, B.; Felgate, P.D.; Laurence, G.S., Aqueous chemistry of thallium(II). Part I. Kinetics of reaction of thallium(II) with cobalt(II) and iron(II) ions and oxidation-reduction potentials of thallium(II), *J. CHEM. SOC., DALTON TRANS.* 1367-73 (1974).
- 75-1027 Buxton, G.V.; Sellers, R.M., Pulse radiolysis study of monovalent cadmium, cobalt, nickel and zinc in aqueous solution. Pt. 1. Formation and decay of the monovalent ions, *J. CHEM. SOC., FARADAY TRANS. 1* 71(3): 558-68 (1975).
- 75-1032 Rao, P.S.; Hayon, E., One electron oxidation of odd-valent metal ions in solution, *J. PHYS. CHEM.* 79(9): 865-8 (1975).
- 75-1044 Fujita, S.; Horii, H.; Mori, T.; Taniguchi, S., Pulse radiolysis of mercuric oxide in neutral aqueous solutions, *J. PHYS. CHEM.* 79(10): 960-4 (1975).
- 75-1049 Armor, J.N.; Hoffman, M.Z., Reactivity of coordinated nitrosyls. IV. One-electron reduction of ruthenium nitrosylpentaammine ( $3+$ ) ion in aqueous solution, *INORG. CHEM.* 14(2): 444-6 (1975).
- 75-1064 Kelm, M.; Lilie, J.; Henglein, A., Pulse radiolytic investigation of the reduction of cadmium(II) ions, *J. CHEM. SOC., FARADAY TRANS. 1* 71(5): 1132-42 (1975).
- 75-1077 Armor, J.N.; Furman, R.; Hoffman, M.Z., Reactivity of coordinated nitrosyls. V. Generation and characterization of a ruthenium(II) alkyl nitroso complex, *J. AMER. CHEM. SOC.* 97(7): 1737-42 (1975).
- 75-1086 O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D., Formation of radical cations from 1,2- and 1,4-dimethoxybenzene by

- electron transfer to  $Ti^{2+}$  and  $Ag^{2+}$  in aqueous solution. A pulse radiolysis and in situ radiolysis EPR study, *ANGEW. CHEM. INT. ED. ENGL.* 14(6): 430-1 (1975)
- 75-1092 Meyerstein, D., Kinetics of complexation of copper(I) ions with maleate and fumarate in aqueous solutions. A pulse radiolytic study, *INORG. CHEM.* 14(7): 1716-7 (1975).
- 75-1128 Lilie, J.; Simic, M.G.; Endicott, J.F., Chemical behavior of rhodium(II)-ammine complexes generated by the pulse radiolytic one-electron reduction of rhodium(III) amines, *INORG. CHEM.* 14(9): 2129-33 (1975).
- 75-1130 O'Neill, P.; Schulte-Frohlinde, D., Evidence for formation of a  $(TiOH)^+$  complex, *J. CHEM. SOC., CHEM. COMMUN.* (10): 387-8 (1975).
- 75-1153 Barkatt, A.; Rabani, J., Kinetics of spur reactions of electrons in ethylene glycol-water glassy ice. A pulse radiolytic study, *J. PHYS. CHEM.* 79(24): 2592-7 (1975).
- 75-1171 O'Neill, P.; Steenken, S.; Schulte-Frohlinde, D., Formation of radical cations of methoxylated benzenes by reaction with OH radicals,  $Ti^{2+}$ ,  $Ag^{2+}$ , and  $SO_4^-$  in aqueous solution. An optical and conductometric pulse radiolysis and in situ radiolysis electron spin resonance study, *J. PHYS. CHEM.* 79(25): 2773-9 (1975).
- 75-1188 Storer, D.K.; Waltz, W.L.; Brodovitch, J.C.; Eager, R.L., A pulse radiolysis study of some platinum(II) and platinum(IV) complex ions in aqueous solutions. The formation and characterization of platinum(I) and platinum(III) transients, *INT. J. RADIAT. PHYS. CHEM.* 7(6): 693-704 (1975).
- 75-1203 Fujita, S.; Horii, H.; Mori, T.; Taniguchi, S., Pulse radiolysis of  $Hg(CN)_2$  in aqueous solutions, *BULL. CHEM. SOC. JPN.* 48(11): 3067-72 (1975).
- 75-1215 Ilan, Y.A.; Czapski, G.; Ardon, M., The formation of  $CrO_2^{2+}$  in the reaction of  $Cr^{2+} + O_2$  in aqueous acid solutions, *ISR. J. CHEM.* 13(1): 15-21 (1975).
- 75-1218 Pikaev, A.K.; Sibirskaia, G.K.; Spitsyn, V.I., Pulsed radiolysis of aqueous solutions of compounds of divalent mercury, *DOKL. PHYS. CHEM. (ENGL. TRANSL.)* 224(1-3): 994-7 (1975). Translated from *DOKL. AKAD. NAUK SSSR* 224(3): 638-41 (1975).
- 75-7093 Falcinella, B.; Felgate, P.D.; Laurence, G.S., Aqueous chemistry of thallium(II) with manganese(II), iron(II), and cobalt(I) ions, *J. CHEM. SOC., DALTON TRANS.* (1): 1-9 (1975).
- 76-1001 Tait, A.M.; Hoffman, M.Z.; Hayon, E., The reactivity of cobalt(I) complexes containing unsaturated macrocyclic ligands in aqueous solution, *J. AMER. CHEM. SOC.* 98(1): 86-93 (1976).
- 76-1003 Baxendale, J.H.; Garner, C.D.; Senior, R.G.; Sharpe, P., The reduction of molybdenum(II) trifluoroacetate by pulse radiolysis in methanol, *J. AMER. CHEM. SOC.* 98(2): 637-8 (1976).
- 76-1016 Faraggi, M.; Leopold, J.C., Pulse radiolysis studies of electron-transfer reaction in molecules of biological interest. II. The reduction of  $Cu(II)$ -peptide complexes, *RADIAT. RES.* 65(2): 238-49 (1976).
- 76-1039 Tait, A.M.; Hoffman, M.Z.; Hayon, E., Reactivity of nickel(I) and copper(I) complex containing 14-membered macrocyclic ligands in aqueous solution, *INORG. CHEM.* 15(4): 934-9 (1976).
- 76-1042 Jungbluth, H.; Beyrich, J.; Asmus, K.-D., Reduction of mercuric halides and pseudohalides in aqueous solution. Formation and some physicochemical properties of  $HgCl$ ,  $HgBr$ ,  $HgI$ ,  $HgSCN$ , and  $HgCN$  radical molecules, *J. PHYS. CHEM.* 80(10): 1049-53 (1976).
- 76-1055 Broszkiewicz, R.K.; Grodkowski, J., Pulse radiolysis studies on aqueous systems  $PtCl_4^{2-}-Cl^-$  and  $PtCl_4^{2-}-Br^-$ , *INT. J. RADIAT. PHYS. CHEM.* 8(3): 359-65 (1976).
- 76-1072 Buxton, G.V.; Sellers, R.M.; McCracken, D.R., Pulse radiolysis study of monovalent cadmium, cobalt, nickel and zinc in aqueous solution. Part 2. Reactions of the monovalent ions, *J. CHEM. SOC., FARADAY TRANS. 1* 72(6): 1464-76 (1976).
- 76-1087 Fujita, S.; Horii, H.; Mori, T.; Taniguchi, S., Pulse radiolysis of  $HgBr_2$  in aqueous solutions, *BULL. CHEM. SOC. JPN.* 49(5): 1250-3 (1976).
- 76-1093 Brodovitch, J.C.; Storer, D.K.; Waltz, W.L.; Eager, R.L., A pulse radiolysis and flash photolysis study of the formation and characterization of platinum(III) amine complex ions, *INT. J. RADIAT. PHYS. CHEM.* 8(4): 465-75 (1976).
- 76-1134 Sellers, R.M.; Simic, M.G., Pulse radiolysis study of the reactions of some reduced metal ions with molecular oxygen in aqueous solution, *J. AMER. CHEM. SOC.* 98(20): 6145-50 (1976).
- 76-1186 Buxton, G.V.; Green, J.C.; Sellers, R.M., Oxidation of copper(I)-olefin complexes in aqueous solution by oxygen and hydrogen peroxide, *J. CHEM. SOC., DALTON TRANS.* (21): 2160-5 (1976).
- 77-0121 Buxton, G.V.; Sellers, R.M., The radiation chemistry of metal ions in aqueous solution, *COORD. CHEM. REV.* 22(3): 195-274 (1977).
- 77-1027 Simic, M.G.; Hoffman, M.Z.; Breznjak, N.V.; Kinetics of ligand-to-metal intramolecular electron transfer in cobalt(III)-ammine complexes containing a coordinated radical, *J. AMER. CHEM. SOC.* 99(7): 2166-72 (1977).
- 77-1500 Buxton, G.V.; Green, J.C., Reactions of some simple  $\alpha$ - and  $\beta$ -hydroxyalkyl radicals with  $Cu^{2+}$  and  $Cu^+$  ions in aqueous solution, *J. CHEM. SOC., FARADAY TRANS. 1* 74: 697-714 (1978).