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Chemical Kinetic Data Needs for Modeling the Lower Troposphere

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Chemical Kinetic Data Needs for Modeling the Lower Troposphere

+ special publication

Proceedings of a Workshop
held at Reston, Virginia
May 15-17, 1978

John T. Herron, Robert E. Huie,
and Jimmie A. Hodgeson, Editors

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Foreword

It is increasingly recognized that the integrity of the data input is one of the most serious limiting factors in modeling complex chemical systems. The reliability of the results generated in modeling studies is critical considering their application to environmental regulation and control.

The purpose of this workshop was to bring together modelers, chemical kineticists, theoreticians and program managers, in order to define the critical data needs for modeling the troposphere. This collection of review papers, comments, and recommendations should serve a wide community of atmospheric scientists in identifying and attacking priority problem areas.

The National Bureau of Standards is pleased to be responsible for this publication, and to have joined with the Environmental Protection Agency as cosponsors of the workshop.

John D. Hoffman, Director
National Measurement Laboratory
National Bureau of Standards

Preface

It used to be said, "At least the air we breathe is free." For about 30 years that has not been the case in the United States. We are now paying about 10 billion dollars a year in an increasingly difficult effort to maintain our atmosphere at a degree of pollution near current levels. That sum will almost certainly increase as we turn towards alternate energy sources such as coal, shale oil and crude oils with high sulfur contents. It will grow even larger as we learn more about the impacts of various chemical substances, both natural and man made, on the complex ecology in which man exists on this planet.

By contrast one can estimate that about 3 million dollars will be spent this year (1978) on basic research, by all government agencies for learning the molecular details of the chemistry of air pollution. It is perhaps very flattering to the scientific community involved in this effort to consider that such a sum will suffice to make significant progress in the understanding of the chemistry of air pollution. But the scientists involved share no such illusions. In 30 years of research effort we have learned a great deal about the chemistry of our "dirty" atmosphere but we can hardly pretend to give quantitative answers to questions which are increasingly being asked, such as, "What will the effect be on our atmosphere of removing or adding X tons per week of substance A?" Yet important economic decisions rest on the answers to such questions. The sums spent on basic research are dwarfed by the sums now being spent on regulation and abatement. Research funds are the least expensive aspect of the problem of air pollution, and without the answers that they might provide, our expensive efforts may be largely squandered.

The present conference brings together many of the leaders in the basic research effort directed towards air pollution. They have examined the scientific details with a fine microscope and come up with what must seem to the layman an endless multitude of unanswered questions. Some of these may never be answered and some of them need urgently to be resolved. Air pollution will not go away. It will become worse even with current efforts. No city on earth will escape its effects. If we hope to ameliorate it, we must devote a more profound and longer range effort to its understanding than we have done so far. The recommendations of this symposium point the direction these efforts must take. As chairman, I would like to take this opportunity to express my appreciation to my fellow colleagues who have given generously of their time and effort towards making this a fruitful meeting.

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Abstract

This is a report of the proceedings of a workshop on chemical kinetic data needs for modeling the lower troposphere, held at Reston, Virginia, May 15-17, 1978. The meeting, sponsored by the Environmental Protection Agency and the National Bureau of Standards, focussed on six key problem areas in tropospheric chemistry: reactions of olefins with hydroxyl radicals and ozone, reactions of aldehydes, free radical reactions, reactions of oxides of nitrogen, reactions of aromatic compounds, and reactions of oxides of sulfur.

The report includes a summary and list of major recommendations for further work, review papers, discussion summaries, contributed comments, recommendations, and an attendance list.

Key words: Aldehydes, aromatics, chemical kinetics, data needs, free radicals, modeling, NO_x, olefins, SO_x, troposphere.

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Introduction

The Environmental Protection Agency and the National Bureau of Standards' Office of Environmental Measurements and Center for Thermodynamics and Molecular Science sponsored a workshop entitled "Chemical Kinetic Data Needs for Modeling the Lower Troposphere," at Reston, Virginia, May 15-17, 1978. The objective of the workshop was to assess and make recommendations on mechanistic and kinetic data needs for modeling chemical transformations occurring in the lower troposphere.

The workshop was organized around six major topics: reactions of olefins with hydroxyl radicals and ozone, the chemistry of aldehydes, free radical chemistry, the chemistry of oxides of mitrogen, the chemistry of aromatic compounds, and the chemistry of the oxides of sulfur. These general topics cover almost all of the important problem areas in homogeneous chemical kinetics of interest to the atmospheric scientist. Heterogeneous processes were not included.

Each technical session opened with a review paper followed by a discussion period. A set of recommendations was prepared based on the review paper and subsequent discussions.

This report of the meeting includes the review papers (with one exception), discussion summaries, written contributions to the discussion, and recommendations. It opens with an overview and summary of the workshop recommendations.

We want to thank all those involved in organizing and running the workshop, and all those who through their participation helped make it a success.

Summary and Recommendations of Workshop

The recommendations of the workshop are given in detail following each session. Here we summarize the major themes of the workshop and list the most important areas requiring additional experimental or theoretical work.

Major advances in the chemistry of the troposphere depend on understanding the chemistry of large molecules and free radicals. Real atmospheres contain large amounts of hydrocarbons C_4 and greater, aromatic compounds, natural products such as terpenes, and large aldehydes, ketones, phenols, etc, which are their photooxidation products, as well as a large class of oxygen containing free radicals which are the intermediates in these photooxidation reactions. These complex molecules are not only involved in the NO-NO conversion process, but almost certainly are important precursors to atmospheric aerosols. We will not understand either oxidant or aerosol formation until we attack the problem of large molecules.

Clearly, moving away from fairly simple surrogate reactants such as propylene, and considering the whole range of atmospheric pollutants creates a problem in scale. There are far too many molecules and potential reactions to measure everything. A proper attack on this problem involves a judicious mix of experiment and theory. We may illustrate this by considering one of the most pressing problems - the chemistry of alkoxy radicals. Large alkoxy radicals can isomerize, decompose, or react with oxygen (as well as NO_x and SO_x, see below). The relative rates of these processes must be known. Even though this problem was extensively considered at this workshop it is doubtful if a convincing solution was given. Measurements are needed to provide a base set to allow for the development of theoretical estimation schemes.

Another class of reactions of great importance both in the atmosphere and in laboratory investigations are alkylperoxy radical reactions. In the absence of NO, these radicals react with themselves to produce aldehydes and alcohols. There is considerable uncertainty as to the mechanism of these reactions. The suggestion made at the meeting that one of their products might be the Criegee intermediate emphasizes the need for much more work in this area. At the same time the peroxy radicals formed in the reactions of OH with olefins in the presence of O_2 need identifying.

In addition we need data on acetyl and acetylperoxy type radicals. There are questions as to formation of acids, particularly from formyl radical reactions, which cannot be explained on the basis of existing data.

Another major deficiency is in the area of reactions of aromatic compounds. Recognition of their importance is fairly recent. In particular we need to know about rates and mechanisms of reaction of aromatics with OH radicals. This will involve extension of existing experimental approaches and development of new ones. The branching ratios for different products need to be measured and the subsequent chemistry of these products needs to be considered.

The possibility of making the Criegee intermediate from alkylperoxy radicals was noted above. The Criegee intermediate is presumably a primary product of an ozone-olefin reaction. Its subsequent fate is of great importance. A crucial question is whether it decomposes or is stabilized, and if stabilized what chemical reactions it can undergo. There is some evidence that small Criegee intermediates decompose. For the large ones however, there is very little quantitative data. This question needs resolution since the Criegee intermediate has been postulated to be a potential oxidizer for NO, SO_2, olefins, etc.

In addition to treating free radical reactions in terms of isomerization, scission, self-reaction, and reaction with O_2, we must consider reactions with NO_x and SO_x. Here we are faced with problems of rates and mechanisms and in particular the problem of the role of association reactions. For peroxy radicals the starting point is the HO_2-NO reaction. The new value for the rate constant has had a dramatic effect on the models. It needs to be studied over a wide range of conditions (temperature, pressure) to confirm this value under atmospheric conditions. The use of the rate constant data for HO_2 + NO for RO_2 + NO reactions may be invalid. Direct measurements are needed. In addition, for large alkylperoxy radicals we need to know if alkyl nitrates are products since this is a chain terminating reaction.

Similar considerations apply in the case of the reactions of alkylperoxy radicals with NO_2, although it is not likely that the peroxynitrates formed in simple association reactions would have a significant lifetime in the atmosphere. However, if the reaction can lead to an aldehyde and nitric acid it could be of considerable importance.

Reactions of alkoxy radicals with NO and NO_2 can also proceed via channels leading to adducts or to HNO or HONO respectively. The overall rate constants and branching ratios need to be determined. Similar considerations apply to OH reactions with NO and NO_2.

A somewhat different approach to the question of the importance of adduct formation is to consider the thermal stability of peroxy radicals. Work of this kind has been done for some PAN

Session I

Reactions of Olefins with Ozone and Hydroxyl Radicals

AN EVALUATION OF CHEMICAL KINETIC DATA NEEDS FOR MODELING THE LOWER TROPOSPHERE: REACTIONS OF OLEFINS WITH HYDROXYL RADICAL AND WITH OZONE

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Needs for improved kinetic and mechanistic data for the reactions of olefinic hydrocarbons with hydroxyl radical and with ozone have been evaluated from the view point of modeling the chemistry of the lower troposphere. Research priorities for removal of various uncertainties in these reactions have been discussed briefly.

Key words: Hydroxyl; kinetics; olefin; ozone; review; troposphere.

1. Introduction

In planning for the abatement and control of air pollution, it is essential to establish the quantitative chemical relationship between source emission and the resulting air quality. At present, concerted modeling efforts are being made to achieve this goal. Chemical interpretation of smog chamber data [1][1], prediction of "ozone-isopleth" [2], and air-shed modeling [3] of Los Angeles Reactive Pollutant Program (LARPP) data [4] are a few of the notable examples of such endeavor. Clearly, the degree of success of modeling work is governed, in large part, by the availability of reliable kinetic data. Despite recent progress, the knowledge of the chemical reactions taking place in the lower troposphere is far from satisfactory. There exist numerous critical uncertainties in the kinetics and mechanisms of reactions involving a large variety of atmospheric constituents. This paper is intended to assess the needs for improved experimental data for olefin reactions with HO and with O_3.

For the purpose of evaluating the existing needs for improved kinetic and mechanistic information for these reactions, their potential role in the lower troposphere is discussed briefly. Further, the current knowledge of these reactions is illustrated by some of the work published within the last few years. This paper is not intended to be an extensive literature review, but rather, to convey the author's thoughts on the future direction and research priorities in the area of tropospheric chemistry. In view of the urgency and long-term interest in establishing firm scientific bases for the abatement of air pollution problems, the more systematic data evaluation efforts, e.g., the "chemical reaction matrix" method [5] used for the evaluation of the stratospheric chemistry, should be made in the future.

2. Atmospheric Role of Olefin Reactions with HO and with O_3.

Olefins are among the most reactive classes of organic compounds present in the lower troposphere. In particular, their possible role in the formation of photochemical smog has been well-recognized over the last three decades [6]. As a result, olefins have been used extensively as surrogate hydrocarbons in laboratory smog studies, and have played the crucial role in the development of smog chemistry [1]. It now appears that the atmospheric fate of olefins are governed primarily by their reactions with HO and with O_3. Conversely, these reactions are responsible for regulating the atmospheric concentrations of HO and O_3. The latter aspect is of primary importance, since HO is the major chain carrier of atmospheric reactions and determines the role of other hydrocarbons and organic compounds in the formation of "oxidant", e.g., O_3. Whether O_3-olefin reactions can lead to the formation of "excess" O_3 or alternatively serve as a sink for O_3 is another key question to be answered.

It must be stressed that a quantitative evaluation of the atmospheric role of the olefin reactions, or for that matter any other reactions, can be made only on the basis of numerical modeling studies for a given source distribution and strength under a variety of meteorological conditions. Clearly, relative importance of HO and O_3 reactions involving various olefins can vary markedly between "fresh" and "aged" air masses because of the chemically and meterologically induced changes in relative and absolute olefin concentrations.

To illustrate the relative importance of various olefinic and other types of hydrocarbons, table 1 shows the results obtained by Calvert [7] for the relative rates of HO-radical attack on hydrocarbons

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[1] Figures in brackets indicate literature references at the end of this paper.

Table 1. Estimated relative rates of HO-radical attack on hydrocarbons and CO present in the 0823 sample (LARPP Operation #33, Smog #2, 425-ft (AGL) Flight).[a]

Compound	(RH), ppb, mol basis	Rel. rate, HO reaction	Compound	(RH), ppb, mol basis	Rel. rate, HO reaction
CH_4	2.010	2.8	3-Methylhexane	6.3	5.8
C_2H_6	49	2.2	*1-Heptene[b]	4.4	∿ 25.9
*C_2H_4	43	11.6	n-C_7H_{16}	4.3	3.8
C_2H_2	38	1.0	Methylcyclohexane	3.7	4.7
C_3H_8	37	4.4	2,2,3- and 2,3,3-Trimethylpentane	1.9	1.4
*C_3H_6	8.7	21.8	2,2,4-Trimethylpentane	2.5	1.8
*iso-C_4H_{10}	12	4.2	Toluene	2.0	17.6
n-C_4H_{10}	37	13.3	*1-Methylcyclohexene	4.7	∿ 6.0
*1-C_4H_8	1.5	8.9	2,2,5-Trimethylhexane	1.0	0.9
iso-C_4H_8	3.0	27.9	n-C_8H_{18}	2.1	2.2
iso-C_5H_{12}	44.3	29.2	EtC_6H_5	4.1	∿ 4.2
n-C_5H_{12}	16.2	8.9	p.m-Xylenes	1.4	∿ 32.1
Cyclo-C_5H_{10}	2.6	2.1	o-Xylene	6.0	11.3
*1-C_5H_{10}	4	∿ 2.4	n-C_4H_{20}	1.3	1.6
*2-Methylbutene	0.8	∿ 7.4	n-PrC_6H_5	1.0	∿ 1.2
*2,2-Dimethylbutene	0.8	∿ 4.7	sec-BuC_6H_5	5.0	∿ 7.0
2-Methylpentane	11.0	9.1	n-$C_{10}H_{22}$	1.1	1.5
3-Methylpentane	10.0	8.3	n-$C_{11}H_{24}$	1.0	1.5
*1-Hexene	1.7	∿ 10.0	n-$C_{12}H_{26}$	0.3	0.5
n-Hexane	10.0	7.1	CO	1,910	47.8 (12.1%)
*Cyclohexene	10.7	∿ 10.7	Total alkane		128.0 (32.5%)
2,2,3-Trimethylbutane	7.7	4.4	Total alkene		138.3 (35.1%)
C_6H_6	8.2	6.3	Total aromatic hydrocarbons		79.7 (20.2%)
2-Methylhexane	6.9	6.3	Grand total		393.8

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[a] Taken from table IV in ref. [7].
[b] Asterisks indicate olefins which contribute significantly to the removal of HO-radical.

in Los Angeles air samples [4]. It should be noted in this table, that a variety of olefins, indicated by asterisks, contribute significantly to the removal of HO-radical. The olefins as a whole are responsible for 35 percent of the HO removal by hydrocarbons. Similarly, relative removal rates of hydrocarbons by O_3 can be estimated for the data given in table 1. The results are shown in table 2. Only the olefinic hydrocarbons are listed in this table, since O_3 reactions with both paraffinic and aromatic hydrocarbons are negligibly slow. Notably, in this particular case, by far the dominant hydrocarbon-ozone reactions involve cyclic olefins, i.e., cyclohexene and 1-methylcyclohexene rather than the straight chain olefins commonly used as surrogates. Calvert [7] also estimated the comparable fractional rates of removal of C_3H_6 by O_3 (3.2 percent h^{-1}) and by HO (4.8 percent h^{-1}) for conditions given in table 1. These examples amply demonstrate that detailed hydrocarbon analyses of air samples are essential to the understanding of atmospheric chemistry.

Because of the close chemical coupling among O_3, NO and NO_2 concentrations via photo-stationary relationship [9], the role of olefins in the oxidant formation can be assessed only in terms of their effects on NO_x chemistry. Specifically, the key question is "how do the atmospheric reactions of olefins with HO and O_3 control NO and NO_2 concentrations?" The relevant chemistry is shown schematically in figure 1, where R represents H atom or hydrocarbon radicals formed, for instance, from olefin reactions with HO and O_3. Thus, to

Table 2. Estimated relative rates of O_3 attack on the olefins given in table 1.

Compound	(RH) ppb	Rel. O_3[a] rate	O_3 Rel. removal rate (%)
C_2H_4	43	.15	2.3
C_3H_6	8.7	1.0	3.2
1-C_4H_8	1.5	1.0	.5
iso-C_4H_8	3	1.0	1.2
1-C_5H_{10}	4	.8	1.2
2-methylbutene	.8	37.9	11.2
2,2-dimethylbutene	.8[b]	1.1	.3
1-hexene	1.7	.9	.5
cyclo-hexene	10.7	13.0	51.4
1-heptene	4.4[b]	.9	1.4
1-methylcyclohexene	4.7[b]	15.4	26.7

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[a] Taken from ref. [8].
[b] Estimated from analogous reactions.

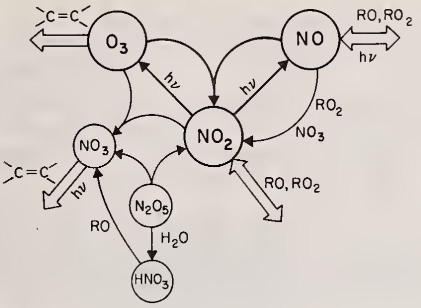

Fig. 1. Reactions controlling O_3 level in the lower troposphere.

account for the behavior of O_3, it is necessary to know the kinetics and mechanism of various RO and RO_2 species interacting with NO_x and all other labile atmospheric constituents. In fact, the predictive capability of modeling work on O_3 formation hinges on the understanding of free radical chemistry involving NO_x [1]. It is fair to state that at present, there is a serious lack of reliable information on the question "how effectively do olefins generate radical species and what is the subsequent fate of these radicals in the atmosphere?" In the following sections the current knowledge on olefin reactions with HO and O_3 will be discussed to address these questions.

3. Current Knowledge of Olefin Reactions With HO and With O_3.

A. HO-olefin reaction

Kinetics: As noted in the preceeding section, the atmospheric life time and radical formation efficiency of olefins are governed, in large part, by the HO reactions. Therefore, these rate constants should be determined with utmost accuracy. In recent years, numerous direct and relative measurements of these rate constants have been made over a wide range of temperatures and diluent pressures [10]. In particular, various direct experimental methods employing flash photolysis-resonance absorption and fluorescence, and discharge-flow-laser magnetic resonance have been successfully used to measure the decay rates of HO in the absence of interferences from secondary reactions. Thus, the overall accuracy of the rate constants determined by these methods is determined by the inherent signal-to-noise ratios in the HO decay curves and by the measurement of the reactant concentrations. Therefore, the highest attainable accuracy should be expected from these measurements as exemplified by the excellent agreement between two recent determinations of HO + C_3H_6 by Atkinson and Pitts [11] $k = 25.1 \pm 2.5 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and by Ravishankara et al. [12] ($k = 25.6 \pm 1.2 \times 10^{-12}$) at 298 K.

An extensive, critical review of previous studies on HO-olefin reactions has been made recently by Atlkinson et al. [10]. In the case of the lightest olefin, C_2H_4, the pressure dependence of k has been well established. The rate constant at 300 K is in the fall-off region between 2nd and 3rd order kinetics below ∿ 225 Torr of Ar and below ∿ 300 Torr of He. Table 3 shows a summary of limiting high pressure data on HO + C_2H_4 taken from the review by Atkinson et al. [10]. There is a spread of a factor of 2 among these values, although the recent values are more consistent but not up to the expected accuracy. The literature values of k for HO + C_3H_6 are also summarized in table 3. The fall-off region for C_3H_6 appears to occur at much reduced pressure of ∿ 1 Torr. Also included in this table are several values derived from relative decay rates of hydrocarbons measured in the photolysis of HC-NO_x mixtures at ppm concentrations. These relative values complement those of direct studies, but must be considered to be less precise (by as much as ± 20 percent).

The most extensive and consistent set of both direct and relative rate data for a large variety of olefins including terpenes and haloalkenes have been obtained recently by Pitts' group [10]. Their values agree, in general, with those determined by others to within ± 25 percent or better. Therefore, the kinetics of HO-olefin reactions should be considered to be reasonably well established. However, it should be noted that thus far, no direct measurements of these constants have been made in the presence of 1 atm air. Therefore, it is desirable to obtain further verification and improvement of these rate constants over wider range of pressures and temperatures.

Mechanism - Primary Step: There have been conflicting mechanistic interpretation of kinetic and product data obtained at low diluent pressures concerning the relative importance of HO-addition to olefinic double bond and H-atom abstraction. However, recent studies show convincingly that HO radicals undergo predominantly, if not exclusively, addition reactions with C_2H_4, C_3H_6 and other methyl-substituted olefins, and that the resulting adducts are collisionally deactivated in 1 atm of air. For example, in the case of C_2H_4, Howard [13] has shown that the rate constant extrapolates to zero at zero diluent pressure. Thus, the abstraction reaction is of negligible importance. In the case of C_3H_6, Cvetanovic [14] has made a comprehensive analysis of products formed in the photolyses of N_2O-CH_4-C_3H_6 and N_2O-H_2-C_3H_6 mixtures, and concluded that the majority of the observed products could be accounted for by reactions of radical species arising from the HO adducts. From these data, Cvetanovic further deduced the extent of the terminal addition being approximately 65 percent. It is interesting to note that Gutman et al. [15] earlier obtained evidence for H-abstraction from C_3H_6 and trans-2-butene under virtual absence of collisional deactivation in their cross-molecular beam - mass spectrometric studies. Thus, H-abstraction does occur to a minor extent. A somewhat puzzling study of the HO-C_2H_4 mechanism is that of Meagher and Heicklen [16]. These investigators photolyzed H_2O_2 in the presence of C_2H_4 and excess N_2 in both the presence and absence of added O_2 at 298 K. The observed quantum yields of products such as CH_2O, HCOOH and C_2H_3OH were taken to imply that the abtraction accounts for 20 percent of the primary reaction. This conclusion is at odds with those of other workers and must be judged to be incorrect.

Table 3. Rate constant data and Arrhenius parameters for the reaction of OH radicals with alkenes.[a]

Alkenes	$10^{12} \times A$ $cm^3 molec^{-1} s^{-1}$ [b]	E cal mol^{-1}	$10^{12} \times k$ $cm^3 molec^{-1} s^{-1}$	At T K	Technique	Reference	Temperature range covered
Ethene	1.26	-903 ± 136	5.33[c]	298-301	FP-KS	Greiner, 1970 (97)[a]	298-498 K
(limiting high	--	--	5.33 ± 0.65[d]	300	FP-RF	Davis et al., 1975 (165)	
pressure data)	--	--	6.23 ± 0.33	381	PR	Gordon & Mulac, 1975 (115)	
	--	--	7.21 ± 0.33	416			
	--	--	8.1 ± 1.6	305 ± 2	Relative rate	Lloyd et al., 1976 (135) (relative to OH+n-butane = 2.82×10^{-12})[e]	
	2.18	-770 ± 300	7.85 ± 0.79	299	FP-RF	Atkinson, Perry & Pitts, 1977 (168)	299-425 K
	--	--	10.0 ± 1.7	296	FP-RA	Overend & Paraskevopoulos, 1977 (103)	
Propene	--	--	17 ± 4	300	DF-MS	Morris, Stedman & Niki, 1971 (78)	
	--	--	5.0 ± 1.7	∿ 300	DF-ESR	Bradley et al., 1978 (151)	
	--	--	14.5 ± 2.2	298	FP-RF	Stuhl, 1973 (169)	
	--	--	13.4 ± 3.4	298	Relative rate	Gorse & Volman, 1974 (123) (relative to OH+CO = 1.50×10^{-13})[e]	
	--	--	14.3 ± 0.7	381	PR	Gordon & Mulac, 1975 (115)	
	--	--	20.0 ± 1.0	416			
	--	--	5 ± 1	300	DF-RA	Pastrana & Carr, 1975 (170)	
	4.1	-1080 ± 300	25.1 ± 2.5	298	FP-RF	Atkinson & Pitts, 1975 (155)	298-424 K
	--	--	25.6 ± 1.2[g]	298	FP-RF	Ravishankara et al., 1978 (105)	
	--	--	27.4 ± 5.5	305 ± 2	Relative rate	Lloyd et al., 1976 (135) (relative to OH-n-butane = 2.82×10^{-12})[e]	
	--	--	20.8	303	Relative rate	Wu, Japar & Niki, 1976 (121) (relative to OH+cis-2-butene = 5.20×10^{-11})[h]	
	--	--	23.5 ± 3.5	305 ± 2	Relative rate	Winer et al., 1976 (136) (relative to OH + isobutene = 4.80×10^{-11})[h]	
	--	--	23.5 ± 4.7	305 ± 2	Relative rate	Winer et al., 1977 (140) (relative to OH + isobutene = 4.80×10^{-11})[h]	

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[a] Taken from ref. [10]. Reference numbers are indicated as they appear in ref. [10].
[b] Mean Arrhenius preexponential factor.
[c] Total pressure not stated, but stated to be the same as in previous work (86), i.e., 100 Torr of helium.
[d] Essentially the high pressure limits from a Lindeman plot (175).
[e] Calculated from the Arrhenius pressure expression of reference (153) for T = 305 K.
[f] Reference (86).
[g] Rate constants at 20 Torr total pressure with helium as the diluent gas. No pressure effects were observed over the total pressure range 3-20 Torr (1-butene and cis-2-butene) or 20-200 Torr (propene).
[h] Calculated from the Arrhenius expressions of reference (155) for T = 303 K or T = 305 K.

In the case of olefins containing weak allylic hydrogens, e.g., 1-butene and 3-methyl-1-butene, Atkinson et al. [17] have postulated, from the correlation of HO and $O(^3P)$-atom reactivities towards olefins, that H-atom abstraction can occur up to 30 percent of the total reaction. Clearly, extensive product studies for larger olefins in the presence of an inert diluent gas at 1 atm pressure are needed to obtain more definitive information on the questions of HO-addition vs. abstraction, and position of the HO-addition.

Secondary Reactions in the Atmosphere: The nature of atmospheric reactions initiated by HO-olefin reactions is, generally, even less certain than the corresponding primary processes. However in the case of C_2H_4, C_3H_6 and $2\text{-}C_4H_8$, for which the HO-addition has been shown to be the predominant primary step, some significant progress has been made on the mechanistic interpretation of secondary reactions involving the HO-adducts in the presence of O_2 and NO_x. In particular, computer-aided numerical analyses of smog chamber data have played a major role.

In computer modeling of smog chamber data, the degree of success in arriving at a unique chemical mechanism may be judged by the extent of agreement

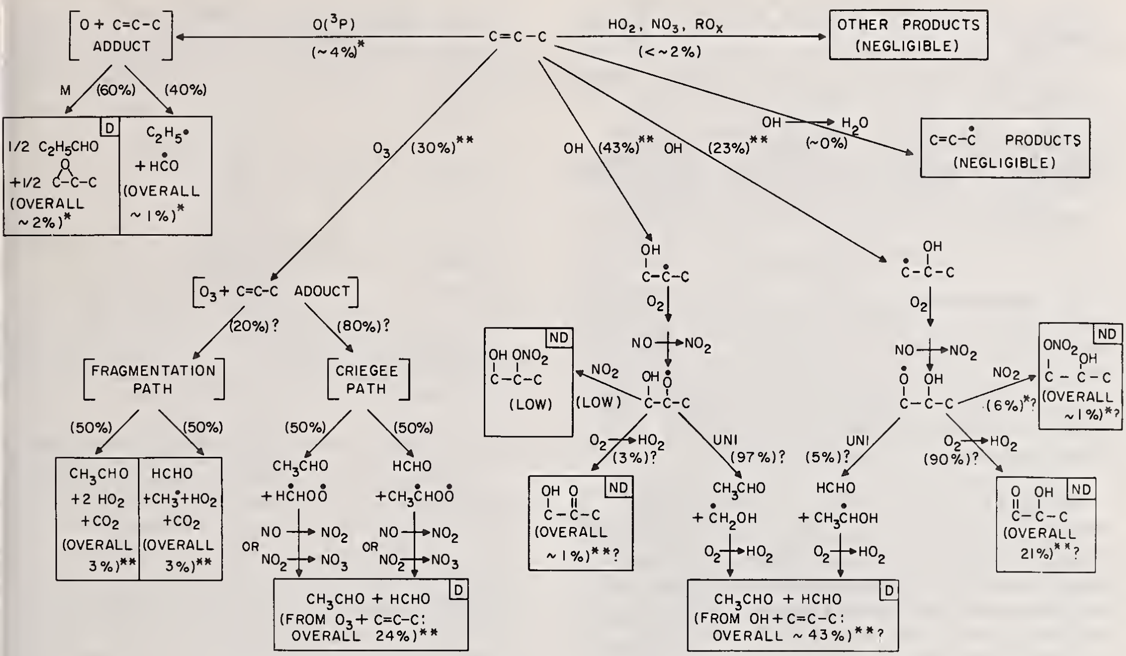


Fig. 2. Atmospheric reactions involving C_3H_6 (from ref. 19).

between computed and experimental concentration-time profiles of all the relevant reactants and products. Unfortunately, many existing smog chamber data have not been designed for the purpose of elucidating detailed reaction mechanisms, and consequently, suffer from the lack of sufficiently accurate and extensive product analyses and other kinetic parameters. In addition, for typical smog chamber data on olefins, both HO- and O_3 - initiated oxidation of olefin and No are of comparable importance. Thus, mechanistic understanding of HO-olefin reactions requires adequate knowledge of the corresponding O_3-olefin reactions or vice versa. Further complication in the interpretation of smog chamber data arises from the highly ill-defined, elusive role of what is commonly known as "chamber effects" [18]. These effects appear to be significant source and sink for chain carriers, e.g., HO and HO_2. It is apparent that better characterization of such effects is a prerequisite to the judicious use of smog chamber data for validating detailed smog mechanisms.

The current state-of-the-art smog chamber data generation and computer modeling can be illustrated by the work of Pitts' group [19] with C_3H_6-C_4H_{10} mixtures as surrogate hydrocarbons. The HO-C_3H_6 mechanism adopted by these investigators is shown in figure 2, together with other atmospheric reactions involving C_3H_6. In this scheme, two of the most important radical intermediates in the oxidation of the terminal HO adduct, ($\overset{\text{OH}}{\overset{|}{\text{C}}}-\dot{\text{C}}-\text{C}$), are $\overset{\text{OH}}{\overset{|}{\text{C}}}-\overset{\text{O}}{\overset{|}{\text{C}}}\text{C}$ and $\dot{C}H_2OH$. The corresponding radicals for the non-terminal HO adduct, ($\dot{\text{C}}-\overset{\text{OH}}{\overset{|}{\text{C}}}-\text{C}$), are $\overset{\text{O}\cdot}{\overset{|}{\text{C}}}-\overset{\text{OH}}{\overset{|}{\text{C}}}-\text{C}$ and $\dot{C}H_3CHOH$. The former oxy-type radicals undergo predominantly unimolecular dissociation, and to a minor extent, bimolecular reactions with O_2 and NO_2. The reactions of the latter hydroxyalkyl radicals with O_2 lead to H-atom transfer from the HO-group rather than the addition of O_2 to form peroxy radicals. Presumably, this mechanism has been deduced from studies of the NO_x-photoxidations of ethanol and 2-butanol. The same conclusion has been reached independently by Niki et al. [20] from Fourier Transform Infrared (FTIR) studies of Cl-atom initiated oxidation of NO_x alcohol mixtures in ppm concentration.

According to the scheme in figure 2, the HO-initiated oxidation of C_3H_6 in the presence of NO leads to the formation of HCHO and CH_3CHO as the major carbon-containing products and to the concomitant conversion of 2NO → $2NO_2$.

Similarly, the major products from C_2H_4 and 2-C_4H_8 are expected to be HCHO and CH_3CHO, respectively. Further evidence to support this conclusion has been recently obtained by Niki et al. [20] from product studies in the photooxidation of these olefins in the presence of HONO and NO. These experiments have been designed to produce HO from a well-defined photochemical source, i.e., HONO + hν → HO + NO, with minimal interference from O_3-olefin reactions by maintaining a large excess of NO over NO_2. Product analyses by the FTIR were made at sufficiently low conversion of the olefins to minimize secondary reactions of HO with the aldehydic products. Thus, this work represents a significant departure from conventional smog chamber-based studies, and should be extended to other olefinic compounds.

In conclusion, there is a great need for kinetic and mechanistic data on the oxidation of free radicals formed from HO-olefin reactions. The above-mentioned studies illustrate a classical photochemical approach to these problems. Clearly, it is highly desirable to study these chemical systems with more direct experimental methods.

B. O_3-olefin reactions

The atmospheric consumption of olefins proceeds, to a large extent, by their reactions with O_3. Furthermore, the question of whether the O_3-olefin reactions serve as an O_3 source or sink hinges on the efficiency of free radical formation by the reaction. Thus, utmost accuracy is required for the kinetic and mechanistic information on O_3-olefin reactions for modeling purpose.

Kinetics: Over the years, there have been numerous determinations of the rate constants for the reactions of O_3 with a large variety of olefins. A summary of literature values for several olefins is given in table 4. Generally, the reported values agree reasonably well for terminal olefins, but scatter far beyond the estimated experimental precision for internally double-bonded olefins. For instance, two of the most recent sets of extensive measurements by Huie and Herron [21] (ref. [1] in table 4), and by Niki et al. [8] (refs. f and k) disagree by as much as 48 percent for trans-2-butene and by an average of 27 percent for the entire set. The individual values in the latter set are all higher than those in the former. Apparently, there are factors other than systematic measurement errors affecting one or both experiments. In these studies as well as most of the others, the rate constants were derived from the decay rates of O_3 in the presence of excess olefins. In addition, the former employed much higher reactant concentrations and lower total pressures (< 10 Torr) than the latter (at 1 atm air). Therefore, the fundamental question is whether the consumption of O_3 is due entirely to the primary process or is interfered with by secondary reactions. Unfortunately, there exist large uncertainties in the reaction mechanisms, and such effects cannot be determined reliably at present.

There are several instances of kinetic evidence for the consumption of O_3 by secondary reactions, e.g., retardation of excess O_3 decay rates by O_2, [21, 22] and dependence of O_3 and olefin decay rates and reaction stoichiometry on reactant mixing ratios [22]. Therefore, all the reported values of the rate constants for O_3-olefin reactions must be considered as upper limit values. In particular, the higher values obtained by Niki et al. [8] might reflect the extent of such effect.

In short, experimental methodologies required for obtaining the "true" rate constants for O_3-olefin reactions have not been firmly established at present, and should be developed in the future. Meanwhile, concerted efforts should be made to minimize systematic errors as revealed in table 4. Concomitantly, kinetic and mechanistic studies of free-radical reactions involving O_3 and olefins should be made to better characterize the relevan secondary reactions as discussed below.

Table 4. Rate constants for gas phase ozone-olefin reactions at room temperature.^{a}

	$k, 10^{-18}$ cm^3 molec^{-1}s^{-1} Literature
Ethylene	1.2^{e}, 1.3^{b}, 1.6^{f}, 2.6^{c}, 2.7^{d}, 3.0^{a}, 1.9^{k}, 1.7^{l}
Propylene	6.2^{a}, 7.5^{c}, 8.2^{b}, 11.0^{c}, 12.5^{f}, 13^{i}, 1.3^{k}, 10.6^{l}
1-Butene	9.0^{c}, 10.0^{d}, 12.3^{k}, 10.3^{l}
1-Pentene	5.3^{a}, 7.5^{b}, 9.0^{c}, 10.7^{k}
1-Hexene	9.2^{a}, $10.0^{a,b}$, 10.2^{c}, $11.0^{d,f,h}$, 16^{i}, 11.1^{k}
Dialkylethylenes	
Isobutene	6.2^{b}, 8.4^{c}, 15^{h}, 23^{d}, 13.6^{k}, 11.7^{k}
cis-2-Butene	28^{c}, 50^{h}, 140^{i}, 340^{d}, 161^{k}, 126^{l}
trans-2-Butene	35^{c}, 166^{h}, 260^{i}, 275^{f}, 430^{d}, 260^{k}, 176^{l}
Trialklethylenes	
2-Methyl-2-butene	29^{c}, 790^{i}, 493^{k}, 400^{l}
cis-3-Methyl-2-pentene	456^{k}
trans-3-Methyl-2-pentene	563^{k}
Tetraalkylethylenes	
2,3-Dimethyl-2-butene	39^{c}, 750^{d}, 1510^{k}, 1060^{l}
Others	
Cyclopentene	813^{k}
Cyclohexene	30^{i}, 59^{a}, 169^{k}
1,3-Butadiene	8.2^{b}, 9.1^{i}, 8.4^{k}

[a] Taken from ref. [8]. References (a) through (k) given in ref. [8]; reference (l) is ref. [23] of this text.

Mechanism: To date, no direct monitoring of reactive intermediates formed in O_3-olefin reactions has been made under atmospheric conditions. Therefore, it is compelling to resor to the deduction of mechanistic models from produ studies. The model will provide a basis for establishing experimental priorities to reduce mechanistic uncertainties. Significant progress has been made recently both in characterizing key reaction products and in computer modeling of these results.

To illustrate, the reaction of O_3 with C_2H_4 ha been studies by Herron and Huie [23], using the stopped-flow mass spectrometry (M.S.) method, at 298 K and 8 Torr total pressure. From the comput modeling of the temporal behaviors of several species, e.g., C_2H_4, CO_2, H_2O, CH_2O, HCOOH and CH_3OH, the role of free radical mechanism involvi 27 steps has been proposed.

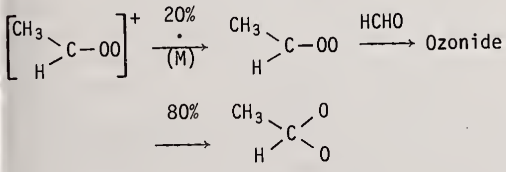
The initial reactions occurring under their experimental conditions have been postulated to be Criegee mechanism [29] followed by the unimolecular dissociation of the methylene peroxide, CH_2OO, to serveral products, i.e.,

$$CH_2O_2 \rightarrow H_2\overline{COO} \xrightarrow{67\%} H_2O + CO$$
$$\xrightarrow{18\%} H_2 + CO_2$$
$$\xrightarrow{9\%} 2H + CO_2$$
$$\xrightarrow{6\%} H\overline{COO}H$$

The formation of intermediate dioxirane (H_2COO) in the above scheme was predicted by Wadt and Goddard [24], and was subsequently verified by Lovas and Sueram [25] using microwave spectroscopy in the low-temperature reaction of O_3 with C_2H_4.

Clearly, the degree of reliability of the above postulated mechanism depends on the accuracy of the input kinetic data for the series of secondary reactions initiated by the product H atoms. On the basis of their modeling work, Herron and Huie [23] have pointed out the needs for improved data for several crucial free radical reactions occurring in O_3-C_2H_4 system. In particular, the mechanistic knowledge of the HO-C_2H_4 reaction is a prerequisite to unraveling the O_3-C_2H_4 mechanism. These investigators further extended their model to high pressure conditions and compared the computed results with the product data on O_3-C_2H_4 reactions obtained by Scott <u>et al</u>. [26] at ppm reactant concentrations in 1 atm air. In general, the agreement should be considered fair considering the uncertainty in both measurements and model.

Very recently, Dodge and Arnts [27] have developed a sufficiently detailed model including 6 steps for the reactions of O_3 with methyl-ubstituted olefins, e.g., C_3H_6 and 2-C_4H_8, which nvolve the formation and subsequent dissociation f a "hot" CH_3 CHOO radical, i.e.,



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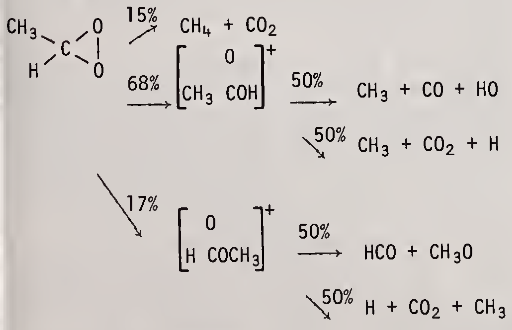

The above scheme for the decomposition of the CH_3CHOO radical to several free radical species was used to model the product studies of Niki <u>et al</u>. [28] in the O_3-air-2 butene - HCHO - air system.

Although these recent experimental and modeling studies are by no means definitive, they do shed new light on the O_3-olefin chemistry, in particular, on the efficiency of radical formation. Some of the O_3-olefin mechanisms adapted for atmospheric modeling incorporate the formation of two free radical species for every olefin molecule reacted with O_3 [9]. This assumption stems from two types of mechanistic conjectures which appeared plausible in the past. One of these was based on the motion that secondary ozonides are not formed from small olefins in air because of chemical instability of the corresponding Criegee intermediates, possibly reacting with O_2 [26]. The recent observation of propene ozonide in a mixture of O_3-2-C_4H_8-HCHO-air precludes this possibility [28]. The other stems from a theoretical treatment of gas phase O_3-olefin reactions by O'Neal and Blumstein [30] which deviates from the Criegee mechanism. At present, there is little experimental evidence that supports their theory uniquely. Thus, the new information suggests the production of fewer radical species than has been assumed previously.

4. Conclusion

Experimental methodologies for the determination of the kinetics of HO-olefin reactions appear to be well established, and should be applied more extensively to numerous olefins under wider range of temperature and diluent pressure. In contrast, derivation of "true" rate constants for O_3-olefin reactions from the decay rates of the reactants may suffer from the interferences due to secondary free radical reactions initiated mainly by "Criegee intermediates," and thus requires better mechanistic knowledge. To elucidate the mechanisms for O_3-olefin reactions, temporal behavior of the reactants and products should be better characterized first. These data can then be utilized for mechanistic modeling. The HO-initiated oxidation of olefin is likely to play a major role in the secondary reactions of O_3-olefin system. Thus, mechanistic studies of HO-olefin reactions in the presence of 1 atm air are prerequisite to the understanding of O_3-olefin reactions, and should assume the highest research priority.

References

[1] Demerjian, K. L., Kerr, J. A., and Calvert, J. C., <u>Adv. Environ. Sci. Technol</u>. <u>4</u>, 1 (1974).

[2] Dodge, M. C., Effect of Selected Parameters on Predictions of a Photochemical Model, EPA-600/3-77/148 (June, 1977).

[3] Echenroeder, A., Development of an Air Quality Model Based on the LARPP Data, (in progress).

[4] Parker, R. O. and Martinez, J. R., Los Angeles Reactive Pollutant Program (LARPP) Data Archiving and Retrieval, Document No.

P-1464-W, 1974, Environmental Research and Technology, Inc. Concord, Massachusetts, (NTIS Accession No. PB 244-298).

[5] Garvin, D. and Hampson, R. F. eds., Chemical Kinetics Data Survey VII, Table of Rate and Photochemical Data for Modelling of the Stratosphere [Revised], NBSIR 74-430, National Bureau of Standards, Washington, D.C. 20234 (May, 1973).

[6] Leighton, P. A., Photochemistry of Air Pollution (Academic Press, New York, 1961).

[7] Calvert, J. G., Environ. Sci. Technol. 10, (1976).

[8] Japar, S. M., Wu, C. H., and Niki, H., J. Phys. Chem. 78, 2318 (1974).

[9] Niki, H., Daby, E. E., and Weinstock, B., Adv. Chem. Ser. 113, 16 (1972).

[10] Atkinson, R., Darnall, K. R., Lloyd, A. C., Winer, A. M., and Pitts, J. N., Jr., Adv. Photochem. (in press).

[11] Atkinson, R. and Pitts, J. N., Jr., J. Chem. Phys. 63, 3591 (1975).

[12] Ravishankara, A. R., Wagner, S., Fischer, S., Smith, G., Schiff, R., Watson, R. T., Tesi, G., and Davis, D. D., Int. J. Chem. Kinet. 10, 783 (1978).

[13] Howard, C. J., J. Chem. Phys., 65 4771 (1976).

[14] Cvetanovic, R. J., 12th Int. Symp. Free Radicals, Laguna Beach, California, Jan. 4-9 (1976).

[15] Slagle, I. R., Gilbert, J. R., Graham, R. E., and Gutman, D., Int. J. Chem. Kinetics, Symp. No. 1, 317 (1975).

[16] Meagher, J. F. and Heicklen, J., J. Phys. Chem. 80, 1645 (1976).

[17] Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., J. Chem. Phys. 67, 3170 (1977).

[18] Bufalini, J., Walter, T., and Bufalini, M., Environ. Sci. Technol. 11, 1181 (1977).

[19] Carter, W. P. L., Lloyd, A. C., Sprung, J. R., and Pitts, J. N., Jr., Computer Modeling of Smog Chamber Data: Progress in Validation of a Detailed Mechanism for the Photooxidation of Propene and μ-Butane in Photochemical Smog, Int. J. Chem. Kinetics 11, 45 (1979).

[20] Niki, H., Marker, P. D., Savage, C. M., and Breitenbach, L. P., J. Phys. Chem. 82, 135 (1978).

[21] Huie, R. E. and Herron, J. T., Int. J. Chem. Kinetics, Symp. 1, 165 (1975).

[22] Japar, S. M., Wu, C. H., and Niki, H., J. Phys. Chem. 80, 2057 (1976).

[23] Herron, J. T. and Huie, R. E., J. Am. Chem. Soc. 99, 5430 (1977).

[24] Wadt, W. R. and Goddard, W. A., III, J. Am. Chem. Soc. 97, 3004 (1975).

[25] Lovas, F. J. and Suenram, R. O., Chem. Phys. Lett. 51, 453 (1977).

[26] Scott, W. E., Stephens, E. R., Hanst, P. L., and Doerr, R. C., Proc. Am. Petroleum Inst. 37, 171 (1957).

[27] Dodge, M. C. and Arnts, R. R., A New Mechanism for the Reaction of Ozone with Olefins, Int. J. Chem. Kinetics 11, 399 (1979).

[28] Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P., Chem. Phys. Lett. 46, 327 (1977).

[29] Criegee, R., Rec. Chem. Progs. 18, 113 (1975).

[30] O'Neal, H. E. and Blumstein, C., Int. J. Chem. Kinetics 5, 397 (1973).

Summary of Session

The discussion centered on the reactivity of OH and O_3 and the mechanisms of reaction of OH and O_3 with olefins. The mechanisms of OH-olefin reactions were treated by Cvetanovic. In his work hydroxyl radicals were produced by the photolysis of N_2O (to produce O'D) in the presence of H_2 or H_2O. In the absence of O_2, the major products of the reaction can be accounted for on the basis of an additions reaction followed by radical-radical and radical substrate reactions. There was no evidence that abstraction was important for ethylene or propylene, e.g., in the case of the propylene reaction only minor amounts of products characteristic of vinyl radicals, its major abstraction product, were found. Heicklen discussed the earlier work which had suggested the possible importance of an abstraction path for $OH + C_2H_4$. As pointed out by Niki in his review paper, larger olefins, particularly those with weak allylic bonds, all could react partially through an abstraction mechanism. Kinetic data support this argument.

Of greater interest is the question of the role of O_2 in the reaction. If the initial reaction is addition, then in the presence of O_2, a peroxy radical would be formed. The subsequent fate of this peroxy radical is one of the key problems in laboratory studies of atmospheric chemical reactions. Cvetanovic reported that, in the presence of O_2, the major products of the $OH + C_2H_4$ reaction were CH_3CHO and C_2H_5OH, and from $OH + C_3H_6$, the major product by far was CH_3CHO. These products are not readily accounted for on the basis of simple radical-radical interactions $2RO_2 \rightarrow R'CHO + R''OH + O_2$, or $2RO_2 \rightarrow 2RO + O_2$. In the atmosphere where NO is available it is generally assumed that the peroxy radicals are converted to alkoxy radicals. The subsequent fate of the alkoxy radicals is not understood. In the mechanism used by Niki (his fig. 2) based on modeling of the Riverside data, the alkoxy radical decomposes (a revised version of the mechanism and figure were supplied by Carter). It was pointed out by Batt and by Golden, however, that the simpler alkoxy radicals were more likely to react with O_2 (see review paper of Golden and susequent discussion). The specific fate of the radical $C_3H_6 \cdot OH \cdot O_2$ produced in the reaction of OH with C_3H_6 in the presence of O_2 was not resolved.

The rate constants for OH reactions are in relatively good shape as discussed by Atkinson. Rate constants for O_3 reactions are still subject to some uncertainty because of problems in measurement methodology. These problems would be resolved if the mechanisms were better understood. The major lack of kinetic data is for cyclic olefins which as Niki pointed out are the most important class with respect to consumption of ozone by olefins.

The mechanisms of ozone-olefin reactions have not been settled. Recent work, as reviewed by Niki, indicates that free radical yields are smaller than had been thought previously. Whitten emphasized that in most cases the radical yields were the important information needed by modelers rather than specific reaction channels. Dodge presented a general model for the reactions based on both high and low pressure experimental observations. This model appears to rule out the O'Neal-Blumstein mechanism. O'Neal agreed to this interpretation, pointing out the reasons for the discrepancy. Golden pointed out that the high and low pressure results used by Dodge might not be compatible because of different quenching rates etc., and the general mechanism should be used with caution. A critical question in this discussion is the chemistry of the Criegee intermediate, RCHOO. In particular what are the rates of reaction with NO_x, SO_x, and aldehydes relative to isomerization and scission. Heicklen commented on the reactions of ozone with chlorinated ethylenes where a π-complex may be involved.

There was considerable interest expressed in extending observations to more complex systems. The importance of cyclozlkenes was noted above. Stedman urged consideration of natural substances such as α-pinene and isoprene. O'Brien pointed out the difference between high and low molecular weight compounds particularly with respect to acid and aerosol formation. This raise unanswered questions as to the stabilization of the Criegee intermediate and their role in the formation of acids. The origin of organic acids is also a puzzling problem in photooxidation studies of aldehydes. Acids are also found in low pressure ozonoalysis studies.

Comments

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Rate Constant Data for the Reaction of OH Radicals with Alkenes: The available rate constant data and Arrhenius parameters are given in tables 1 (alkenes), 2 (monoterpenes) and 3 (dialkenes) which are taken from the review article of Atkinson, Darnall, Lloyd, Winer and Pitts, to be published in Advances in Photochemistry. The relative rate constant data of Cox [1] for ethane, propene and trans-2-butene, obtained from the photolysis of HCHO-alkene mixtures in air at 760 Torr total pressure, have not been included in table 1 as the stoichimetry factor was not known. The data from relative rate studies have been reevaluated on the basis of what is felt (however biased) by the authors to be the "best" rate constant for the reference reaction at the temperatures employed in the respective relative rate studies. The abbreviations used for the techniques are: DF-RF: discharge flow-resonance fluorescence; DR-RA: discharge flow-resonance absorption; DF-ESR: discharge flow-esr detection; DF-LMR: discharge flow with laser magnetic resonance detection of OH; DF-MS: discharge flow-mass spectrometry; FP-KS flash photolysis-kinetic spectroscopy; FP-RA: flash photolysis-resonance absorption; FP-RF: flash photolysis-resonance fluorescence; MPS: modulation-phase shift; PR: pulsed radiolysis. The tables list the literature data expressed in the form of $k = A\ e^{-E/RT}$ with k being given at room temperature, and A and E are the Arrhenius preexponential factor and Arrhenius activation energy, respectively.

For ethane the rate constant at room temperature (and up to 425 K) is in the falloff region between second order and third order kinetics [3,6,7,27,31] below ∿ 225 Torr of argon [6] and below ∿ 300 Torr of helium [3]. The rate in table 1 for ethene are limited to the high pressure results, although the rate constants of Greiner [2] (apparently obtained at 100 Torr total pressure of helium) have been included.

For ethane and propene the limiting high pressure room temperature rate constants appear to be reasonably well defined (table 1) at about 8 x 10^{-12} cm^3 $molec^{-1}$ s^{-1} and 2.5 x 10^{-11} cm^3 $molec^{-1}$ s^{-1}, respectively. For the higher alkenes the data do not appear to be as consistent. The rate constants obtained by Ravishankara et al. [18] for cis-2-butene and, especially, for 2,3-dimethyl-2-butene appear to be low; that for 2,3-dimethyl-2-butene [18] being a factor of 2 lower than the room temperature rate constants determined by Morris and Niki [19], Perry [25], and Atkinson, Darnall and Pitts [23]. It is probable that wall adsorption problem (as observed for propene in a metal reaction cell [18]) in the static system used by Ravishankara et al. [18] is the cause of these apparently low rate constants.

It would then appear that the flash photolysis-resonance fluorescence rate constant data of Atkinson and Pitts [14,22] and Atkinson, Perry, and Pitts [6,20] (which are generally in good

Table 1. Rate constant data and Arrhenius parameters for the reaction of OH radicals with alkenes.

Alkenes	$10^{12} \times A$ cm^{3}molec^{-1}s^{-1} ^{a}	E cal mol^{-1}	$10^{12} \times k$ cm^{3}molec^{-1}s^{-1}	At T K	Technique	Reference	Temperatu range covered
Ethene (limiting high pressure data)	1.26	-903 ± 136	5.33^b	298-301	FP-KS	Greiner, 1970 [2]	298-498
	--	--	5.33 ± 0.65^c	300	FP-RF	Davis et al., 1975 [3]	
	--	--	6.23 ± 0.33	381	PR	Gordon & Mulac, 1975 [4]	
	--	--	7.31 ± 0.33	416			
	--	--	8.1 ± 1.6	305 ± 2	Relative rate	Lloyd et al., 1976 [5] (relative to OH+n-butane = $2.82 \times 10^{-12})^d$	
	2.18	-770 ± 300	7.85 ± 0.79	299	FP-RF	Atkinson, Perry & Pitts, 1977 [6]	299-425
	--	--	10.0 ± 1.7	296	FP-RA	Overend & Paraskevopoulos, 1977 [7]	
Ethene-d_4	--	--	8.24 ± 0.48	298 ± 2	Relative rate	Niki et al., 1978 [8] (relative to OH + C_2H_4 = $8.00 \times 10^{-12})^e$	
Propene	--	--	17 ± 4	300	DF-MS	Morris, Stedman & Niki, 1971 [9]	
	--	--	5.0 ± 1.7	∿ 300	DF-ESR	Bradley et al., 1973 [10]	
	--	--	14.5 ± 2.2	298	FP-RF	Stuhl, 1973 [11]	
	--	--	13.4 ± 3.4	298	Relative rate	Gorse & Volman, 1974 [12] (relative to OH+OC = $1.50 \times 10^{-13})f$	
	--	--	14.3 ± 0.7	381	PR	Gordon & Mulac, 1975 [4]	
	--	--	20.0 ± 1.0	416			
	--	--	5 ± 1	300	DF-RA	Pastrana & Carr, 1975 [13]	
	4.1	-1080 ± 300	25.1 ± 2.5	298	FP-RF	Atkinson & Pitts, 1975 [14]	298-424 K
	--	--	27.4 ± 5.5	305 ± 2	Relative rate	Lloyd et al., 1976 [5] (relative to OH-n-butane = $2.82 \times 10^{-12})^d$	
	--	--	20.8	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH+cis-2-butene = $5.20 \times 10^{-11})^g$	
	--	--	23.5 ± 3.5	305 ± 2	Relative rate	Winer et al., 1976 [16] (relative to OH + isobutene = $4.80 \times 10^{-11})^g$	
	--	--	23.5 ± 4.7	305 ± 2	Relative rate	Winer et al., 1977 [17] (relative to OH + isobutene = $4.80 \times 10^{-11})^g$	
	--	--	25.6 ± 1.2^h	298	FP-RF	Ravishankara et al., 1978 [18]	
Propene-d_6	--	--	18.7	298	DF-MS	Morris & Niki, 1971 [19]	
	--	--	16.8	298	FP-RF	Stuhl, 1973 [11]	
1-Butene	--	--	40.8	298	DF-MS	Morris & Niki, 1971 [19]	
	--	--	15 ± 1	300	DF-RA	Pastrana & Carr, 1975 [13]	
	7.6	-903 ± 300	35.3 ± 3.6	298	FP-RF	Atkinson & Pitts, 1975 [14]	298-424 K
	--	--	27.0	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = $5.20 \times 10^{-11})^g$	
	--	--	29.4 ± 1.4^h	298	FP-RF	Ravishankara et al., 1978 [18]	

Table 1. Rate constant data and Arrhenius parameters for the reaction of OH radicals with alkenes. (continued)

Alkenes	$10^{12} \times A$ $cm^3 molec^{-1} s^{-1}$ [a]	E cal mol^{-1}	$10^{12} \times k$ $cm^3 molec^{-1} s^{-1}$	At T K	Technique	Reference	Temperature range covered
Isobutene	--	--	64.6	298	DF-MS	Morris & Niki, 1971 [19]	
	9.2	-1000 ± 300	50.7 ± 5.1	297	FP-RF	Atkinson & Pitts, 1975 [14]	297-424 K
	--	--	47.8	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	
cis-2-Butene	--	--	61.2	298	DF-MS	Morris & Niki, 1971 [19]	
	10.4	-970 ± 300	53.7 ± 5.4	298	FP-RF	Atkinson & Pitts, 1975 [14]	298-425 K
	--	--	61.5 ± 12.3	305 ± 2	Relative rate	Lloyd et al., 1976 [5] (relative to OH + n-butane = 2.82×10^{-12})[d]	
	--	--	58.6 ± 8.8	305 ± 2	Relative rate	Winer et al., 1976 [16] (relative to OH + isobutene = 4.80×10^{-11})[g]	
	--	--	42.6 ± 2.5[h]	298	FP-RF	Ravishankara et al., 1978 [18]	
trans-2-Butene	--	--	71.4	298	DF-MS	Morris & Niki, 1971 [19]	
	--	--	12 ± 10	300	DF-RA	Pastrana & Carr, 1975 [13]	
	11.2	-1090 ± 300	69.9 ± 7.0	298	FP-RF	Atkinson & Pitts, 1975 [14]	298-425 K
	--	--	67.6	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	
1-Pentene	--	--	42.5	298	DF-MS	Morris & Niki, 1971 [19]	
	--	--	29.1	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	
2-Methyl-	--	--	90.1	298	DF-MS	Morris & Niki, 1971 [19]	
1-butene	--	--	57.2	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	
3-Methyl-	5.23	-1060 ± 300	31.0 ± 3.1	299	FP-RF	Atkinson, Perry & Pitts, 1977 [20]	299-423 K
2-Methyl-	--	--	119	298	DF-MS	Morris & Niki, 1971 [19]	
2-butene	36	-450 ± 400	78 ± 8	298	FP-RF	Atkinson, Perry & Pitts, 1976 [21]	298-425 K
	19.1	-895 ± 300	87.3 ± 8.8	299	FP-RF	Atkinson & Pitts, 1978 [22]	299-426 K
	--	--	87 ± 6	300 ± 1	Relative rate	Atkinson, Darnall & Pitts, 1978 [23] (relative to OH + cis-2-butene = 5.29×10^{-11})[g]	
cis-2-Pentene	--	--	62.4	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	

Table 1. Rate constant data and Arrhenius parameters for the reaction of OH radicals with alkenes.[a] (continued)

Alkenes	$10^{12} \times A$ $cm^3 molec^{-1} s^{-1}$ [a]	E cal mol^{-1}	$10^{12} \times k$ $cm^3 molec^{-1} s^{-1}$	At T K	Technique	Reference	Temperatu range covered
2-Pentene (mix. cis, trans)	--	--	90.1	298	DF-MS	Morris & Niki, 1971 [19]	
1-Hexene	--	--	31.2	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	
Cyclohexene	--	--	62.4	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	
	--	--	73.4 ± 14.7	305 ± 2	Relative rate	Darnall et al., 1976 [24] (relative to OH + isobutene = 4.80×10^{-11})[g]	
3,3-Dimethyl-1-butene	--	--	27.0	303	Relative rate	Wu, Japar & Niki, 1976 [15] (relative to OH + cis-2-butene = 5.20×10^{-11})[g]	
2,3-Dimethyl-2-butene	--	--	153	298	DF-MS	Morris & Niki, 1971 [19]	
	--	--	110 ± 22	298	FP-RF	Perry, 1977 [25]	
	--	--	56.9 ± 1.3[h]	298	FP-RF	Ravishankara et al., 1978 [18]	
	--	--	122 ± 8	300 ± 1	Relative rate	Atkinson, Darnall & Pitts, 1978 [23] (relative to OH + cis-2-butene = 5.29×10^{-11})[g]	
1-Heptene	--	--	35.0 ± 7.0	305 ± 2	Relative rate	Darnall et al., 1976 [24] (relative to OH + isobutene = 4.80×10^{-11})[g]	
1-Methyl-cyclohexene	--	--	91.7 ± 18.3	305 ± 2	Relative rate	Darnall et al., 1976 [24] (relative to OH + isobutene = 4.80×10^{-11})[g]	

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[a] Mean Arrhenius preexponential factor.
[b] Total pressure not stated, but stated to be the same as in previous work [26], i.e., 100 Torr of helium.
[c] Essentially the high pressure limit from a Lindemann plot [27].
[d] Calculated from the Arrhenius expression of reference [28] for T = 305 K.
[e] Calculated from the Arrhenius expression of reference [6] for T = 298 K.
[f] Rate constant determined for OH + CO at room temperature and low pressure [29].
[g] Calculated from the Arrhenius expression of reference [14] for T = 300, 303 or 305 K.
[h] Rate constants at 20 Torr total pressure with helium as the diluent gas. No pressure effects were observed over the total pressure range 3-20 Torr (1-butene and cis-2-butene) or 20-200 Torr (propene).

In addition to the above data, Simonaitis and Heicklen [30] obtained rate constant data for propene relative to those for the reaction of OH radicals with CO at 373 and 473 K at total pressures of ∿ 400-800 Torr (mainly H_2O). They obtained $k(OH + C_3H_6)/k(OH + CO)$ (± 10%) = 75 at 373 K and 55 at 473 K. Assuming that $k(OH + CO) = 3.0 \times 10^{-13}$ cm^3 $molec^{-1}s^{-1}$, independent of temperature under these conditions (which is subject to large uncertainties), then by extrapolation a value of $k(OH + C_3H_6) = 3.3 \times 10^{-11}$ cm^3 $molec^{-1}s^{-1}$ at 298 K and an Arrhenius activation energy of E = -1090 cal mol^{-1} may be obtained. It is evident that this data (which is obviously subject to large uncertainties because of the assumptions made) is in general agreement with that obtained by references [5,14-18], as quoted in the table above.

Table 2. Rate constant data for the reaction of OH radicals with monoterpenes.

Terpene	10^{11} × k $cm^3molec^{-1}s^{-1}$	At T K	Technique	Reference
α-Pinene	5.5 ± 0.8	305 ± 2	Relative rate	Winer et al., 1976 [16] (relative to OH + isobutene = 4.80 × 10^{-11})[a]
β-Pinene	6.4 ± 1.0	305 ± 2	Relative rate	Winer et al., 1976 [12] (relative to OH + isobutene = 4.80 × 10^{-11})[a]
d-Limonene	14.2 ± 2.1	305 ± 2	Relative rate	Winer et al., 1976 [16] (relative to OH + isobutene = 4.80 × 10^{-11})[a]

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[a] Calculated from the Arrhenius expression of reference [14] for T = 305 K.

Table 3. Rate constant data and Arrhenius parameters for the reaction of OH radicals with dialkenes.

Dialkenes	10^{12} × A $cm^3molec^{-1}s^{-1}$[a]	E cal mol^{-1}	10^{12} × k $cm^3molec^{-1}s^{-1}$	At T K	Technique	Reference	Temperature range covered
Propadiene	--	---	4.5 ± 2.5[b]	∿ 300	DF-ESR	Bradley et al., 1973 [10]	
	5.59	-305 ± 300	9.30 ± 0.93	299	FP-RF	Atkinson, Perry, & Pitts, 1977 [20]	299-421 K
1,3-Butadiene	--	---	72.8 ± 14.6	305 ± 2	Relative rate	Lloyd et al., 1976 [5] (relative to OH + n-butane = 2.82 × 10^{-12})[c]	
	14.5	-930 ± 300	68.5 ± 6.9	299	FP-RF	Atkinson, Perry, & Pitts, 1977 [20]	299-424 K

---

[a] Mean Arrhenius preexponential factor.
[b] May be in the fall-off region between second order and third order kinetics (see text and reference [20]).
[c] Calculated from the Arrhenius expression of reference [30] at 305 K.

greement with the relative rate data [5,15-17,23] nd with the discharge flow-mass spectrometric ata of Morris and Niki [19]), together with the ate constant for 2,3-dimethyl-2-butene recently btained by Atkinson, Darnall, and Pitts [23] rom a relative rate study, should be viewed as he most consistent set of rate constant data. his is especially so as this set of absolute rate onstant data [14,20,22] also comprises the only emperature dependence studies for the alkenes ther than for ethene.

Finally, it should also be noted that with the lash photolysis systems used to determine OH adical rate constants for the alkenes, problems ave been encountered due to secondary reactions nd due to wall absorption of the reactants. hus, although the [reactant]/[OH] ratios are easonably similar with FP-RA and FP-RF, because f the higher flash energies used with RA etection (∿ 1000 joules per flash compared with 100 joules per flash for RF detection), secondry reactions of OH radicals with the larger mounts of photolysis products generated by the ore intense flash may be encoutered with flash hotolysis-resonance absorption systems.

References

[1] Cox, R. A., Int. J. Chem. Kinet. Symp. No. 1, 378 (1975).

[2] Greiner, N. R., J. Chem. Phys. 53, 1284 (1970).

[3] Davis, D. D., Fischer, S., Schiff, R., Watson, R. T., and Bollinger, W. , J. Chem. Phys. 63, 1707 (1975).

[4] Gordon, S. and Mulac, W. A., Int. J. Chem. Kinet., Symp. No. 1, 289 (1975).

[5] Lloyd, A. C., Darnall, K. R., Winer, A. M., Pitts, J. N., Jr., J. Phys. Chem. 80 and Pitts, J. N., Jr., J. Phys. Chem. 80, 789 (1976).

[6] Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., J. Chem. Phys. 66, 1197 (1977).

[7] Overend, R. and Paraskevopoulos, G., J. Chem. Phys. 67, 674 (1977).

[8] Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P., J. Phys. Chem. 82, 132 (1978).

[9] Morris, E. D., Jr., Stedman, D. H., and Niki, H., J. Amer. Chem. Soc. 93, 3570 (1971).

[10] Bradley, J. N., Hack, W., Hoyermann, K., and Wagner, H. Gg., J. Chem. Soc. Faraday Trans. I 69, 1889 (1973).

[11] Stuhl, F., Ber. Bunsenges, Phys. Chem. 77, 674 (1973).

[12] Gorse, R. A. and Volmam, D. H., J. Photochem. 3. 115 (1974).

[13] Pastrana, A. V. and Carr, R. W., Jr., J. Phys. Chem. 79, 765 (1975).

[14] Atkinson, R. and Pitts, J.N., Jr., J. Chem. Phys. 63, 3591 (1975).

[15] Wu, C. H., Japar, S. M., and Niki, H., J. Environ. Sci. Health A11, 191 (1976).

[16] Winer, A. M., Lloyd, A. C., Darnall, K. R., and Pitts, J. N., Jr., J. Phys. Chem. 80, 1635 (1976).

[17] Winer, A. M., Lloyd, A. C., Darnall, K. R., Atkinson, R., and Pitts, J. N., Jr., Chem. Phys. Lett. 51, 221 (1977).

[18] Ravishankara, A. R., Wagner, S., Fischer, S., Smith, G., Schiff, R., Watson, R. T., Test, G., and Davis, D. D., Int. J. Chem. Kinet., in press (1978).

[19] Morris, E. D., Jr. and Niki, H., J. Phys. Chem. 75, 3640 (1971).

[20] Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., J. Chem. Phys. 67, 3170 (1977).

[21] Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., J. Chem. Phys. 38, 607 (1976).

[22] Atkinson, R. and Pitts, J. N., Jr., J. Chem. Phys. 68, 2992 (1978).

[23] Atkinson, R., Darnall, K. R., and Pitts, J. N., Jr., J. Phys. Chem., submitted for publication (1978).

[24] Darnall, K. R., Winer, A. M., Lloyd, A. C., and Pitts, J. N., Jr., Chem. Phys. Lett. 44, 415 (1976).

[25] Perry, R. A., Ph.D. Thesis, University of California, Riverside, August 1977.

[26] Greiner, N. R., J. Chem. Phys. 51, 5049 (1969).

[27] Palmer, H. B., J. Chem. Phys. 64, 2699 (1976).

[28] Perry, R. A. Atkinson, R., and Pitts, J. N., Jr., J. Chem. Phys. 64, 5314 (1976).

[29] Perry, R. A., Atkinson, R., and Pitts, J.N., Jr., J. Chem. Phys. 67, 5577 (1977).

[30] Simonaitis, R. and Heicklen, J., Int. J. Chem. Kinet. 5, 231 (1973).

[31] Howard, C. J., J. Chem. Phys. 65, 4771 (1976).

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All workers agree that at room temperature and atmospheric pressure the predominant reaction of HO with C_2H_4 is addition. The only evidence for abstraction is given by Meagher and Heicklen (J. Phys. Chem. 80, 1645, 1976) who photolyzed H_2O_2 at 2537 Å to produce HO radicals. They found C_2H_5OH as the major product at high pressures and that this product became less important as the pressure was reduced, as expected for the pressure-sensitive addition reaction of HO with C_2H_4.

However they also found that CH_2O and HCOOH were produced in a pressure-insensitive reaction. From this they concluded that abstraction occurred 26 percent of the time for $[C_2H_4] \sim 2$ to 5 Torr, $[H_2O_2] \sim 2$ Torr, and $N_2 = 40$ Torr. They further estimated that in the high pressure limit, this fraction would further drop below 22 percent. Since then, the high pressure limit rate constant has been evaluated, and this fraction becomes 7 percent at the high pressure limit.

This value is still higher than indicated by some other studies, and may be due to energetic HO radicals in Meagher and Heicklen's system, since the photolyzing radiation provices an excess of ∿ 23 kcal/mol over that needed to photodissociate H_2O_2. It is apparent that if the HO radicals become significantly energetic (either thermally or by other means), and the pressure is low enough, then the abstraction reaction must become dominant. Thus pressure and temperature studies should be done to determine the conditions when the two competitive paths are important.

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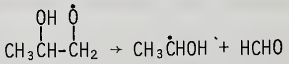
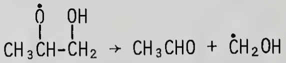
At the present time, the major uncertainties we have found in developing and validating the mechanisms for the OH-olefin system concerns the rate constant for the decomposition of β-substituted alkoxy radicals, relative to the rate of their reaction with O_2. For example, in the OH-propene system, the question concerns the rates of



$$CH_3\overset{OH}{C}H-\overset{\dot{O}}{C}H_2 \rightarrow CH_3\dot{C}HOH + HCHO \qquad (1)$$



$$CH_3\overset{\dot{O}}{C}H-\overset{OH}{C}H_2 \rightarrow CH_3CHO + \dot{C}H_2OH \qquad (2)$$

relative to the competing reactions with atmospheric O_2, forming β-hydroxy carbonyl products (see Niki's figure 2[1]). There appears to be some

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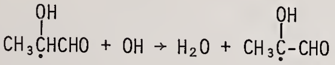
[1] Editor's note. Figure 2 in Dr. Niki's review paper is a revised version provided by Dr. Carter The change does not significantly affect Dr. Niki's conclusions.

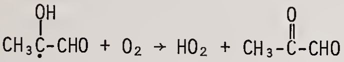
conflicts concerning this. The study of Niki et al. [1] on olefin-HONO-NO systems indicates that both reactions are fast, while we found, in modeling [2] the more recent U.C. Riverside smog chamber data [3] that the acetaldehyde and formaldehyde yields in propene-containing NO_x-air systems are better fit by models which assume that reaction (1) is slow and reaction (2) is fast. (The assumption that reaction (2) is much faster than reaction (1) is consistent with the theoretical estimates of Baldwin et al. [4]). Assuming that both reactions are fast results in the model overpredicting the most recently determined acetaldehyde and formaldehyde yields by ∿ 25 to 50 percent.

Our results [2] could be reconciled with those of Niki et al. [1] if there were systematic calibration errors in the determination of the acetaldehyde and formaldehyde yields in the UCR smog chamber runs. However, the yields of these products monitored in n-butane-NO_x-air UCR chamber runs using the same techniques [3] agree well with our n-butane model predictions [2]. Since in the n-butane system, the photooxidation mechanism is less uncertain; this tends to indicate that the reported yields of these products in the recent UCR chamber experiments are probably not in error.

It should be noted that our smog chamber modeling results are completely inconsistent with <u>both</u> reactions (1) and (2) being slow. Not only do models assuming this consistently underpredict acetaldehyde and formaldehyde, they also overpredict overall reactivity because both acetol and 2-hydroxy propanal, which would be the major products if reactions (1) and (2) were slow, are expected to react with OH to form methylglyoxyl



$$CH_3\underset{\bullet}{\overset{OH}{C}}HCHO + OH \rightarrow H_2O + CH_3\underset{\bullet}{\overset{OH}{C}}\text{-}CHO$$



$$CH_3\underset{\bullet}{\overset{OH}{C}}\text{-}CHO + O_2 \rightarrow HO_2 + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CHO$$

hose rapid photolysis would contribute significanly to radical initiation [2].

eferences

1] Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P., <u>J. Phys. Chem</u>. <u>82</u>, 135 (1978).

[2] Carter, W. P. L., Lloyd, A. C., Sprung, J. L., and Pitts, J. N., Jr., Computer modeling of smog chamber data: Progress in validation of detailed mechanisms for the photooxidation of propene and n-butane in photochemical smog, <u>Int. J. Chem. Kinetics</u> <u>11</u>, 45 (1979).

[3] Darnall, K. R., Winer, A. M., and Pitts, Jr., J. N., A smog chamber study of the propene-n-butane-NO_x systems, in preparation (1978).

4] Baldwin, A. C., Barker, J. R., Golden, D. M., and Hendry, D. G., <u>J. Phys. Chem</u>. <u>81</u>, 2483 (1977).

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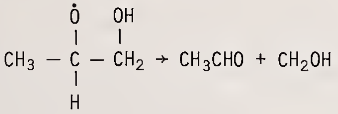
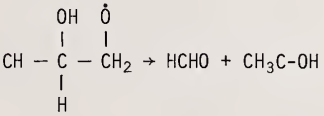
By analogy with our studies on the decomposition and other reactions of alkoxy radicals we are able to make some prediction about the two unimolecular steps



$$CH_3-\underset{H}{\overset{\dot{O}}{C}}-\overset{OH}{CH_2} \rightarrow CH_3CHO + CH_2OH$$



$$CH-\underset{H}{\overset{OH}{C}}-\overset{\dot{O}}{CH_2} \rightarrow HCHO + CH_3C\text{-}OH$$

given by Dr. Niki in his figure 2. The predictions indicate that the decompositions compete with difficulty with their reaction with oxygen, if at all. (See more detailed comments in session on free radical chemistry).

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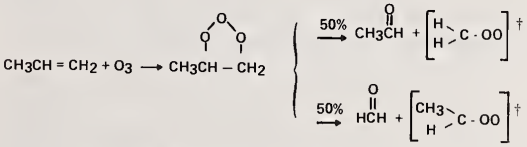
We recently developed a mechanism for the propylene-O_3 reaction to use in our modeling studies. The mechanism we formulated is based on the results of the two most recently published studies of olefin-O_3 reactions. These are Herron and Huie's study of the ethylene-O_3 reaction and the Niki <u>et al</u>. study of the reaction of cis-2-butene with O_3 in the presence of HCHO. The results of both of these studies can be explained in terms of the Criegee mechanism, which is given below for the propylene-O_3 reaction:



We used the mechanism developed by Herron and Huie to explain the fate of the HCHOO radical. Our treatment of the CH_3CHOO radical is based on an analysis of the product yields obtained by Niki <u>et al</u>. in their study. In our model, a fraction of the "hot" CH_3CHOO radical is assumed to be collisionally-stabilized at atmospheric pressure. The rest of the biradical undergoes rearrangement to form a "hot" acid and ester. The acid and ester subsequently decompose to various free radical species.

This mechanism was used to model data collected in our laboratory on the ozonolysis of propylene. Four experiments were conducted in Teflon bags in air at atmospheric pressure. An example of the type of fits obtained when we modeled these data is shown in figure 1. The simulated propylene and O_3 decay curves are in good agreement with

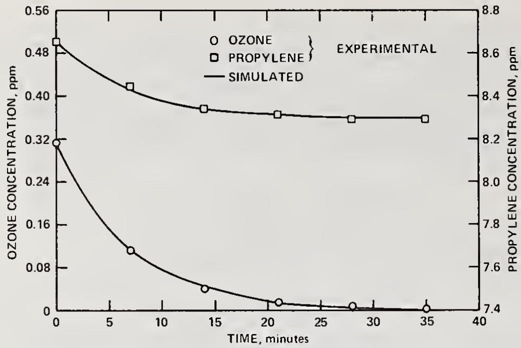
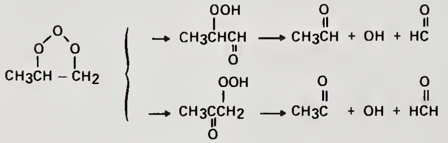


Fig. 1. Experimental and simulated results using the new mechanism for olefin-ozone reactions.

the experimental profiles. The fits obtained for the other three experiments were equally as good.

Although the new mechanism adequately explains the observed decay of propylene and O_3, the mechanism favored by many modelers in the past does not fit the data. In the last few years, many modelers have used a mechanism based on the O'Neal and Blumstein treatment of olefin-O_3 reactions. In this mechanism, the primary ozonide, after ring-opening, can undergo a number of rearrangements, the most likely of which is α-hydrogen abstraction to form unstable hydroperoxides. These peroxides can then fragment to an aldehyde and two free radicals:



When this mechanism was used to model the data, we obtained the type of fit shown in figure 2. The simulated rate of propylene disappearance is significantly faster than the observed rate of loss. Clearly, the data do not support this trea ment of propylene-O_3 chemistry.

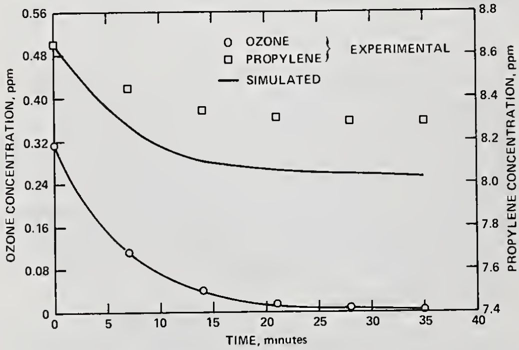


Fig. 2. Experimental and simulated results using mechanism based on the O'Neal-Blumstein treatment of olefin-ozine reactions.

Although the mechanism developed in this study adequately explains the observed decay of propylene and O_3, the results should not be construed as definitive. Additional work is needed in order to fully elucidate the mechanism of ozone-olefin reactions.

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Many modeling studies appear to have as their goal the matching of some particular set of experimental results (smog chamber data). Considering the non-existence of a proper data base for such an effort, it is not clear what suc fits demonstrate. Certainly with the available number of adjustable parameters it does not take a very ingeneous investigator to fit the data. To the unwary it may well appear that the entire problem has been solved. We know that this is nc the case and it would be more worthwhile to highlight disagreements and inability to fit the data This will immediately highlight the important questions that must be settled.

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Concerning the O'Neal-Blumstein mechanism, it should be noted that in the original formulation, the rate of reaction from the molozonide to the Criegee intermediate was estimated using (for an analogy) the then available t-butoxy radical decomposition rate constant. This is now known to have an A-factor about 100 times higher than that used in the estimate. The Criegee reaction pathway is therefore corresponding more important and relative to the competing intramolecular H-abstraction pathways, is now expected to be the dominant process under many reaction conditions.

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In an ozone-olefin reaction, it is the yield c free radicals that is important and not necessari the kind of radicals. Our recent modeling work indicates that for ethylene the yield of free rad icals should not exceed about 10 percent. We wer very pleased to see the results of Herron and Hui which confirm that estimate. In the case of the prophlene reaction we were pleased to see Niki's recent results which indicated a 30 percent radical yield, and Dodge's estimate of about 38 percent. In our air models we are using a value of 30 to 35 percent. Anything greater leads to a marked decay of propylene.

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The reaction of O_3 with olefins proceeds by irst forming the primary ozonide which then ecomposes to give either the Criegee zwitterion lus a carbonyl compound or free radicals. owever O_3 does react with olefins to form a eversible π-complex (E. Sanhueza, I. C. Hisatsune, nd J. Heicklen, Chem. Rev., 76, 801, 1976). here is no evidence that this species plays any ole in olefins containing only carbon and hydro- en. However this may not be the case with chlor- ated ethylenes, where kinetic evidence with HClCHCl gives a reaction rate law second order in oth CHClCHCl and O_3 at very low pressures. This as interpreted as meaning that the reversible -complex was the active species. This view is upported by the fact that the primary ozonides ere not seen in the reactions of O_3 with cis- and rans-CHClCHCl, CH_2Cl_2, and C_2Cl_4 (I. C. Hisatsune, . H. Kolopajilo, and J. Heicklen, J. Am. Chem. oc., 3704, 1977). The possible role of the -complex should be considered in O_3 reactions nvolving substituted olefins.

Recommendations

Reactions of Ozone and Hydroxyl Radicals with Olefins

Reactions of olefins with ozone and hydroxyl adicals are of fundamental importance for the hemistry of photochemical smog and although sub- tantial progress is being made in this field, uch further work remains to be done. This work hould involve both determinations of rate onstants and mechanistic studies. The latter hould be based on detailed product analysis, upplemented by computer modeling.

It is convenient to discuss ozone-olefin and H-olefin reactions separately.

1. Reactions of Ozone with Olefins

. Mechanism of ozone-olefin reactions

While significant progress is being made in the nvestigation of the mechanism of ozone-olefin eactions, it is clear that the mechanism is not et fully understood. Its full understanding is f crucial importance for an understanding of the hemistry of photochemical smog. Some of the hemistry involved in the O_3-olefin interaction in he gas phase is probably the same or is similar o the chemistry of the oxygenated free radicals eacting with O_2, as for example the radicals ormed by addition of OH to olefins in the presence f O_2. Further progress in this very difficult iled will require therefore imaginative studies ot only of ozone-olefin reactions but also of the eactions of O_2 with the oxygen containing free adicals produced in these systems. Photolysis of organic acids and esters and generation of selected oxygenated free radicals by other means are examples of the techniques which could be utilized for this purpose in future work.

Recommendations:

1) Selected ozone-olefin reactions, including cycloolefins, should be investigated under atmospheric conditions over a wide range of experimental parameters and with time resolved analysis of the concentrations of the reacting species and as many products as possible.

2) Techniques should be developed to generate and study the chemical behavior of the Criegee intermediates in the gas phase.

3) New approaches should be explored for studying the reactions of oxygen containing free radicals under atmospheric conditions to obtain information needed to understand the mechanism of ozone-olefin reactions in the gas phase.

4) The formation of aerosols induced by ozone-olefin reactions should be studied, the key intermediates isolated, and the critical chemical reactions studied.

B. Rates of ozone-olefin reactions

The phenomenological "rate constants" of the reactions of O_3 with a number of simple terminal olefins in the gas phase, show good mutual agreement and describe well the rates of consumption of these olefins. However, their exact relation to the "true" bimolecular rate constants will only be resolved when the mechanism of ozone-olefin reactions in the gas phase becomes fully understood. The "rate constants" for internal olefins measured in different laboratories show greater discrepancies. These discrepancies may be largely due to the fact that the range of experimental conditions has not been sufficiently broad to establish potential trends in the values. A better understanding of the reaction mechanism will no doubt also help to resolve these discrepancies.

The difference between the data obtained at high O_3-olefin concentrations in the gas phase and in non-polar solvents those obtained at low O_3-olefin concentrations in the gas phase and in non-polar solvents those obtained at low O_3-olefin concentrations under conditions similar to those in the polluted troposphere is puzzling. Further work with the object of resolving this discrepancy, while not of the highest priority, could help in the understanding of the mechanism of the O_3-olefin reactions in the gas phase.

Recommendations:

1) Measurements of the rates of O_3-olefin reactions in the gas phase should be extended to cover a substantially broader range of experimental conditions.

2) In view of the reportly very large O_3 consuming effect of some olefins (e.g. cyclo-olefins, terpenes) in the atmosphere, their reaction rates should be redetermined.

2. Reactions of Hydroxyl Radicals with Olefins

A. Mechanism of OH-olefin reactions

The mechanism of the OH reactions with ethylene and propylene in the absence of O_2 appears now to be reasonably well understood. Hydroxyl radicals add to these two olefins and there is little or no H atom abstraction at room temperature. (A suggestion that there is approximately 8 percent H atom abstraction from ethylene at atmospheric pressure, possibly due to "hot" OH radicals, is given in a separate comment further below). The mechanism of OH-olefin reactions in the presence of O_2, a process of crucial importance for the chemistry of photochemical smog, is unfortunately very incompletely understood.

Recommendations:

1) Study of the mechanism of the OH-olefin reactions in the absence of O_2 should be extended to olefins other than C_2H_4 and propylene, especially to the olefins known to be present in the polluted atmosphere.

2) Very high priority should be attached to detailed studies of the OH-olefin reactions in the presence of O_2, especially for olefins known to be present in polluted atmosphere.

3) Studies of the OH-olefin reactions under atmospheric conditions in the presence of varying amounts of NO_x (and possibly of other pollutants, such as SO_2, etc.) should be carried out with as detailed analysis of the reaction products as possible.

B. Rates of OH-olefin reactions

Good experimental techniques for the determination of OH-olefin reaction rates are now available. However, caution has to be exercised to assure accurate determination of the very small reactant concentrations used in some experiments and to establish the extent of the interfering secondary reactions, in particular of the OH-free radical secondary reactions.

2) A set of accurate values of the rate constants of the OH reactions with selected olefins (including ethylene under conditions similar to those in the lower atmosphere would be desirable in order to establish whether the rates are affected by oxygen in the air. The case of ethylene is of special interest in this respect because of a possibility of interception (and consumption by reaction) of the "hot" CH_2CH_2OH radicals by O_2. Such an interception could result in an appreciable increase in the rate constant of the OH-C_2H_4 reaction in air relative to the value obtained in laboratory measurements in the absence of O_2.

3) An ongoing critical review of the rate constants would be very useful.

Rate constants for the simple olefins are now probably known to within ± 20 percent. The value of the rate constant for C_2H_4 at 1 atm is probably also accurate within ± 20 percent. Rate constants for higher olefins and cycloolefins are less satisfactory, especially the values obtained by the competitive technique. No values are available for some important naturally occurring olefins such as terpenus and isoprene, although the latter could be roughly estimated from the value of the rate constant for 1,3-butadiene. The range of the literature values of the rate constan for acetylene is large (a factor of about 5-6) and further determinations are required.

Recommendations:

1) Further determinations of the rate constant are required for higher olefins, cycloolefins, isoprene, terpenes and acetylene.

Session II

Aldehydes

TROPOSPHERIC CHEMISTRY OF ALDEHYDES

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This paper presents a survey of the current published literature on aldehydes, and to a lesser extent, the other oxygenated hydrocarbons, as related to their role in modeling the troposphere. Sources, ambient levels, photochemistry, and free radicals, reactions of these substances are treated.

Key words: Aldehyde; free radical; photolysis; reactions; review; troposphere

1. Introduction

Aldehydes are major products in the oxidation of hydrocarbons and play a rather unique role in the photochemistry of the polluted troposphere. For example, they can contribute to photochemical smog, eye irritation, and odor problems. Their importance has been recognized for over a decade (Leighton, 1961; Altshuller and Cohen, 1963; Altshuller and Bufalini, 1965). While significant progress has been made in defining the photochemistry, kinetics, and mechanism of aldehyde photooxidation, much remains to be learned about their ambient concentrations as a function of time, season and location. Since aldehydes, both aliphatic and aromatic, occur as primary and secondary pollutants and are direct precursors of free radicals in the atmosphere, aldehyde chemistry represents an important subject area. The understanding of this topic is necessary to meet the objective of modeling tropospheric chemical reactions. In this context, the major objective of this paper is to consider the historical interest in aldehydes; their sources and atmospheric concentrations; the photochemistry, kinetics and mechanism of their reactions and finally to delineate current measurement needs and recommend research priorities based on assessment of the current status of knowledge of the chemistry of aldehydes in the troposphere.

In addition, the role of other oxygenated hydrocarbons in tropospheric chemistry will be addressed briefly. Although aldehydes are the main oxygenated hydrocarbons generally considered, and will receive major considerations here, other classes of oxygenated hydrocarbons merit consideration and should be assessed in terms of their involvement in the chemistry of the polluted troposphere. Thus ketones, esters, ethers and alcohols will be briefly considered to assess their possible importance in modeling the troposphere. The major areas of uncertainty will be discussed and research priorities suggested.

This paper is an attempt to survey the current published literature on aldehydes (and, to a lesser extent, other oxygenated hydrocarbons) as the work relates to modeling the troposphere. It is hoped that the discussion periods will extend the coverage to include unpublished work, preliminary results, and peripheral studies which have a direct bearing on the overall thrust of this paper.

2. Previous Work and Importance of Aldehydes

Initial impetus for the interest in the role of aldehydes in photochemical air pollution stemmed largely from the possibility that they were connected with eye irritation which became a major phenomenon and problem in the Los Angeles basin during the 1940's. However, an early Stanford Research Institute study (SRI 1950) concluded that "concentrations of aldehydes have rarely exceeded 0.2 parts per million by weight and the high concentrations did not coincide with periods of eye irritation. This lack of correlation tends to indicate that aldehydes alone are not responsible for eye irritation." Subsequent work indicated that acrolein was present on highly polluted days and this compound is known to be a potent eye irritant (Los Angeles Air Pollution Control District, 1950; Altshuller and McPherson, 1963; Scott Research Labs, 1969). Acrolein and formaldehyde were shown to be produced upon irradiation of dilute automobile exhaust and olefin-NO_x mixtures (Schuck, 1957; Schuck and Doyle, 1959).

Aside from the possible relationship of aldehydes to eye irritation, it was subsequently proposed (Leighton and Perkins, 1956; Leighton, 1961) that aldehydes could act as precursors to radicals which could either directly form oxidant or oxidize NO to NO_2. This possibility received support from the results of several experimental studies focused on the photooxidation of aldehydes under laboratory and simulated atmospheric conditions and generally employed formaldehyde and the lower molecular weight aliphatic aldehydes (Haagen-Smit and Fox, 1956; Altshuller and Cohen, 1963; Altshuller, Cohen et al., 1966; Johnston and Heicklen, 1964; Altshuller, Cohen et al., 1967; Cohen, Purcell et al., 1967; Purcell and Cohen, 1967; Bufalini and Brubaker, 1969).

Recently Dimitriades et al., (1972) and Pitts et al., (1976) carried out experiments in a smog chamber illustrating the effect of initial aldehyde concentrations on oxidant production under simulated atmospheric conditions. Figure 1 shows the significant impact of initial aldehyde concentrations on ozone formation in a nine-hour irradiation of a surrogate hydrocarbon mixture (Pitts et al., 1976). Thus an approximately 100 percent increase in initial formaldehyde concentration from 91 to 185 ppb increases the maximum ozone concentration by approximately 25 percent from about 0.39 to nearly 0.5 ppm in nine hours. Clearly, the rate of formation of O_3 is enhanced but it is possible that the O_3 maximum value would not be significantly increased if the irradiations were carried out sufficiently long.

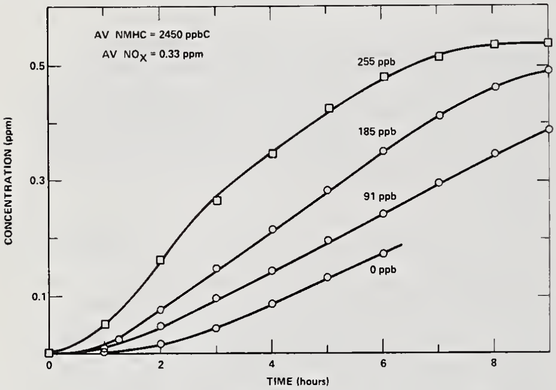

Fig. 1. Effect of added HCHO on ozone formation in long-term irradiations of surrogate mixture (from Pitts et al., 1976).

Aldehydes can provide significant sources of radicals such as HO_2, OH and RO_2 which can influence the rate at which photochemical oxidants are formed under ambient conditions. With the advent of appropriate computer calculation facilities to handle complex kinetic mechanisms, a number of workers demonstrated this effect by carrying out computer simulations of atmospheric chemistry both with and without initial aldehydes (Niki, Daby and Weinstock, 1972; Calvert et al., 1972; Demerjian, Kerr and Calvert, 1974; Dodge and Hecht, 1975; Levy, 1974; Whitten and Dodge, 1976; Graedel, 1976; Carter et al., 1978). Many of these calculations have focused on formaldehyde which photodissociates to produce significant amounts of HO_2 radicals under ambient conditions. Thus Demerjian et al., (1974) have shown that this route is the most important source of HO_2 radicals in the atmosphere.

Although there is some uncertainty attached to the quantum yields for photodissociation into radicals of HCHO as a function of wavelength (vide infra), aldehydes are well established as important ingredients in photochemical smog formation.

The role of aldehydes as eye irritants and radical precursors has been given above. An additional role for aldehydes is as precursors to the formation of peroxyacyl nitrates. These can be formed by the reaction mechanism

$$RCHO + OH \rightarrow RCO + H_2O$$

$$RCO + NO_2 \xrightarrow{O_2} RCO_3NO_2$$

peroxyacyl nitrate

Peroxyacyl nitrate type compounds have been found in many parts of the world e.g., Penkett et al. (1975) in England, van Ham and Nieboer (1972) in Netherlands, in Japan (Akimoto and Kondo, 1975) and in the U.S.A. (Stephens, 1969; Lonneman et al. (1976)).

3. Sources and Ambient Concentrations

Sources. There are primary and secondary sources of aldehydes in the atmosphere. The primary sources are related to combustion and result from incomplete combustion in, for example, internal combustion engines, diesel engines and stationary sources, such as incinerators, etc. (Altshuller et al., 1961; Linnell and Scott, 1962; Elliot et al., 1955). Automobiles are a significant source of aldehydes and the latter account for up to one-tenth of the hydrocarbon emissions (Black 1977). Oberdorfer (1964) and Seizinger and Dimitriades (1972) have analyzed the individual aldehydes emanating from pre-controlled automobiles. Table 1 shows the percentage of aldehydes from automobile exhaust as determined by several workers (Oberdorfer, 1964; Fracchio et al., 1967; Wodkowski and Weaver, 1970; Wigg et al., 1972). It is evident from these emission sources that formaldehyde is the largest aldehyde component. Similar but more extensive results are shown in table 2 which were obtained by Seizinger and Dimitriades (1972).

It can be seen that in addition to the saturated aliphatic aldehydes, acrolein--a potent eye irritant--is also present. In addition, benzaldehyde and formaldehyde are produced, along with alcohols, ethers and ketones. One would of course expect variations in the relative amounts of these compounds depending on the fuel used, e.g., see table 1.

With the advent of hydrocarbon control measures for automobiles, the aldehyde concentrations have been reduced along with the hydrocarbons. However, different control techniques apparently have varying effects upon the percentage reduction of aldehydes compared with the remaining hydrocarbons. Thus, Black (1977) shows interesting data for emissions from automobiles using thermal reactors, lean burn technology and catalysts of various kinds to reduce hydrocarbons. Table 3 shows a comparison of absolute and relative hydrocarbon class reductions for various automobiles employing different hydrocarbon control systems. It is apparent that cars using the catalyst system, rather than the lean burn system, effect greater reductions of aldehydes.

Table 1. Exhaust aldehyde analyses (adapted from National Academy of Sciences, 1976).

	Fraction of total exhaust aldehydes, volume percent					
Aldehyde	Wigg et al. (1972)[a]		Oberdorfer (1964)	Wodkowski and Weaver (1970)[a]		Fracchio et al. (1967)
Formaldehyde	66.7	72.5	70.2	59.9	69.3	72.9
Acetaldehyde	9.3	8.7	7.2	14.3	7.5	8.5
Propionaldehyde[b]	15.7	--	0.4	7.0	0.7	6.4
Acrolein	3.2	--	9.8		2.6	
Butyraldehydes	--	4.3	0.4	3.0	1.0	1.7
Crotonaldehyde	--	--	0.4	1.4	0.4	0.4
Valeraldehydes	--	--	0.4	--	--	--
Benzaldehyde	3.2	7.0	8.5	3.3	5.4	4.3
Tolualdehydes	1.9	7.2	--	5.9	3.1	--
Other	--	0.3	2.5	5.2	10.0	5.8
TOTAL	100	100	100	100	100	100

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[a] Exhausts from two different gasolines.

[b] Also includes acetone of unknown proportion.

Table 2. Oxygenates in exhaust from simple hydrocarbon fuels (from Seizinger and Dimitriades, 1972.).

Oxygenate	Concentration range, ppm[a]
Acetaldehyde	0.8- 4.9
Propionaldehyde (+ acetone)[b]	2.3-14.0
Acrolein	0.2- 5.3
Crotonaldehyde (+ toluene)[c]	0.1- 7.0
Tiglaldehyde	<0.1- 0.7
Benzaldehyde	<0.1-13.5
Tolualdehyde	<0.1- 2.6
Ethylbenzaldehyde	<0.1- 0.2
o-Hydroxybenzaldehyde (+ C_{10} aromatic)[d]	<0.1- 3.5
Acetone (+ propionaldehyde)[b]	2.3-14.0
Methylethylketone	<0.1- 1.0
Methylvinylketone (+ benzene)[e]	0.1-42.6
Methylpropyl (or isopropyl) ketone	<0.1- 0.8
3-Methyl-3-buten-2-one	<0.1- 0.8
4-Methyl-3-penten-2-one	<0.1- 1.5
Acetophenone	<0.1- 0.4
Methanol	0.1- 0.6
Ethanol	<0.1- 0.6
C_3 alcohol (+ C_3 aromatic)[f]	<0.1- 1.1
2-Buten-1-ol (+ C_3H_8O)	<0.1- 3.6
Benzylalcohol	<0.1- 0.6
Phenol + cresol(s)	<0.1- 6.7
2,2,4,4-Tetramethyltetrahydrofuran	<0.1- 6.4
Benzofuran	<0.1- 2.8
Methylphenylether	<0.1
Methyl formate	<0.1- 0.7
Nitromethane	<0.8- 5.0
C_4H_3O	<0.1
C_5H_5O	<0.1- 0.2
$C_5H_{10}O$	<0.1- 0.3

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[a] Values represent concentration levels in exhaust from all test fuels.

[b] Data represent unresolved mixture of propionalydehyde + acetone. Chromatographic peak shape suggests acetone to be the predominant component.

[c] Tuolene is the predominant component.

[d] The C_{10} aromatic hydrocarbon is the predominant component.

[e] Benzene is the predominant component.

[f] The aromatic hydrocarbon is the predominant component.

Aldehydes are also emitted from some stationary sources (EPA-AP42). These include power plants burning oil and coal and sources such as incinerators, animal rendering facilities, or gasoline and diesel engines operated at stationary source facilities. Typical levels from stationary combustion sources are given in table 4 (National Academy of Sciences, 1976).

Secondary. Sources of aldehydes include the oxidation of hydrocarbons in the presence of NO_X under ambient atmospheric conditions. Figure 2 shows a concentration time plot for the formation of secondary pollutants including aldehydes from an irradiated hydrocarbon-NO_x mixture under simulated atmospheric conditions. Major sources in such systems are the reactions of ozone and OH radicals with olefins, and radical decomposition products, e.g.,

$$O_3 + C_3H_6 \rightarrow HCHO + CH_3O + \text{radical products}$$
$$RCHOH + O_2 \rightarrow RCHO + HO_2$$

In addition, aromatic aldehydes can be formed by the reaction of OH with aromatics, i.e., benzaldehyde.

Ketones and hydroxyaldehydes or hydroxy-ketones can obviously also be formed in such oxidation systems.

Ambient Concentrations. The major problem in measuring atmospheric concentrations of aldehydes is the lack of an appropriate monitoring technique applicable to this low concentration regime. For example, wet chemical techniques, such as the chromatropic acid method for measuring formaldehyde. are subject to interferences and uncertainties in the results can be large. Consequently, results of studies in the Los Angeles area in the 1940's and 50's may be subject to large error. For example, levels of 1.87 ppm in 1956 reported for total aldehydes by the Los Angeles County Air Pollution Control District are suspiciously high. More typical values of around 0.4 ppm were reported for lower molecular weight aldehydes on days of significant air pollution in Los Angeles in the late 1940's and early 50's (Katz, 1961).

Table 3. Automobile exhaust hydrocarbon (and aldehyde) emission patterns (from Black, 1977).

Vehicle	Control system	Total exhaust Hydrocarbon, g/mi.	Percentage of total hydrocarbon, wt.%								
			Methane	Paraffin	Acetylene	Benzene	Aromatic	Ethylene	Olefin	Formaldehyde	Total aldehydes
1972 350 CID	non-catalyst	1.15	9.29	40.68	11.04	2.43	22.30	12.97	26.00	3.28	7.00
1974 Mazda rotary 40 CID	thermal reactor	1.47	8.99	41.62	6.20	2.04	18.04	17.45	33.70	6.83	11.00
1975 Chev. Impala, 350 CID	single oxidation catalyst	.25	15.44	57.09	2.72	1.44	19.68	8.76	20.44	1.60	3.64
Honda CVCC (proto.) 91 CID	stratified charge (lean)	.28	4.64	37.82	7.29	1.79	22.24	15.11	32.46	6.00	11.29
Volvo (proto) 130	three-way reduction-oxidation catalyst	.16	19.91	56.59	4.73	1.47	21.60	5.17	17.10	.94	3.25

Table 4. Typical emission of several classes of compounds including aldehydes from stationary combustion sources (from National Academy of Sciences, 1976).

Compounds	Emission, lb/ton of fuel		
	Coal	Oil	Gas
Hydrocarbons	0.3	1.0	1.0
Aldehydes	unknown	0.5	0.5
Formaldehyde	0.003	0.006	0.008
Organic acids	10	∿5	2

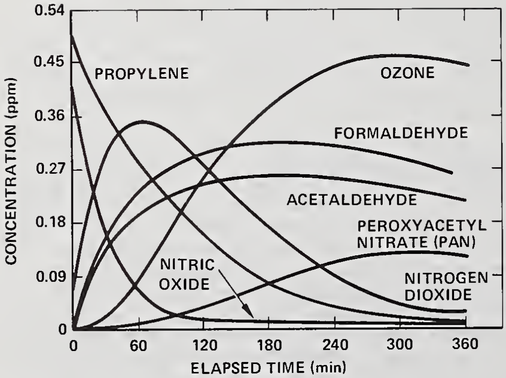

Fig. 2. Results of a typical smog chamber experiment (SAPRC evacuable chamber). Irradiation of a propylene-NO-NO_2 mixture in air. Initial experimental conditions--0.5 ppm propylene, 0.45 ppm NO, and 0.05 ppm NO_2 in 760 Torr of highly purified air.

Aldehydes have been measured in various parts of the world, but the most extensive body of data exists for Los Angeles (Stanford Research Institute 1950; Renzetti and Bryan, 1961; Altshuller and McPherson, 1963; Scott Research Laboratories, 1969; California Air Resources Board, 1972). The studies of Altshuller and McPherson showed typical formaldehyde and acrolein levels of ∿ 0.04 ppm and ∿ 0.07 ppm respectively during September to November 1961. More recently, the California Air Resources Board (1972) measured formaldehyde at levels up to 0.1 ppm, while daily average levels were around .035 ppm. Acetaldehyde exhibited an average concentration of .02 ppm, while no other aldehydes or ketones were detected above their threshold of 0.1 ppm. The Air Resources Board found that aldehyde levels in the eastern part of the Los Angeles basin were significantly lower than those in downtown Los Angeles: specifically, formaldehyde was found to average less than 0.2 ppm and acetaldehyde less than .015 ppm at Azusa. Figure 3 shows hourly concentrations measured at two locations in the Los Angeles area in 1968 by Scott Research Laboratories. Both locations show sharp decreases in afternoon levels of total aliphatic aldehydes.

The advent of Fourier transform infrared spectroscopy (FTIR) has added a significant new dimension to the measurement of trace pollutants, including aldehydes, in ambient air. The technique is specific and sensitive. Hanst and coworkers (1975) first applied the method in Pasadena in 1972. They measured HCOOH at surprisingly high levels but detected no significant amounts of HCHO. More recently, low levels of formaldehyde ($\leq$ 10 ppb) have been observed in the eastern part of the Los Angeles basin by Tuazon et al. (1978a) also using FT-IR spectroscopy. These workers detected levels of formic acid up to 10 ppb and there was no obvious correlation between the HCHO and HCOOH ambient concentrations. However, this study has been largely superceded by more recent results using improved absorptivi-

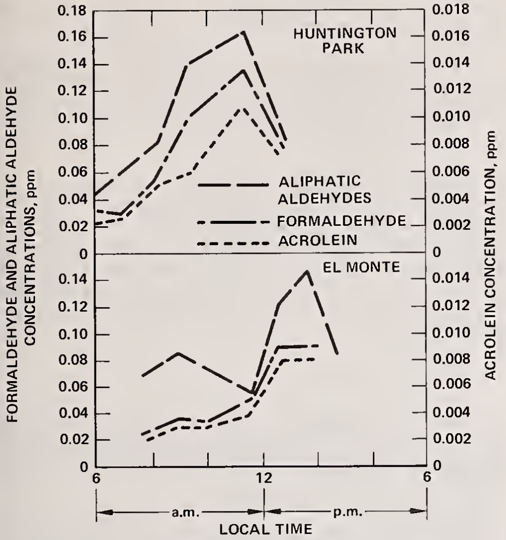

Fig. 3. Hourly aldehyde concentrations at two Los Angeles sites, October 22, 1968 (from Air Quality Criteria Document for Hydrocarbons, 1970).

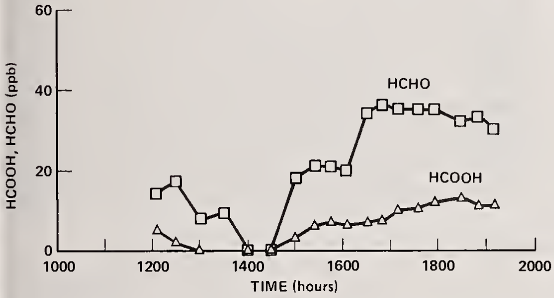

Fig. 4. Ambient concentrations of HCHO and HCOOH as a function of time measured in Riverside, October 14, 1977 (from Tuason et al., 1978).

ties for several species including HCHO and HCOOH (Tuazon et al., 1978b). Some of the results from this 1977 study are shown in figure 4. The ambient levels of HCHO for this October 14, 1977 day (∿ 36 ppb) are significantly higher than measured in the previous study. This is partly due to the improved absorptivities used in the 1977 study. There is some evidence that the new absorptivities would also reduce the levels of HCOOH reported by Hanst el al. (1973) in the Pasadena study (Winer, 1978).

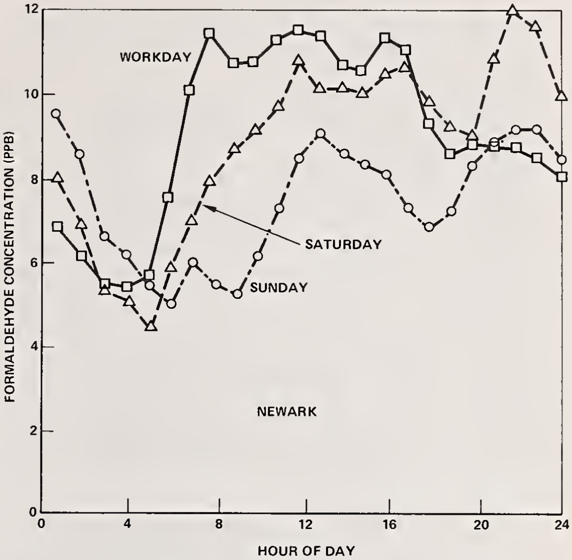

Fig. 5. Diurnal concentrations of formaldehyde at Newark, New Jersey for different days of the week, from June 1 to August 31 for the years 1972, 1973, and 1974 (from Cleveland et al., 1977).

In the last few years continuous measurements for formaldehyde have been undertaken in certain areas of New Jersey (Cleveland et al., 1977). This continuous monitoring showed a correlation with vehicle traffic and a seasonal variation with higher levels in summer than in winter. Peak formaldehyde concentrations were in the range of 14 to 20 ppb at four sites monitored. For example, figure 5 shows formaldehyde levels reported for Newark as a function of the day of the week. In Japan, Katou, (1972), observed high levels of the unsaturated aldehyde, acrolein. The average concentration measured was 7.2 ppb, but maximum levels as high as 273 ppb were reported.

With the advent of FT-IR spectroscopy employed by several groups of workers (e.g., Calvert et al.; Hanst et al.; Niki et al. and Pitts, Winer et al. more reliable data for aldehydes should become available for both ambient and simulated atmospheric conditions. Of necessity, the geographical area covered will be limited in the near future by the complexity and expense of the instrumentation.

4. Kinetics and Mechanism

This section is divided into two parts -- the first discusses the primary attack of radicals on aldehydes and the second part discusses the fate in the atmosphere of the radicals produced.

The aldehydic hydrogen in aldehydes is relatively weak (C-H bond strength is 86 kcal mol^{-1}, Trotman-Dickinson and Kerr, 1975). Consequently, this hydrogen atom will be susceptible to attack by radical species present under atmospheric conditions. Possible species are $O(^3P)$, $O(^1D)$, OH, HO_2, NO_3 and HSO_4. Of these OH is likely to be by far the most dominant.

A. Radical and Atom Reactions with Aldehydes

OH Radical Reactions. OH is generally thought to abstract an H atom from aldehydes -- chiefly the aldehydric H atoms, i.e., the reaction

$$OH + RCHO \rightarrow H_2O + RCO \quad (1)$$

Niki and coworkers have carried out rate studies for the largest number of aldehydes ranging from the C_1-C_3 aliphatic aldehydes to benzaldehyde (Morris and Niki, 1971; Morris et al., 1971; Niki et al., 1978). The two former studies were carried out at low pressure using a discharge flow-mass spectrometer technique for the generation of reactants and analysis of products respectively. In their latest study, Niki et al. used the photolysis of HONO to generate OH radicals in the presence of the aldehyde and C_2H_4 or C_2D_4 at close to atmospheric pressure and monitored the decay of reactants by Fourier transform infrared spectroscopy. In this way, rates of reaction of aldehydes relative to ethylene were determined. These values were placed on an absolute basis using the appropriate rate constant for the OH reaction with C_2H_4 at atmospheric pressure (Niki et al., 1978). These values are shown in table 5 with the modification that the rate constant for the OH + C_2H_4 reaction obtained by Atkinson et al., (1977) was used to reduce the relative values of Niki et al. (1978).

Also included are the recent results for HCHO and CH_3CHO obtained by Atkinson and Pitts (1978) using a technique yielding absolute rate constants. These latter workers used a flash photolysis-resonance fluorescence technqiue and carried out the first study of aldehydes over a range of temperature (299-426 K). Arrhenius activation energies for the two aldehydes studied are small with acetaldehyde exhibiting a negative value.

Table 5 allows a comparison among the results obtained by the various workers employing three different techniques. The agreement between the earlier work of Niki and coworkers (1971) and the most recent study of Niki et al. (1978) is excellent for HCHO and CH_3CHO but only fair for C_2H_5CHO. These results agree well with those of Atkinson and Pitts (1978) for CH_3CHO but are about 50 percent higher for HCHO.

If one assumes an atmospheric OH concentrations of 10^6 radicals cm^{-3}, the rates of decay of HCHO and CH_3CHO by reaction with OH are $\sim$ 4.2 percent and 5.8 percent h^{-1} respectively.

O Atom Reactions. Attention here will be focused on ground state atomic oxygen, (O^3P) since this more abundant than $O(^1D)$ in the lower troposphere. $O(^3P)$ reacts with aldehydes in the same manner as OH, by abstracting the aldehydic H atom. However, the reaction is a chain branchin one compared with a chain transfer reaction in the case of OH

$$O + RCHO \rightarrow RCO + OH \qquad (2)$$

Results of several studies of $O(^3P)$ reacting with a variety of aldehydes are shown in table 6. No results are shown from purely high temperature studies such as shock tubes.

The most extensive data are those obtained by Singleton et al. (1977) for four aldehydes-acetaldehyde, propionaldehyde, n- and iso-butyraldehyde. These workers used a phase shift technique and covered a temperature range of 298-472 K. They reported that at the high end of their temperature range, abstraction of the alkyl group H atoms became significant for the higher molecular weight aldehydes. However, under atmospheric conditions, abstraction of the aldehydric H atom is likely to dominate. The room temperature rate constants in table 6 show that there is generally good agreement among the different workers for acetaldehyde but significant differences for propionaldehyde and butyraldehyde. The technique used by Singleton et al., would suggest that their results should be mor reliable and should be used in any modeling studies

Table 5. Rate constant data and Arrhenius parameters for the reaction of OH radicals with aldehydes.

Reactant	10^{12} x A $cm^3molec^{-1}s^{-1a}$	E cal mol^{-1}	10^{12} x k $cm^3molec^{-1}s^{-1}$	at T K	Reference	Temperature range covered
HCHO	--	--	$\geq$6.6	300	Herron and Penzhorn, 1969	
	--	--	14 ± 3.5	298	Morris and Niki, 1971	
	12.5	175 ± 300	9.4 ± 1.0	299	Atkinson and Pitts, 1978	299-426 K
	--	--	14.4 ± 0.8	298 ± 2	Niki et al.,1978 (relative to OH + C_2H_4 = 8.00 x 10^{-12} (Atkinson et al., 1977))	
CH_3CHO	--	--	15 ± 3.8	300	Morris, Stedman and Niki, 1971	
	--	--	$\leq$20	295 ± 2	Cox et al., 1976 (relative to OH + HONO = 6.6 x 10^{-12} (Cox, et al., 1976))	
	6.87	-510 ± 300	16.0 ± 1.6	299	Atkinson and Pitts, 1978	299-426 K
	--	--	15.2 ± 1.6	298 ± 2	Niki et al., 1978 (relative to OH + C_2H_4 = 8.00 x 10^{-12} (Atkinson et al., 1977))	
C_2H_5CHO	--	--	31	298	Morris and Niki, 1971	
	--	--	20.8 ± 0.8	298 ± 2	Niki et al., 1978 (relative to OH + C_2H_4 = 8.00 x 10^{-12} (Atkinson et al., 1977))	
C_6H_5CHO	--	--	12.8 ± 0.8	298 ± 2	Niki et al, 1978 (relative to OH + C_2H_4 = 8.00 x 10^{-12} (Atkinson et al., 1977))	

Table 6. Arrhenius parameters and rate constants for the reaction of oxygen atoms (O^3P) with aldehydes.

Reactant	A (cm^3 $molec^{-1}s^{-1}$)	E ($kcal$ mol^{-1})	k (cm^3 $molec^{-1}s^{-1}$)	TK	Technique	Reference
HCHO			1.5×10^{-13}	300	Discharge flow-mass spectrometry (DF-MS)	Herron and Penzhorn (1969)
			1.6×10^{-13}	300	DF-MS	Niki, Daby, and Weinstock (1969)
			1.5×10^{-13}	300	Discharge flow-product analysis, epr and chemiluminescence	Mack and Thrush (1973)
CH_3CHO	1.20×10^{-11}	1.460 ± 0.153		298-472	Hg sensitization-chemiluminescence	Singleton et al. (1977)
			4.3×10^{-13}	298		
			4.8×10^{-13}	298	Discharge flow-product analysis, epr and chemiluminescence	Mack and Thrush (1974)
	2.3×10^{-11}	2.36		300-480	Discharge flow-chemiluminescence	Cadle and Powers (1967)
			4.5×10^{-13}	298		
			5.0×10^{-13}	298	Hg sensitization-product analysis	Cvetanovic (1956)
C_2H_5CHO	1.30×10^{-11}	1.727 ± 0.066		298-472	Hg sensitization chemiluminescence	Singleton et al. (1977)
			7.0×10^{-13}	298		
	1.41×10^{-11}	3.8		300-480	Discharge flow-chemiluminescence	Cadle et al. (1972)
			2.3×10^{-13}	298		
C_3H_7CHO	1.66×10^{-11}	1.702 ± 0.040		298-472	Hg sensitization-chemiluminescence	Singleton et al. (1977)
			9.5×10^{-13}	298		
			2.5×10^{-13}	298	NO_2 photooxidation-quantum loss of NO_2	Jaffee and Wan (1974)
$i\text{-}C_3H_7CHO$	1.32×10^{-11}	1.445 ± 0.091		298-472	Hg sensitization-chemiluminescence	Singleton et al. (1977)
			1.2×10^{-12}	298		
$CH_2 = CHCHO$ (acrolein)	7.8×10^{-12}	2.0		300-480	Discharge flow-chemiluminescence	Cadle et al. (1972)
			2.7×10^{-13}	298		
	6.0×10^{-11}	2.84		296-423	Relative rate relative to O + propylene	Gaffney, Atkinson, and Pitts (1975)
			4.9×10^{-13}	296		
Crotondehyde	3.3×10^{-11}	2.3		?	Discharge flow-chemiluminescence	Cadle et al. (1974)
			8.3×10^{-13}	298		
	6.4×10^{-11}	2.43		296-423	Relative rate relative to O + propylene	Gaffney, Atkinson, and Pitts (1975)
			1.09×10^{-12}	296		

The three major studies of formaldehyde at room temperature show excellent agreement. The rate constant appears to be about one third that of acetaldehyde which reflects the weaker aldehydric H bond in acetaldehyde.

If one assumes an $O(^3P)$ atom concentration of 10^5 atoms cm^{-3}, for the lower troposphere, the rates of reaction of HCHO and CH_3CHO with $O(^3P)$ are 5.4×10^{-3} and 1.5×10^{-2} percent h^{-1} respectively. Thus this route will be unimportant for the atmospheric chemistry of aldehydes.

Measurements have been reported for the unsaturated aldehydes acrolein, $CH_2 = CHCHO$ and crotonaldehyde, $CH_3CH = CHCHO$. Cadle et al. (1972, 1974) used a discharge flow technique over the approximate temperature range of 300-480 K. The values shown in table 6 are in reasonable agreement with those of Gaffney et al. (1975). The latter workers used a relative rate technique using the mercury photosensitized decomposition of N_2O at 2537 Å to generate $O(^3P)$ atoms. Product analysis was by gas chromatography.

HO₂ Radicals. No room temperature rate constants have been reported for the reaction of HO_2 radicals with aldehydes, although Baldwin and coworkers (1972) have obtained a value of 1.6×10^{-15} cm³ molecule^{-1}s^{-1} at 773 K for formaldehyde. In addition, Hendry and Mabey (1973) reported a value for HCHO of 7.1×10^{-18} cm³ molecule^{-1}s^{-1} at 373 K. In order to obtain an estimate for the rate of reaction of

$$HO_2 + HCHO \rightarrow H_2O_2 + CHO \qquad (3)$$

one may employ the expression suggested by Lloyd (1974) of $1.7 \times 10^{-12} \exp(-4700/T)$ cm³ molecule^{-1}s^{-1} to produce $k_3 = 2.8 \times 10^{-18}$ cm³ molecule^{-1}s^{-1} at 298 K.

Combining this value with a typical HO_2 concentration of 10^9 radicals cm³ for the polluted troposphere one obtains a value of 1×10^{-3} percent h^{-1} for the rate of disappearance of HCHO by reaction with HO_2. This rate would be about an order of magnitude smaller in the unpolluted troposphere.

Although measurements of the rate constant for HO_2 reacting with HCHO would be desirable from a scientific viewpoint, unless current measurements at higher temperatures are grossly in error, it does not appear from an atmospheric modeling viewpoint that this reaction plays a significant role in the chemistry of the polluted troposphere.

Alkoxy Radicals. Kelly and Heicklen (1978) have recently measured the rate constant for the lowest molecular weight compound in the series, methoxy radicals reacting with acetaldehyde

$$CH_3O + CH_3CHO \rightarrow CH_3OH + CH_3CO \qquad (4)$$

This is a radical transfer reaction. The authors photolyzed azomethane in the presence of acetaldehyde and oxygen at 298 K and from a product analysis obtained $k_4/k_5 = 1.4 \pm 2.8$ where k_5

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (5)$$

Using the value of 6×10^{-16} cm³ molecule^{-1} s^{-1} obtained by Barker et al. (1977) for k_5, the authors quoted $k_4 = (8.3 \pm 1.7) \times 10^{-15}$ cm³ molecule^{-1} s^{-1} at 298 K.

The steady state concentration of CH_3O in the lower polluted troposphere is around 5×10^6 radicals cm^{-3}. Thus the rate of disappearance of acetaldehyde by reaction with CH_3O in the lower troposphere is about 1.5×10^{-2} percent h^{-1}.

NO₃ Radicals. Morris and Niki (1974) studied the reaction

$$NO_3 + CH_3CHO \rightarrow HNO_3 + CH_3CO \qquad (6)$$

using a long path length IR cell operated at 300 K and near atmospheric pressure. The results from studying the reaction of mixtures of N_2O_5 and CH_3CHO were interpreted using numerical integratio for the participating reactions. A value of

$$k_6 = 1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 300 \text{ K}$$

was obtained by varying k_6 until a good match of the calculated and observed N_2O_5 decay was obtained.

Assuming an NO_3 concentration of 10^9 radicals cm^{-3} for the polluted troposphere, one can estimat that the rate of disappearance of CH_3CHO by reaction 6 is 0.4 percent h^{-1}.

HSO₄ Radicals. This radical is given some consideration here although no experimental data are available for the relevant reaction:

$$HSO_4 + RCHO \rightarrow H_2SO_4 + RCO \qquad (7)$$

Benson (1978) has suggested that the HSO_4 radical could be more reactive than RO radicals in either adding to the double bond of olefins or in H-abstraction reactions. Since aldehydes have a relatively weak C-H bond, reaction 7 is a logical candidate to consider in HC-NO_x-SO_x photooxidation systems.

HSO_4 can be formed in the sequence of reactions

$$OH + SO_2 + M \rightarrow HSO_3 + M$$

$$HSO_2 + O_2 \rightarrow HSO_5$$

$$HSO_5 + NO \rightarrow HSO_4 + NO_2$$

Using $\Delta H_f(HSO_4) = -125$ kcal mol^{-1} (Benson, 1978) one can estimate that reaction 7 for HCHO is 17.1 kcal mol^{-1} exothermic. (The similar reaction for OH radicals reacting instead of HSO_4 is 32.30 kcal mol^{-1} exothermic and for CH_3O is 17.5 kcal mol^{-1} exothermic). Thus, by comparison with the sole experimental measurement of k_4, one would expect $k_7 \geq 8.3 \times 10^{-15}$ cm³ molecule^{-1} s^{-1} at 300 K. However, this reaction should be studie experimentally since thermochemistry is not always a reliable guide for estimating kinetic data.

B. Atmospheric Reactions of Radicals Produced from Attack of Radicals on Aldehydes

We have seen above that radicals of the form RCO are produced from the reaction of atoms and free radicals with aldehydes. In this section, the subsequent fate of these radicals under atmospheric conditions will be discussed. Differentiation is made between the acyl radicals and their aromatic equivalents since there is evidence (Niki et al., 1978) that the radical produced from benzaldehyde react differently from their aliphatic equivalents.

The simplest acyl radical is formyl produced from formaldehyde. Three reaction paths are possible for its reaction under atmospheric conditions. These are:

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (8)$$

$$HCO + O_2 \rightarrow OH + CO_2 \qquad (9)$$

$$HCO + O_2 + M \rightarrow HCO_3 + M \qquad (10)$$

The following results support the conclusion that reaction (8) is the main route for this reaction:

- the reaction obeys second order kinetics at low pressures (Washida et al., 1974),
- the rate constant for $HCO + O_2$ is independent of pressure over the range 20-500 Torr (Shibuya et al., 1977),
- the direct identification of HO_2 formation from HCO by laser magnetic resonance (Radford et al., 1974),
- the observation of HO_2 formation from $HCO + O_2$ at 1 atmosphere (Hunziker, 1975).

However, results from recent studies by Osif and Heicklen (1976) and Niki et al., (1977) suggested that reaction (10) was the dominant pathway. Both of these studies used the Cl atom sensitized decomposition of formaldehyde in the presence of O_2. They assumed that formic acid formation was a good indicator of reaction (10), since HCO_3 radicals would be converted to HCO_2 radicals and subsequently HCOOH by H-abstraction from the aldehyde, thus

$$HCO_3 + HCO_3 \rightarrow 2HCO_2 + O_2 \tag{11}$$

$$HCO_2 + HCHO \rightarrow HCO_2H + HCO. \tag{12}$$

Osif and Heicklen measured $k_{10}/k_8 \simeq 5 \pm 1$ independent of pressure over the range studied (70-700 Torr) while Niki[1] et al., obtained a value > 9 for the same ratio at atmospheric pressure. Hanst and Gay (1977) also used the Cl atom catalyzed oxidation of HCHO. They irradiated low concentrations of $Cl_2/HCHO/NO_2$ mixtures in 1 atmosphere of air and the analysis performed using FT-IR spectroscopy. From the small yield of HCOOH and the observations of peroxynitric acid HO_2NO_2, they concluded that reaction (10) was unimportant in their system.

Horowitz et al. (1978) have subsequently suggested that formic acid can be formed by routes other than those involving reaction (10), specifically

$$OH + HCHO \rightarrow (HOCH_2O) \rightarrow HCO_2H + H \tag{13}$$

$$HO_2 + HCHO \rightarrow (HO_2CH_2O) \rightarrow HCO_2H + OH \tag{14}$$

they state that reactions (13) and (14) are 22 and 60 kcal mol^{-1} exothermic respectively. These workers photolyzed mixtures of HCHO at 3130 Å at low pressures in the presence of O_2 and added CO_2, and measured the quantum yields of formation of H_2, CO and CO_2 and the loss of O_2. A lower limit for k_{10} of 1.21×10^{-28} cm^6 $molecule^{-2}$ s^{-1} was obtained from the measured ratio $k_{10}M/(k_{10}M + k_8) \geq 0.049 \pm 0.017$ (obtained from experiments using $P_{HCHO} = 8$ Torr and $P_{O_2} = 1\text{-}4$ Torr) and Washida et al.'s (1974) value of k_8. Contrary to Osid and Heicklen (1976) and Niki et al. (1977), Horowitz et al. conclude that reactions (8) and (10) assume about equal importance under atmospheric conditions. Clearly, further work is needed to clarify this discrepancy.

Table 7. Rate constants for $HCO + O_2 \rightarrow HO_2 + CO$ at 298 K.

Rate constant, k_8 ($cm^3 molec^{-1} s^{-1}$) x 10^{12}	Pressure Torr	Reference
5.7 ± 1.2	4	Washida, et al. (1974)
6.0 ± 0.9	20	Shibuya, et al. (1977)
5.3 ± 0.7	530	Shibuya, et al. (1977)
3.8 ± 0.6	?	More, quoted in Shibuya (1977)

Table 7 shows the generally good agreement for results of rate constant determinations of k_8. Washida et al. (1974) used a photoionization mass spectrometer coupled to a flow system to obtain $k_8 = (5.7 \pm 1.2) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature. Recently, Shibuya et al (1977) generated HCO radicals in the absence and presence of O_2 by the flash photolysis of CH_3CHO

$$CH_3CHO + h\nu(> 2000\ \text{Å}) \rightarrow CH_3 + HCO.$$

From an analysis of the behavior of HCO radical decay, a value of $k_8 = (5.6 \pm 0.9) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K was obtained. This value is essentially independent of pressure (see table 7) and is in excellent agreement with that of Washida et al. (1974) but larger than the value obtained by Moore quoted in Shibuya et al.

Under atmospheric conditions, acyl radicals other than formyl are generally assumed to react with O_2 by addition:

$$RCO + O_2 \rightarrow RCO \cdot O_2.$$

Subsequent reactions in the polluted atmosphere with NO and NO_2 occur

$$RCO \cdot O_2 + NO \rightarrow NO_2 + RCO_2 \rightarrow R + CO_2 \tag{15}$$

$$RCO \cdot O_2 + NO_2 \rightarrow \underset{\text{peroxyacyl nitrate}}{RCO \cdot O_2 \cdot NO_2} \tag{16}$$

The most commonly studied member of the peroxyacyl nitrate family is peroxyacetyl nitrate (PAN) (Stephens, 1969; Pate, Atkinson and Pitts, 1976; Hendry and Kenley, 1977; Cox and Roffey, 1977). The kinetics and mechanism of PAN formation and thermal decomposition have been discussed recently (Pate et al., 1976; Hendry and Kenley, 1977; Baldwin et al., 1977; Carter et al. 1978) and is beyond the scope of this paper.

Niki et al. (1978) note that, based on OH reactivity, aliphatic and aromatic aldehydes,

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[1] Niki (1978) suggests that formation of HCOOH in his system may be explained by Reaction (14) as suggested by Horowitz et al. (1978). This would reduce the importance of Reaction (10) in the system used by Niki et al. (1977).

should be equally efficient at converting NO to NO_2. However, they note that smog chamber studies show that benzaldehyde is far less reactive than the aliphatic aldehydes in producing ozone (Dimitriades, 1974). They suggest that radicals formed by H abstraction from benzaldehyde are efficient NO_x scavengers. Support for these suggestions would significantly aid the understanding and computer modeling of aromatic hydrocarbon photooxidation.

5. Photochemistry of Aldehydes

The photodissociation of aldehydes is an important radical generation mechanism in the formation of photochemical air pollution (Leighton, 1961; Altshuller and Bufalini, 1965, 1971; Pitts, 1969; Calvert et al., 1972; Demerjian et al., 1974; Levy, 1974; Hecht, Seinfeld and Dodge, 1974; Dodge and Hecht, 1975; Whitten and Dodge, 1976).

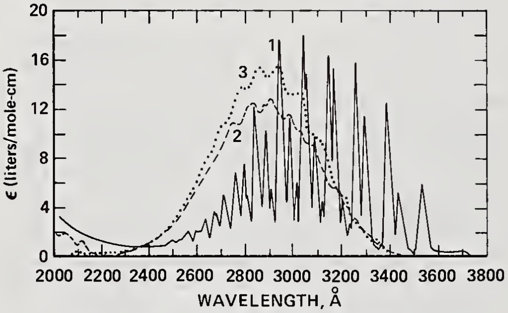

Fig. 6. Absorption spectra of formaldehyde (1), acetaldehyde (2), and propionaldehyde (3) (from Calvert and Pitts, 1966).

Figure 6 shows the absorption spectra for some common aldehydes which illustrates that they will absorb well beyond 3000 Å. The two reactions of most significance can be generalized in terms of a radical and molecular route:

$$RCHO + h\nu \begin{array}{l} \rightarrow R + HCO \\ \rightarrow RH + CO \end{array}$$

The radical route is the more important one for modeling tropospheric chemistry. The rate constant for a particular primary process is an important quantity in assessing the importance of the process in the atmosphere. It is given by

$$k_i(\Theta,h) = \sum_{\lambda} J(\lambda,\Theta,h) \cdot \sigma_i(\lambda) \cdot \Phi_i(\lambda)$$

where Θ is the solar zenith angle, h is the height above ground, λ is the wavelength, J is the actinic flux, σ is the cross section and Φ is the quantum yield for species i. Of these parameters, the quantum yield Φ as a function of wavelength has been subject to major uncertainty; for example, singificant differences among experimentally determined values have been reported for formaldehyde (McQuigg and Calvert, 1969; Sperling and Toby, 1973).

Quantum Yields for HCHO photolysis as a Function of wavelength. Considerable attention has been given to formaldehyde photolysis in recent years, partly because of its importance in photochemical air pollution. There appears to be general agreement that:

a. the major final products are H_2 and CO (in the absence of O_2),

b. the primary reaction paths are

$$HCHO + h\nu \rightarrow H + HCO \quad (17)$$

$$\rightarrow H_2 + CO \quad (18)$$

However, differences have arisen in the determinations of the variation of the ratio of the quantum yields of reactions (17) and (18), Φ_{17}/Φ_{18}, as a function of wavelength. The earlier studies (pre 1975) showed no consistent trend with wavelength variation (Gorin, 1939; Klein and Schoen, 1956; DeGraff and Calvert, 1967; McQuigg and Calvert, 1969; Sperling and Toby, 1973). The results of these studies have been superceded by results from more recent and definitive studies and can be discounted (Horowitz and Calvert, 1978; Lewis and Lee, 1978). Consequently, only the recent studies (post 1975) will be discussed here and emphasis will be on the radical production route, reaction (17).

As pointed out by Horowitz and Calvert (1978), all the recent studies show that the quantum yield for the radical process, Φ_{17}, increases more steeply with decreasing wavelength below about 3400 Å. This is illustrated in figure 7. This figure is similar to that given by Horowitz and Calvert (1978b) but it has the additional results of Moortgat et al. (1978). These results give slightly higher values of Φ_{17} and show a lesser tendency to level off below about 3200 Å.

The results for Φ_{17} reported by Lewis et al. (1976) should be corrected by a factor of 1.89 according to Lewis and Lee (1978). Lewis et al. irradiated a mixture of HCHO and NO with monochromatic radiation (= 1 Å bandwidth) from a tunable laser and measured the intensity of chemiluminescence produced from excited HNO* formed in the three-body recombination H + NO + M. H atoms were produced in reaction (17). Relative values of Φ_{17} were obtained and were converted to absolute values using $\Phi_{17} = 0.36 \pm 0.04$ at 3035 Å determined in a separate experiment (Lewis and Lee, 1976). It is this value which has been redetermined by Lewis and Lee (1978) and increased to 0.68 ± 0.05. This change brings the earlier results of Lewis et al. (1976) into line with the most recent determinations discussed below.

Horowtiz and Calvert (1978a and b) have recently determined Φ_{17} at 3130 Å and over the wavelength range 2890 to 3380 Å at 398 K. They obtained Φ_{18} values by measuring the quantum yields for H_2 production, Φ_{H_2}, in the photolysis of HCHO-isobutene mixtures assuming that the high concentrations of isobutene scavenged the H atom production by reaction (17). Values of Φ_{17} and Φ_{18} were obtained from Φ_{H_2} in the photolysis of pure HCHO. These authors found Φ_{17} and Φ_{18} to be essentially 1 until the longest wavelength studied (3380 Å). Φ_{17} was found to increase from 0 at 3370 Å to = 0.7 at 3175 Å in general agreement with other recent studies. Results of experiments at 3380 Å with added oxygen lead the authors to conclude that little if any dissociation of HCHO into radicals occurred at 3380 Å and longer wavelengths, in contrast to earlier results.

Marling (1977) photolyzed 4 Torr of HDCO using either a high pressure mercury arc coupled with a monochromater of monochromatic laser irradiation in the wavelength range 3040 to 3530 Å. He measured the relative yields of H_2, D_2 and HD as a function of wavelength using a mass spectrometer and noted that the (H_2 + D_2) yield is a measure of radical production via reaction (17), since H_2 and D_2 can only be formed following reaction (17). Marling found that radical production reached 55 percent at wavelengths less than a 3200 Å, but no measurements of the absolute decomposition yield were reported. Horowitz and Calvert (1978) have placed Marling's results on an absolute basis using their value of $\Phi_{17} = 0.76$ at 3030 Å and applied the ratio of 0.55 measured at 3040 Å by Marling. They find that, within the uncertainties introduced by isotopic differences in the HCHO and HDCO molecules, Marling's reduced results agree reasonably well with their own (see fig. 7 and table 8).

Clark (1976) photolyzed HCHO in the presence of NO using a tunable laser. The NO was employed as a radical trap for HCO radicals and H atoms and was used in both small and large quantities and the effect on Φ_{H2} and Φ_{CO} measured. He observed the same sharp increase in Φ_{17} in the 3200 to 3300 Å range as other recent studies, and concluded that $\Phi_{17} + \Phi_{18} = 1.0$. Different results were obtained in experiments with low NO and high NO. Clark assigned more credibility to results obtained with low NO and suggested that high NO enhanced HCHO decomposition by reaction (17). However, Horowitz and Calvert (1978) have questioned this interpretation as a consequence of the results of their studies with added NO which showed little effect on Φ_{H2}. They conclude that Clark's results for Φ_{H2} at high NO are more appropriate estimates of Φ_{18}, and find that when these results for Φ_{18} are used, Clark's results for Φ_{17} are in excellent agreement with their own studies. In view of the results of other recent studies, the suggested reworking of Clark's results appears valid.

Moortgat et al. (1978a) have studied the photolysis of HCHO at several wavelengths in the range 2700 to 3600 Å. They employed two types of experiment -- HCHO in a mixture of N_2 with a small amount of C_3H_6 added, and HCHO in a 20:80 mixture of O_2 and N_2 -- and both systems were operated at atmospheric pressure. Consequently, results from the latter should be directly applicable to modeling the lower troposphere. A Xenon arc monochromater was used to isolate the desired wavelengths. Measurements of the ratio of H_2 and CO production yielded values for the ratio $\Phi_{18}/\Phi_{17} + \Phi_{18}$. Subsequent work (Moortgat et al., 1978b) reported values for $\Phi_{17} + \Phi_{18}$, and consequently, Φ_{17}. Although initially the values for Φ_{17} obtained from the C_3H_6 added experiment were lower than those for the N_2:O_2 system, subsequent allowance for a small contribution to the H_2 formation by H abstraction from C_3H_6 (Moortgat, 1978) gave excellent agreement between the two sets of results as shown in table 8.

Examination of figure 7 shows that results of recent studies show a consistent trend although there remains some scatter in the results of different studies. However, it is possible to draw a line or band which incorporates most of the results within their experimental error. This significant improvement in our knowledge of Φ_{17} is very helpful in improving our capability to model atmospheric chemistry in the polluted troposphere.

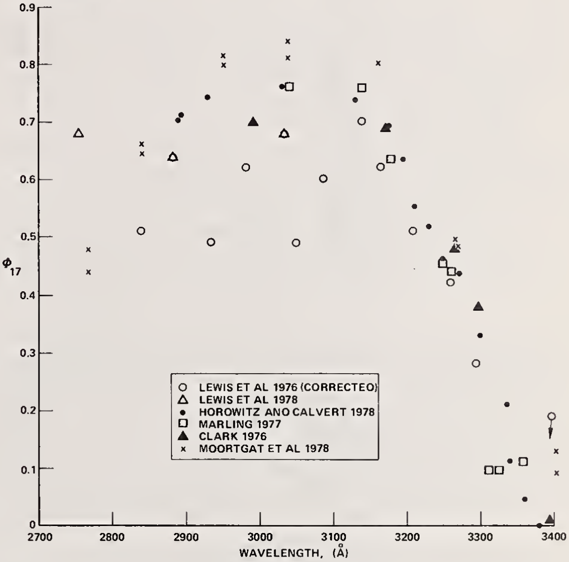

Fig. 7. Primary Quantum Yield, Φ_{17}, for process HCHO + hν → H + HCO, as a function of wavelength. Data of Marling and Clark plotted using interpretation of Horowitz and Calvert.

In order to compare the rate of photolysis with the depletion of formaldehyde by radical processes one can calculate a photolysis rate of ~ 13 percent h^{-1} for a solar zenith angle of 20° and using the value of k_{17} given by Horowitz and Calvert (1978b).

Photolysis of Acetaldehyde. Acetaldehyde is commonly used as a surrogate for aldehydes of higher molecular weight than formaldehyde. Its absorption spectrum is shown in figure 6, which is taken from Calvert and Pitts (1966). As with formaldehyde, major uncertainty is concentrated in the quantum yields of the primary processes (Calvert and Pitts, 1966).

Parmenter and Noyes (1963) carried out emission studies and Archer et al. (1973) used the triplet state induced cis-trans isomerization of butene-2 to study the primary processes in acetaldehyde photolysis. These studies have been summarized by Weaver et al. (1976, 77). In a comprehensive study, these latter workers obtained results which are consistent with the previous studies. Weaver et al photolysed CH_3CHO vapor at 3130 Å in the presence of O_2 or O_2 - N_2 mixtures at 298 K. The products formed at a function of pressure and added O_2 were measured over the pressure range 20 to 640 Torr. Weaver et al. postulated the following

Table 8. Wavelength dependence for the quantum yield Φ, of HCHO photodecomposition into H and HCO.

Wavelength λÅ	Quantum Yield Φ'						
	Lewis et al.[a]	Lewis and Lee	Horowitz and Calvert	Marling[b]	Clark[c]	Moortgat et al.	
2767						0.48	0.44
2754		0.68 ± 0.10					
2840	0.51						
2841						0.65	0.66
2882	0.64	0.64 ± 0.10					
2890			0.701				
2894			0.711				
2930			0.740				
2934	0.49						
2950						0.80	0.81
2982	0.62						
2991					0.70 (0.48)		
3030			0.760				
3035	0.68	0.68 ± 0.05					
3039						0.84	0.81
3040				0.760			
3050	0.49						
3088	0.60						
3130			0.735				
3140	0.70			0.760			
3163						0.80	0.80
3166	0.62						
3172					0.64 (0.42)		
3175			0.692				
3180				0.636			
3195			0.635				
3210	0.51		0.554				
3230			0.519				
3250			0.460	0.456			
3260	0.42			0.442			
3264					0.48 (0.42)		
3267						0.48	0.49
3270			0.438				
3296	0.28						
3298					0.38 (0.31)		
3300			0.330				
3310				0.097			
3324				0.097			
3335			0.212				
3340			0.113				
3360			0.048				
3378				0.111			
3380			0.00				
3392	< .19				0.01 (-0.03)		
3402						0.13	0.09
3550						0.04	0.03

---

[a] Original results multiplied by 1.89 as recommended by Lewis and Lee (1978).
[b] Results quoted by Horowitz and Calvert from Marlings experimental data.
[c] Values quoted are those from high NO data reinterpreted by Horowitz and Calvert. Numbers in parentheses are those given by Clark for low NO pressures.

reactions to account for their results

$$CH_3CHO + h\nu \rightarrow {}^1[CH_3CHO]_n \quad (19)$$

(quenchable part of excited singlet state)

$$\rightarrow {}^1[CH_3CHO]' \quad (20)$$

(non-quenchable part of excited singlet state)

$${}^1[CH_3CHO]' \rightarrow CH_3 + HCO \quad (21)$$

$$\rightarrow CH_3CHO \quad (22)$$

$${}^1[CH_3CHO]_n + M \rightarrow {}^1[CH_3CHO]_0 + M \quad (23)$$

(vibrationally equilibrated electronically-excited single state)

$${}^1[CH_3CHO]_0 \rightarrow {}^3[CH_3CHO] \quad (24)$$

$${}^3[CH_3CHO] + O_2 \rightarrow [complex] \quad (25)$$

$$[complex] \rightarrow CH_3 + CO + HO_2 \quad (26)$$

Weaver et al. found no CH_4 produced at 3130 Å in the presence of NO and so concluded that the other primary process, reaction (27), was negligible at 3130 Å.

$$CH_3CHO + h\nu \rightarrow CH_4 + CO \quad (27)$$

The quantum yields obtained are shown in table 9, which is taken from Weaver et al. (1976, 77).

Reactions (24) through (26) which predict a pressure dependent reaction between the excited

Table 9. Quantum yields of the primary processes in acetaldehyde photo-oxidation as a function of excitation wavelength (Weaver et al., 1976).

λ(Å)	$\phi\{CO + CH_4\}$	$\phi\{CH_3 + HCO\}$	ϕ\{triplet\}
3340	0	0	1.0^d
3130	0	0.05^b	0.84^e
2967	---	---	0.59^d
2804	0.15^a	$\leq 0.30^c$	0.48^d
2654	0.28^a	0.36^a	--
2537	0.64^a	0.36^a	--

---

[a] From Calvert and Pitts (1966).

[b] This work and Archer, et al. (1973).

[c] Calculated from the total quantum yield of the free radical process ($\phi\ \{CH_3 + HCO\} = 0.39$, Calvert and Pitts (1966); the fraction of that from the triplet, 0.18; and ϕ\{triplet\} at 2804 Å = 0.48.

[d] From Parmenter and Noyes (1963).

[e] From Parmenter and Noyes (1963) and Archer, et al. (1973).

triplet state and O_2, form the novel part of Weaver et al.'s results. Although they were able to fit their results with their suggested mechanism, the quantum yields obtained are subject to uncertainty since the mechanism for secondary reactions may affect the results. For example, it was assumed that HCO reacted with O_2 by addition (contrary to the conclusion of our discussions above) and the reaction of CH_3O_2 with HO_2 had to be omitted in order to fit the data.

Weaver et al calculate the rate of CH_3CHO photolysis in the atmosphere for a solar zenith angle of zero (i.e. the maximum photolysis rate) and find the rates for reactions (21) and (26) to be 2.8×10^{-6} and 8.7×10^{-6} s^{-1} respectively. They report the overall rate constant for all free radical processes to be 2.3×10^{-5} s ≡ 8.3 percent h^{-1}. This may be compared with the role of depletion of CH_3CHO by reaction with OH radicals (assumed [OH] = 10^6 radicals cm^{-3}) of 5.8 percent h^{-1}.

6. Other Oxygenates

In addition to aldehydes, there are several other classes of oxygenated hydrocarbons known or suspected to be present in urban areas of the troposphere. These include ketones, alcohols, esters and ethers. Their possible role in atmospheric chemistry will be discussed briefly.

Discussion of radical reactions with these oxygenates will be limited to the OH radical. This was shown to be the major species attacking aldehydes and is likely to be the most important intermediate for the remaining oxygenates. Of the four classes of oxygenated hydrocarbons mentioned above, only ketones undergo photolysis under ambient conditions and this process is discussed later.

Sources and Ambient Concentrations of Ketones, Alcohols, Esters and Ethers. All of these classes of compounds are used in commercial solvents (Burnelle et al. 1966; Wilson and Doyle, 1970; Levy and Miller 1970; Laity et al. 1973). These compounds occur in paints, degreasing solvents, etc. Additionally, automobile exhaust contains small quantities of all the above mentioned classes as illustrated by table 2. Ketones and alcohols are also formed via secondary reactions in the atmosphere in a manner similar to that for the aldehydes.

Data on ambient concentrations of these compounds are scarce and the only available quantitative measurements appear to be for selected ketones. Acetone measurements of 0.3 to 0.9 ppb have been reported by Robinson et al. (1973) for remote areas of California, Idaho, Vermont and Washington. Methyl ethyle ketone (MEK) has been observed in Riverside, California at concentrations of 1 to 6 ppb (Stephens and Burleson, 1976). Smoyer et al. (1971) report the detection of 94 ppm of MEK in ambient air near a chemical reclamation plant in Maryland. Grob and Grob (1971) detected acetophenone in ambient air in Zurich, Switzerland.

Reactions of Oxygenated Hydrocarbons with the Hydroxyl Radicals. The results of studies of the reactions of OH radicals with individuals oxygenated hydrocarbons are summarized in table 10, which is a modified version of that given by Atkinson et al. (1978). Most of these determinations are for one temperature (around 300 K) and were obtained using a relative rate technique. Absolute values were obtained as indicated in table 10.

The rates of disappearance of these oxygenates due to reaction with OH radicals are given in table 11, assuming an [OH] of 10^6 radicals cm^{-3}. The rates given for the ketones will underestimate their disappearance rates in the atmosphere since they can photodissociate under solar radiation indicdent at the earth's surface. Of the remaining classes, the ethers appear the most reactive and the acetates the least reactive.

Photodissociation of Ketones Under Ambient Conditions. Ketones play a similar role to aldehydes in that they photolyse to produce radicals which promote the oxidation of NO to NO_2 with the concomitant formation of photochemical smog. Ketones were suggested to be precursors of peroxyalkyl radicals by Purcell and Cohen (1967) who examined the photoxidation of 2-methyl-1-butane in the presence of acetone. They found the rate of oxidation of the olefin increased as the ratio of ketone to olefin increased. The reactivity of ketones and other oxygenates under simulated atmospheric conditions has been studied by several workers (Burnelle et al. 1966; Wilson and Doyle, 1970; Levy and Miller, 1970; Laity et al. 1973).

Ketone photolysis has been described by Calvert and Pitts (1966) and the photolysis and photooxidation of ketones have been summarized recently by Lande et al. (1976). The absorption spectra of some common ketones are shown in figure 8 (Calvert and Pitts 1966). Due to uncertainty in the behavior of ketones under atmospheric conditions, radical production is often assumed to be 100 percent efficient. For example for MEK, the reactions are

Table 10. Rate constant data for the reaction of OH radicals with other oxygen-containing organics.

Reactant	10^{12} x k $cm^3 molec^{-1} s^{-1}$	at T K	Technique	Reference
Ketones				
Methyl ethyl ketone	3.4 ± 1.0	305 ± 2	Relative rate	Winer et al. (1976) (relative to OH + isobutene = 4.80 x 10^{-11})[a]
Methyl isobutyl ketone	14 ± 4	305 ± 2	Relative rate	Winer et al. (1976) (relative to OH + isobutene = 4.80 x 10^{-11})[a]
Diisobutyl ketone	24 ± 7	305 ± 2	Relative rate	Winer et al. (1976) (relative to OH + Isobutene = 4.80 x 10^{-11})[a]
Ketene	>1.7	∿ 295	Relative rate	Faubel, Wagner, and Hack (1977) (relative to OH + C_3O_2 = 1.4 x 10^{-12} Faubel et al. (1977)
Ethers				
CH_3OCH_3	3.5 ± 0.35	299	FP-RF	Perry, Atkinson, and Pitts (1977) Covered T range 299-424 K obtained A = 1.29 x 10^{-11} $cm^3 molec^{-1} s^{-1}$ and E = 770 ± 300 cal mol^{-1}
Diethyl ether	8.9 ± 1.8	305 ± 2	Relative rate	Lloyd et al. (1976) (relative to OH + Isobutene = 4.80 x 10^{-11})[a]
Di-n-propyl ether	16.3 ± 3.3	305 ± 2	Relative rate	Lloyd et al. (1976) (relative to OH + Isobutene = 4.80 x 10^{-11})[a]
Tetrahydrofuran	13.9 ± 2.8	305 ± 2	Relative rate	Winer et al. (1977) (relative to OH + isobutene = 4.80 x 10^{-11})[a]
$CH_2 = CHOCH_3$	33.5 ± 3.4	299	FP-RF	Perry, Atkinson, and Pitts (1977) Covered T range 299-427 K. Obtained A = 6.10 x 10^{-12} $cm^3 molec^{-1} s^{-1}$ and E = -1015 ± 300 cal mol^{-1}
Alcohols				
CH_3OH[b]	1.06 ± 0.11	292	Relative rate	Campbell, McLaughlin, and Handy (1976) (relative to OH + n-butane = 2.60 x 10^{-12})[c]
	1.06 ± 0.11	296	FP-RA	Overend and Paraskevpopulos (1978)
C_2H_5OH	3.3 ± 0.4	292	Relative rate	Campbell, McLaughlin, and Handy (1976) (relative to OH + n-butane = 2.60 x 10^{-12})[c]
	3.74 ± 0.37	296	FP-RA	Overend and Paraskevpopulos (1978)
n-Propanol	4.3 ± 0.4	292	Relative rate	Campbell, McLaughlin, and Handy (1976) (relative to OH + n-butane = 2.60 x 10^{-12})[c]
	5.33 ± 0.53	296	FP-RA	Overend and Paraskevpopulos (1978)
Isopropanol	6.7 ± 1.3	305 ± 2	Relative rate	Lloyd et al. (1976) (relative to OH + isobutene = 4.80 x 10^{-11})[a]
	5.48 ± 0.55	296	FP-RA	Overend and Paraskevopoulos (1978)
n-Butanol	7.6 ± 1.1	292	Relative rate	Campbell, McLaughlin, and Handy (1976) (relative to OH + n-butane = 2.60 x 10^{-12})[c]
$CH_2 = CH - CH_2OH$	25.9 ± 3.3	440	Pulse radiolysis	Gordon and Mulac (1975)
Acetates				
Methyl acetate	0.18 ± 0.05	292	Relative rate	Campbell and Parkinson (1977) (relative to OH + n-butane = 2.60 x 10^{-12})[c]
Ethyl acetate	1.94 ± 0.22	292	Relative rate	Campbell and Parkinson (1977) (relative to OH + n-butane = 2.60 x 10^{-12})[c]
n-Propyl acetate	4.1 ± 0.8	305 ± 2	Relative rate	Winer et al. (1977) (relative to OH + isobutene = 4.80 x 10^{-11})[a]
sec-Butyl acetate	5.3 ± 1.1	305 ± 2	Relative rate	Winer et al. (1977) (relative to OH + isobutene = 4.80 x 10^{-11})[a]
Methyl propionate	0.29 ± 0.10	292	Relative rate	Campbell and Parkinson (1977) (relative to OH + n-butane = 2.60 x 10^{-12})[c]
Ethyl propionate	1.77 ± 0.25	292	Relative rate	Campbell and Parkinson (1977) (relative to OH + n-butane = 2.60 x 10^{-12})[c]

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[a] Calculated from the Arrhenius expression of Atkinson and Pitts (1975).

[b] Osif, Simonaitis, and Heicklen (1975) determined rate constants relative to that for OH + CO of k(OH + CH_3OH)/k(OH + CO) = 0.63 ± 0.10 at 298 K and 0.98 ± 0.20 at 345 K. However, total pressures (CH_3OH + N_2O + CO) of 28-203 Torr were used. Since no data are available for the pressure dependence of the OH + CO rate constant with CH_3OH or N_2O as the diluent gas, no quantitative estimate of k(OH + CH_3OH) can be made, apart from setting k(OH + CO) $\geq$ 1.5 x 10^{-13} $cm^3 molec^{-1} s^{-1}$ at 298 K (Perry et al. (1978)) and hence k(OH + CH_3OH) $\geq$ (0.95 ± 0.15) x 10^{-12} $cm^3 molec^{-1} s^{-1}$ at 298 K.

[c] Calculated from the Arrhenius expression of Perry et al. (1976) for T = 292 K, which is also in excellent agreement with the value obtained by Campbell, Handy, and Kirby (1975).

Table 11. Rates of reaction of selected oxygenated hydrocarbons with the OH radical (assumed $[OH] = 10^6$ radicals cm^{-3}) at around 300 K.

Compound	Reaction Rate (% h^{-1})
Ketones	
MEK	1.2
Methyl isobutyl ketone	5.0
Diisobutyl ketone	8.6
Ethers	
Dimethyl ether	1.3
Diethyl ether	3.2
Di-n-propyl ether	5.9
Tetrahydrofuran	5.0
$CH_2 = CHOCH_3$	12.1
Alcohols	
CH_3OH	0.38
C_2H_5OH	1.3
$n\text{-}C_3H_7OH$	1.7
$i\text{-}C_3H_7OH$	2.2
$n\text{-}C_4H_9OH$	2.7
CH_2CHCH_2OH	9.3
Acetates	
Methyl acetate	0.06
Ethyl acetate	0.70
n-Propyl acetate	1.5
s-Butyl acetate	1.9
Methyl propionate	0.10
Ethyl propionate	0.64

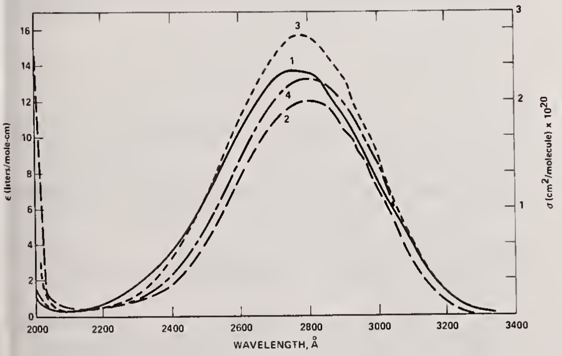

Fig. 8. UV absorption spectra for acetone (1), diethyl ketone (2), MEK (3), and methyl n-butyl ketone (4) (from Calvert and Pitts, 1966).

$$CH_3COC_2H_5 + h\nu \rightarrow CH_3CO + C_2H_5 \qquad (27)$$

$$\rightarrow CH_3 + COC_2H_5 \qquad (28)$$

Carter et al. (1978) suggest that triplet formation is the dominant initial process under ambient conditions and this species reacts with atmospheric O_2 to give ethyl radicals and acetyl peroxy radicals, i.e., reaction (27). They state that the alternative route, reaction (28) is less favored thermodynamically.

However, major uncertainty remains concerning the photolysis of ketones under ambient conditions including the quantun efficiency of radical production in the presence of O_2.

If one compared the realtive rates of aldehydes and ketone photolysis under simulated atmospheric conditions given by Carter et al. (1978), and uses the atmospheric aldehyde photolysis rates given earlier, one may estimate that the photolysis rate of MEK in the atmosphere is ∿ 10 percent h^{-1}.

7. Importance of Aldehydes and Other Oxygenates in Modeling Atmospheric Chemistry

The smog chamber studies carried out under simulated atmospheric conditions have been mentioned earlier and adequately demonstrate the importance of aldehydes and other oxygenates in promoting photochemical smog formation. Computer modeling studies have further emphasized the importance of these compounds. Computer results have been shown to be significantly impacted by uncertainties in initial concentrations and photochemical parameters such as quantum yields (Niki et al., 1972; Demerjian et al., 1974; Dodge and Hecht 1975; MacCracken and Sauter, 1975; Graedel et al. 1976; Whitten et al. 1976; Dodge and Whitten 1976; Baldwin et al. 1977; Carter et al. 1978). Thus Dodge and Hecht (1975) state that aldehyde photolysis is among the most critical reactions for quantitative photochemical smog modeling when one combines the sensitivity with the uncertainty in the rates and mechanism of the reactions.

The situation is more complex for modeling atmospheric conditions. Uncertainties in the photochemistry and ambient concentrations are compounded by ill-defined emission rates for aldehydes and other oxygenates. These combined uncertainties can have a significant impact upon model calculations. For example, figure 9 shows the results of two runs carried out with an atmospheric trajectory model being developed by Environmental Research and Technology (ERT), under Coordinating Research Council (CRC) funding. The photodissociation rates used in the model are those given by Peterson (1976). This model is being developed using data taken during the Los Angeles Reactive Pollutant Program (LARPP) carried out in 1973 (Martinez and Parker, 1976). The model partitions the hydrocarbons into five classes including separate classes for HCHO and other aldehydes, RCHO. It is evident from the results shown in figure 9, that the two parameters which we varied in this calculation can have a significant impact on the results. Of course, each parameter must be caried separately to isolate individual effects. The choice of initial aldehyde concentrations is important in controlling the radical concentration available to promote NO_2 formation, but the absolute effect is modified

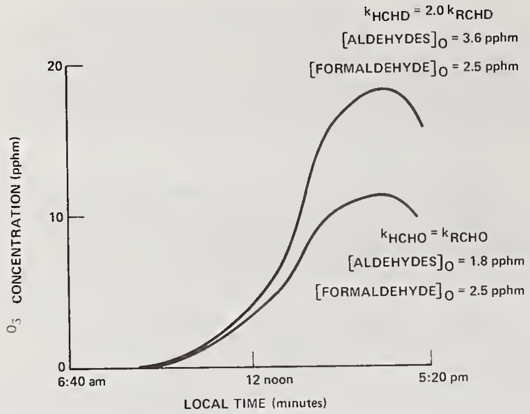

Fig. 9. Effect of aldehyde photolysis rates and initial concentrations on a trajectory model run for November 5, 1973 in the Los Angeles basin.

by the source input fluxes for aldehydes.

8. Summary

The above discussions have covered the sources, ambient concentrations, radical reactions and photochemistry of aldehydes, and to a lesser extent, ketones, alcohols, ethers and esters. In general, the photolysis and reactions with the OH radical appear to be the major sinks for oxygenated hydrocarbons in the lower atmosphere. The state of knowledge of OH radical reactions with these oxygenates is currently adequate for modeling purposes given the uncertainties in other areas. Consequently, a major thrust towards further refinement in these rate constants specifically for tropospheric modeling purposes has little merit and attention should be focused on other areas. These areas may be summarized under the general categories below.

Ambient Concentrations. Much greater emphasis should be placed upon obtaining concentration-time profiles for aldehydes and ketones in the atmosphere as a function of location, season and time of day. The increase in chemical sophistication of atmospheric models, which have been validated using well characterized smog chamber data, places increased demands on the quality and extent of ambient air quality measurements. This is typified in the case of aldehydes and ketones for which chemical reactions may exist in the computer model mechanism, but for which no ambient air quality data are available either for initial conditions or to test the predicted concentration-time behavior of these pollutants.

A greater knowledge of aldehyde and other oxygenate emissions is also needed to form the basis of a good emission inventory for modeling purposes.

It is realized, of course, that the above requirements have not been met in many locations for the common hydrocarbon classes of alkenes, alkenes and arenes and in some cases, not even for non-methane hydrocarbons.

Photooxidation. The photodissociation of aldehydes and ketones appears to be the major depletion mechanism for these compounds in the lower atmosphere based on the calculations presented earlier. Although there has been significant advances in our knowledge of formaldehyde quantum yields, the ambient photolysis rates of other aldehydes, and particularly ketones, are poorly known. Consequently, further studies of the photolysis of aldehydes and ketones as a function of pressure up to atmospheric, and in the presence of O_2 should be carried out. The uncertainty in quantum yields need to be reduced substantially to about ± 25 percent, since the oxygenate photolysis steps are important in radical production.

Kinetics and Mechanism. As indicated above, the general status of knowledge for the most important free radical, OH, is satisfactory for modeling purposes. The mechanism of reaction should receive further attention in the areas of: HCO oxidation under ambient conditions; OH and HO_2 addition to formaldehyde as suggested by Horowitz, Su and Calvert (1978); the oxidation of aromatic aldehydes under ambient conditions, and the photooxidation of ketones and other oxygenates under ambient conditions.

Finally, the kinetics of the possible HSO_4 radical reactions with aldehydes and ketones should be studied to test the suggestion of Benson (1978).

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References

Akimoto, H. and Kondo, J., Advan. Env. Sci. and Tech. 5, 1 (1975).

Altshuller, A. P. and Bufalini, J. J., J. Photochem. and Photobiol. 4, 97 (1965).

Altshuller, A. P. and Bufalini, J. J., Environ. Sci. and Technol. 5, 39 (1971).

Altshuller, A. P. and Cohen, I. R., Presented at the 145th National Meeting of the American Chemical Society, New York, (1963).

Altshuller, A. P., Cohen, I. R., and Purcell, T. C., Can. J. Chem. 44, 2973 (1966).

Altshuller, A. P., Cohen, I. R., and Purcell, T. C., Science 156, 937 (1967).

Altshuller, A. P. and McPherson, S. P., J. Air Poll. Control Assoc. 13, 109 (1963).

Altshuller, A. P., Miller, D. L., and Sleva, S. E., Anal. Chem. 33, 621 (1961).

Archer, A. S., Cundall, R. B., and Palmer, T. F., Proc. Roy Soc. A334, 411 (1973).

Atkinson, R., Darnall, K. R., Lloyd, A. C., Winer, A. M., and Pitts, J. N., Jr., Advances in Photochemistry, in press (1978).

Atkinson, R., Perry, R. A., and Pitts, J. N., Jr., J. Chem. Phys. 66, 1197 (1977).

Atkinson, R. and Pitts, J. N., Jr., J. Chem. Phys. 63, 3591 (1975).

Atkinson, R. and Pitts, J. N., Jr., J. Chem. Phys., accepted for publication (1978).

Baldwin, A. C., Barker, J. R., Golden, D. M., and Hendry, D. G., J. Phys. Chem. 81, 2483 (1977).

Baldwin, R. R., Fuller, A. R., Longthorn, D., and Walker, R. W., J. Chem. Soc., Faraday Trans. I 68, 1362 (1972).

Barker, J. R., Benson, S. W., and Golden, D. M., Int. J. Chem. Kinetics 9, 31 (1977).

Benson, S. W., Chemical Reviews 78, 23 (1978).

Black, F., Proceedings of the International Conference on Phtochemical Oxidant Pollution and Its Control, Volume II, 1053 (1977).

Brunelle, M. F., Dickinson, J. E. and Hamming, W. J., Effectiveness of Organic Solvents in Photochemical Smog Formation, Solvent Project Final Report, County of Los Angeles Air Pollution Control District, July 1966.

Bufalini, J. J. and Brubaker, K. L., The Photo-oxidation of Formaldehyde at Low Partial Pressures, in Chemical Reactions in Urban Atmospheres, C. S. Tuesday, ed., p. 225 (American Elsevier Publishing Co., New York, 1971).

Cadle, R. D. and Powers, J. W., J. Phys. Chem. 71, 1702 (1967).

Cadle, R. D., Lin, S. S., and Hausman, R. F., Jr., Chemosphere 1, 15 (1972).

California Air Resources Board, Staff Report (January 1972).

Calvert, J. G., Kerr, J. A., Demerjian, K. L., and McQuigg, R. D., Science 175, 751 (1972).

Calvert, J. G. and Pitts, J. N., Jr., Photochemistry (John Wiley and Sons, Inc., New York, 1966).

Campbell, I. M., Handy, B. J., and Kirby, R. M., J. Chem. Soc. Faraday Trans. I 71, 867 (1975).

Campbell, I. M., McLaughlin, D. F., and Handy, B. J., Chem. Phys. Lett. 38, 362 (1976).

Campbell, I. M. and Parkinson, P. E., Chem. Phys. Lett., in press (1977).

Carter, W. P., Lloyd, A. C., Sprung, J. L., and Pitts, J. N., Jr., Accepted for publication in Int. J. of Chem. Kinetics, (1978).

Clark, J. H., Ph.D. Thesis, University of California, Berkeley (1976).

Cleveland, W. S., Graedel, T. E., and Kleiner, B., Atmos. Environment 11, (1977).

Cohen, I. R. and Purcell, T. C., Atmos. Environment 1, 689 (1967); Environmental Science and Technology 1, 845 (1967).

Cox, R. A., Derwent, R. G., Holt, P. M., and Kerr, J. A., J. Chem. Soc. Faraday Trans. I 72, 2061 (1976).

Cox, R. A. and Roffey, M. J., Environ. Sci. and Tech. 11, 900 (1977).

Cvetanovic, R. J., Can. J. Chem. 34, 775 (1956).

DeGraff, B. A. and Calvert J. G., J. Amer. Chem. Soc. 89, 2247 (1967).

Demerjian, K. L., Kerr, J. A., and Calvert, J. G., Advan. Environ. Sci. Technol. 4 (1974).

Dimitriades, B. and Wesson, T. C., J. Air Pollution Control Assoc. 22, 33 (1972).

Dodge, M. C. and Hecht, T., Int. J. Chem. Kin. Symp. No. 1, 155 (1975).

Elliot, M. A., Nebel, G. V., and Rounds, F. G., J. Air Pollution Control Assoc. 5, 103 (1955).

Faubel, C., Wagner, H. Gg. and Hack, W., Ber. Bunsenges. Phys. Chem. 81, 689 (1977).

Fracchio, M. F., Schuetts, F. J., and Mueller, P. K., Environ. Sci. Technol. 1:915-922 (1967).

Gaffney, J. S., Atkinson, R., and Pitts, J. N., Jr., J. Amer. Chem. Soc. 97, 5049 (1975).

Gordon, S. and Mulac, W. A., Int. J. Chem. Kinet. Symp. No. 1, 289 (1975).

Gorin, E., J. Chem. Phys. 7, 256 (1939).

Graedel, T. E., Farrow, L. A., and Weber, T. A., Atmos. Env. 10, 1095 (1976).

Grob, K. and Grob, G., J. Chromatogr. 62, (1), 1-13 (1971).

Haagen-Smith, A. J. and Fox, M. M., Ind. Eng. Chem. 48, 1484 (1956).

Hanst, P. L. and Gay, B. W., Env. Sci. and Tech. 11, 1105 (1977).

Hanst, P. L., Wilson, W. E., Patterson, R. K., Gay, B. W., Chaney, L. W., and Burton, C. S., A Spectroscopic Study of California Smog, U. S. Environmental Protection Agency, EPA Publication No. 650/4-75-0006 (February 1975).

Hecht, T., Seinfeld, J., and Dodge, M. C., Environ.

Sci. and Tech. 8, 327 (1974).

Hendry, D. G. and Mabey, Private Communication (1973).

Hendry, D. G. and Kenley, R. A., J. Amer. Chem. Soc. 99, 3198 (1977).

Herron, J. T. and Huie, R. E., J. Phys. Chem. Ref. Data 2, 467 (1974).

Herron, J. T. and Penzhorn, R. D., J. Phys. Chem. 73, 191 (1969).

Horowitz, A. and Calvert, J. G., Int. J. Chem. Kin., in press (1978a).

Horowitz, A., Su, F., and Calvert, J. G., in press (1978).

Hunziker, H. E. and Wendt, H. R., Near Infrared Electronic Absorption of Organic Peroxyl Radicals, Paper No. 48, 12th International Symposium on Free Radicals, Laguna Beach, California, (January 4-9, 1976).

Jaffe, S. and Wan, E., Environ. Sci. Technol. 8, 1024 (1974).

Johnston, H. S. and Heicklen, J., J. Amer. Chem. Soc. 86, 4254 (1964).

Katou, T., Proceedings of the Int. Symp. on Air Pollution, p. 419, Tokyo (1972).

Katz, M., in Air Pollution (Columbia Univ. Press, New York, 1961).

Kelly, N. and Heicklen, J., J. of Photochemistry 8, 83 (1978).

Klein, R. and Schoen, L. J., J. Chem. Phys. 24, 1094 (1956).

Laity, J. L., Burstein, I. G., and Appel, B. R., in Solvents: Theory and Practice, Advances in Chemistry Series No. 124, American Chemical Society, Washington, D.C., (1973).

Lande, S. S., Durkin, P. R., Christopher, D. H., Howard, P. H., and Saxena, J., Investigation of Selected Environmental Contaminants: Ketonic Solvents, prepared for EPA, Office of Toxic Substances, PB 252 970 (May 1976).

Leighton, P. A., Photochemistry of Air Pollution (Academic Press, New York, 1961).

Leighton, P. A. and Perkins, W. A., Conference on Chemical Reactions in Urban Atmospheres, Air Pollution Foundation, Report No. 15 (1956).

Levy, H., Advances in Photochemistry 9, 364 (1974).

Levy, A. and Miller, S. W., Final Technical Report on the Role of Solvents in Photochemical Smog Formation, National Paint, Varnish, and Lacquer Association, Washington, D.C. (1970).

Lewis, R. S. and Lee, E. K. C., J. Phys. Chem. 82, 249 (1978).

Lewis, R. S., Tang, K. Y., and Lee, E. K. C., J. Chem. Phys. 65, 2910 (1976).

Linell, R. H. and Scott, W. E., Arch. Environ. Health 5, 616 (19620.

Lloyd, A. C., Int. J. Chem. Kinetics 6, 169 (1974).

Lloyd, A. C., Darnall, K. R., Winer, A. M., and Pitts, J. N., Jr., Chem. Phys. Lett. 42, 205 (1976).

Lonneman, W. A., Bufalini, J. J., and Seila, R. L. Environ. Sci. and Tech. 10, 374 (1976).

Los Angeles Control District, Second Technical and Administrative Report, (1950-51).

MacCagken, M. C. and Sauter, G. D., ed., Development of an Air Pollution Model for the San Francisco Bay Area, Final Report to the NSF, Vol. II, (October 1975).

Mack, G. P. R. and Thrush, B. A., J. Chem. Soc. Faraday Trans. I 69, 1 (1973).

Mack, G. P. R. and Thrush, B. A., J. Chem. Soc. Faraday Trans. I 69, 208 (1973).

Mack, G. P. R. and Thrush, B. A., J. Chem. Soc. Faraday Trans. I 70, 178 (1974).

Marling, J., J. Chem. Physics 66, 4200 (1977).

Martinez, J. R. and Parker, R. O., Los Angeles Reactive Pollutant Program (LARPP) Data Archiving and Retrieval, ERT Doc, No. P-1464W prepared for Coordinating Research Council (1975).

McQuigg, R. D. and Calvert, J. G., J. Amer. Chem. Soc. 91, 1590 (1969).

Moortgat, G., Private Communication, (March, 1978)

Moortgat, G. K., Slemr, F., Seiler, W., and Warneck, P., Chem. Physics Lett., in press (1978a).

Moortgat, G. K., Slemr, F., Seiler, W., and Warneck, P., Presented at the 13th Informal Photochemistry Conference, Tampa, FL, (January 1978b).

Morris, E. D., Jr. and Niki, H., J. Chem. Phys. 55, 1991 (1971).

Morris, E. D., Jr. and Niki, H., J. Phys. Chem. 75, 3640 (1971).

Morris, E. D., Jr. and Niki, H., J. Phys. Chem. 78, 1337 (1974).

Morris, E. D., Jr., Stedman, D. H., and Niki, H., J. Amer. Chem. Soc. 93, 3570 (1971).

National Academy of Sciences Vapor Phase Organic Pollutants, National Research Council (1976).

Niki, H., Private Communication, (1978).

Niki, H., Maker, P., Savage C., and Breitenbach, L., Presentation at the 173rd ACS National Meeting, New Orleans, Louisiana, (March 20-25, 1977).

Niki, H., Daby, E. E., and Weinstock, B., Advances in Chemistry Series No. 113, 16 (1972).

Niki, H., Daby, E. E., and Weinstock, B., 12th Symp. Combustion p. 277 Comb. Institute (1969).

Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P., J. Phys. Chem, in press (1978).

Oberdorfer, P. E., Automotive Engineering Congress, Detroit, January 9-13, 1967.

Osif, T. L. and Heicklen, J., J. Phys. Chem. 80, 1526 (1976).

Osif, T. L., Simonaitis, R., and Heicklen, J., J. Photochem 4, 233 (1975).

Overend, R. P. and Paraskevopoulos, G., Private Communication (1978).

Parmenter, C. S. and Noyes, W. A., Jr., J. Amer. Chem. Soc. 85, 416 (1963).

Pate, C. T, Atkinson, R., and Pitts, J. N., Jr., J. Environ. Sci. Health, Environ. Sci. Eng. A11, 19 (1976).

Penkett, S. A., Sandalls, F. J., and Lovelock, J. E., Atoms. Env. 9, 139 (1975).

Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., J. Chem. Phys. 64, 5314 (1976).

Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., J. Chem. Phys. 67, 611 (1977).

Peterson, J. T., Demerjian, K. L., and Schere, K. L., Proceedings of the International Conf. on Photochemical Oxidant and Its Control, Raleigh, N.C. (1977).

Pitts, J. N., Jr., J. Air Poll. Control Assoc. 19, 658 (1969).

Pitts, J. N., Jr., Winer, A. M., Darnall, K. R., Doyle, G. J., and McAfee, J. M., Chemical Consequences of Air Quality Standards and of Control Implementation Programs: Roles of Hydrocarbons, Oxides of Nitrogen and Aged Smog in the Production of Photochemical Oxidant, University of California, Riverside: California Air Resources Board, Contract No. 4-214, Final Report (May 1976).

Purcell, T. C. and Cohen, I. R., Atmospheric Environment 1, 689 (1967).

Radford, H. E., Evenson, K. M., and Howard, C. J., J. Chem. Phys. 60, 3178 (1974).

Renzetti, N. A. and Bryan, R. J., J. Air Pollution Control Assoc. 11, 421 (1961).

Robinson, E., Rasmussen, R. A., Westberg, H. H., and Holdren, M. W., J. Geophys. Res. 78, 5345 (1973).

Schuck, E. A., Eye Irritation from Irradiated Auto Exhaust. Air Pollution Foundation, San Mario, CA, Technical Report No. 18 (1957).

Schuck, E. A. and Doyle, G. J., "Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogen and Sulfur Dioxide". Air Pollution Foundation, San Marino, CA., Report No. 29 (October 1959).

Scott, W. E. and Reckner, L. R., "Atmospheric Reaction Studies in the Los Angeles Basin". Progress Report. (November 15, 1968 to January 15, 1969). Scott Research Laboratory. APRAC Project CAPA 7-68 (1969).

Seizinger, D. E. and Dimitriades, B., Journal of the Air Pollution Control Assoc. 22, 47 (1972).

Shibuya, K., Ebata, T., Obi, K., and Tanaka, I., J. Phys. Chem. 81, 2292 (1977).

Singleton, D. L., Irwin, R. S., and Cvetanovic, R. J., Can. J. Chem. 55, 3321 (1977).

Smoyer, J. C., Shaffer, D. E., and DeWitt, I. L., Inst. Environ. Sci., Tech. Meet., Proc., 17, 339-45 (1971).

Sperling, H. P. and Toby, S., Can. J. Chem. 51 471 (1973).

Stanford Research Institute, Third Interim Report on Studies to Determine the Nature and Sources of Smog to the Western Oil and Gas Association, p. 12, (November 1950).

Stephens, E. R., Adv. in Environ. Sci. and Tech. 1, 119 (1960).

Stephens, E. R. and Burneson, F., Private communication quoted in Winer et al. (1976).

Tadasa, K., Imai, N., and Inaba, T., Bull. Chem. Soc. Japan 49, 1758 (1976).

Trotman-Dickenson, A. F. and Kerr, J. A., in Handbook of Chemistry and Physics, 57th ed. (The Chemical Rubber Company, Cleveland, 1976/77).

Tucazon, E. C., Graham, R. A., Winer, A. M., Easton, R. R., Pitts, J. N., Jr., and Hanst, P. L., Atmos. Envir., (1978a).

Tucazon, E. C., Winer, A. M., Graham, R. A. and Pitts, J. N., Jr., Advances in Envir. Sci. and Tech. 10 in press (1978b).

Van Ham and Nieboer, H., T. NO Nieuws. 5, 170 (1972).

Washida, N., Martinez, R. I., and Bayes, K. D., Z. Naturforsch. 29A, 251 (1974).

Weaver, J., Meagher, J., and Heicklen, J., J. Photochem. 6, 111 (1977).

Whitten, G. and Dodge, M. C., 197th American Chemical Society Meeting, New York, (1976).

Wigg, E. E., Campion, R. J., and Petersen, W. L., The Effect of Fuel Hydrocarbon Composition on Exhaust and Oxygenate Emissions. SAE Paper No. 720251 Presented at the Society of Automotive Engineers Automotive Engineering Congress, Detroit, Michigan, January 10-14, 1972.

Wilson, K. W. and Doyle, G. J., "Investigation of Photochemical Reactivities of Organic Solvents", Stanford Research Institute Report, EPA Contract HCPA 22-61-125 (September 1970).

Winer, A. M., Private Communication. (1978).

Winer, A. M., Lloyd, A. C., Darnall, K. R., and Pitts, J. N., Jr., J. Phys. Chem. 80, 1635 (1976).

Winer, A. M., Lloyd, A. C., Darnall, K. R., Atkinson, R., and Pitts, J. N., Jr., Chem. Phys. Lett. 51, 221 (1977).

Wodkowski, C. S. and Weaver, E. E., The Effects of Engine Parameters, Fuel Composition, and Control Devices on Aldehyde Exhaust Emissions. Paper presented at West Coast Section, Air Pollution Control Association Meeting, San Francisco, CA, October 8, 1970, 32 pp.

Summary of Session

The discussion centered on the photolysis of formaldehyde - with and without added oxygen. Heicklen began the discussion by characterizing the photooxidation of aldehydes as the most important unresolved problem in air pollution chemistry. He pointed out that there appears to be general agreement on the mechanism and quantum yield for the photolysis of formaldehyde in the absence of oxygen, but that when oxygen is added, results from various studies suggest that the system is actually poorly understood. Of particular concern is that the results appear to differ from laboratory to laboratory, and sometimes within the same laboratory, as emphasized in additional remarks by Calvert.

Warneck reported on results obtained in his laboratory (with Moortgot, Glens, and Seiler) on the uv photolysis of CH_2O. These experiments were unique in that low formaldehyde concentrations were used, and both synthetic air and pure nitrogen buffer gasses were added at pressures up to atmospheric. These results (see fig. 7 of Lloyd's review paper) appear to be in general agreement with other recent results, within the uncomfortably large scatter of the data. At 355 nm, a pressure effect was observed, and there no longer was 1 to 1 relation between H_2 and CO production. Warneck suggested this may be due to an interaction of O_2 with excited formaldehyde, possibly by hydrogen abstraction.

Parkes noted that, during his study of the photooxidation of methyl radicals using a Phillips dark lamp (peak emission at 360 nm), the photolysis of formaldehyde was a complication. The addition of an atmosphere of isopentane quenched the photolysis.

At shorter wavelengths, Calvert noted that they observed no quenching with up to 50 Torr of added isobutene. At longer wavelength (∿ 390 nm) the addition of 360 Torr of CO_2 resulted in quenching, as measured by the decrease in H_2 yield. The addition of isobutene resulted in no further change.

There was some discussion of the state from which formaldehyde dissociated. Ravishankara asked if a triple state could be involved, in light of the effect of O_2.

Calvert replied that Ed Lee had tried to distinguishe between triplet and singlet formaldehyde by making the triplet via energy transfer from mercury. Apparently both dissociation processes still occur. Calvert felt that the evidence does not support triplet involvement, but that the excited singlet crosses to high vibrational levels of the ground state which then dissociate.

Heicklen questioned this explanation since the addition of an atmosphere of nitrogen resulted in no quenching of the formaldehyde dissociation.

Ravishankara mentioned some work by George Atkinson on dye laser photolysis of H_2CO, monitoring CO production by resonance emission.

The question of HCO oxidation, which is directl related to the observation of HCOOH in the photooxidation of CH_2O, was discussed by Heicklen and Niki. In his contributed remarks, Heicklen, discussed the problems associated with the reactio of HCO with O_2. The direct evidence suggests that the reaction products are CO and HO_2.

The photolysis of Cl_2-O_2-CH_2O system leads to HCOOH, however, which has been interpreted as evidence for the production of HCO_3. Niki reveale that they have found peroxynitric acid by adding NO_2 to the Cl_2-O_2-CH_2O system, further supporting the production of HO_2. In addition, they have investigated the possibility that HCOOH is produce in the reaction OH + CH_2O. They photolyzed nitrou acid and formaldehyde and found very little formic acid, suggesting that OH + CH_2O is not the source of HCOOH. The reaction HO_2 + CH_2O is still considered a possibility.

The discussion ended with some remarks about some sources of aldehydes which could become more important in the future. Calvert noted that the use of CH_3OH as a fuel in internal combustion engines leads to large CH_2O emission. Demerjian added that diesels produce large amounts of heave aldehyde.

Comments

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Moortgat et al. (presented at 13th Informal Conference on Photochemistry, Clearwater Beach, Florida, 1978) have determined the primary photochemical processes in CH_2O photooxidation in an excellent study. At 3130 Å they find the free radical process (HCO + H) to occur with $\phi = 0.80$ and the molecular process (H_2 + CO) to occur with $\phi = 0.20$. However there are still some naging problems.

The ratio of the two paths of 4.0 is consistent with the value of 3.2 found by Osif (Ph.D. thesis, Pennsylvania State University, 1976), but is sufficiently greater than the value of 2.1 found in the absence of O_2 (A. Horowitz and J. G. Calvert, Intern. J. Chem. Kinetics, in press) to suggest that the primary process must be altered in the presence of O_2. This is not unexpected since the photochemistry does not occur from the initially formed excited singlet state but proceeds with an induction period (P. Avouris, W. M. Gelbart, and M. A. El-Sayed, Chem. Rev., 77, 793, 1977). Presumably the photochemistry proceeds through a triplet (as in other aldehydes) or another intermediate ($H\dot{C}OH$) which can be attacked by O_2. If so the formation of molecular H_2 is surprising.

A further baffling point is the results reported by Osif; and Horowitz and Calvert; and Su, Horowitz, and Calvert (13th Informal Conference on Photochemistry, Clearwater Beach, Florida, January, 1978) that $\phi\{CO\}$ could exceed 6 in the presence of O_2. Clearly these high yields indicate some chain process which may be due to surface affects.

Finally Morrison in our laboratory has studied CH_2O photooxidation at 3130 Å in a Teflon-lined 11-liter cell and finds that O_2 quenches all CO and H_2 formation with a half-quenching pressure of 4 Torr. However HCOOH is produced. This result appears to be completely at variance with all other studies.

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There are two problems in HCO oxidation to be considered here: the rate coefficient and products of the reaction. There are three measurements of the rate coefficient. Washida, Martinez, and Bayes (Z. Naturforsch 29A, 1974 and Shibuya, Ebata, Obi, and Tanaka (J. Phys. Chem. 81, 2292, 1977) reported 5.6×10^{-12} cm^3/s at room temperature while Clark, Moore, and Reilly (Int. J. Chem. Kinetics 10, 427, 1978) obtain $4.0 \pm 0.8 \times 10^{-12}$ cm^3/s. Thus there is about a 30 percent uncertainty in this number.

Of more significance is the fact that Shibuya et al., obtain no pressure dependence for this rate coefficient, and conclude that there is no addition reaction of O_2 to HCO and that H abstraction is the sole reaction path. This conforms to Hunziker's observation reported at the 12th Informal Conference on Photochemistry (June, 1976) that he could not find an absorption due to HCO_3 in the HCO-O_2 reaction.

This leaves a puzzling phenomenon since both Osif and Heicklen (J. Phys. Chem. 80, 1526, 1976) and Niki, Maker, Savage, and Breitenbach (reported at the 173rd American Chemistry Society Meeting, New Orleans, March, 1977) found HCOOH in the Cl-CH_2O-O_2 system, which they considered as evidence for HCO_3 as a precursor. HCOOH has also been seen in other systems, as well as in polluted atmospheres If HCOOH does not come from HCO oxidation, then where does it come from?

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George Atkinson has measured CO production in H_2CO flash photolysis and it seems to agree with most other data.

We have measured OH + CH_3OH (and also OH + C_2H_5OH) using flash photolysis - resonance fluorescence. It agrees well with the indirect measurements of Campbell. So the rate constants for the other alcohols (measured by Campbell) are also probably correct.

Recommendations

1. Role of Aldehydes

1.1 Kinetics. We have classified the status of the rate data into the following caegories:

Satisfactory (S) - no need for further work

Less Satisfactory (L.S.) - further work is desirable but not of high priority

Deficient (D) - more work is needed

Insufficient Data (I.D.)

1.1.(a) Hydroxyl Radical Reactions HO + RCHO → H_2O + RCO

HCHO	L.S.
CH_3CHO	S
C_2H_5CHO	S
$CH_2 = CHCHO$	I.D.
C_6H_5CHO	S

In the case of C_2H_5CHO and C_6H_5CHO the rate constants are from single studies which are probably reliable, since the same authors have also studied HCHO and CH_3CHO with consistent results. It would be useful to have a second, independent determination (say be flash photolysis experiments) to confirm the data for these aldehydes.

1.1.(b) Oxygen Atom Reactions $O(^3P)$ + RCHO → HO + RCO

HCHO	S
CH_3CHO	D
C_2H_5CHO	D
n-C_3H_7CHO	I.D.
i-C_3H_7CHO	I.D.
$CH_2 = CHCHO$	L.S.
$CH_3CH = CHCHO$	S

1.1.(c) HO_2 Reactions

There are no experimental data available, and the present estimated kinetic paramters need to be substantiated by experiment.

1.1.(d) CH_3O Reactions

It would be useful to confirm the relative rate data relating to the reaction CH_3O + CH_3CHO with absolute rate data on CH_3O + aldehydes. Such reactions are probably more of kinetic interest than of importance to atmospheric modeling.

1.1.(e) NO_3 Reactions

More data are needed on this class of reactions, which might be of importance under special conditions.

1.1.(f) HSO_4 Reactions

No kinetic data exist for this species, which could be important in atmospheric chemistry.

1.1.(g) Formyl Radical Reactions

The major reaction appears to be

$$HCO + O_2 \rightarrow CO + HO_2$$

for which there are reasonably consistent room temperature data. More work is needed on this reaction, particularly in relation to the formation of HCOOH.

1.2 Photolysis

1.2.(a) HCHO

The photooxidation of HCHO is tied in with the above reaction: $HCO + O_2 \rightarrow CO + HO_2$. The mechanism of HCOOH formation appears to be dependent upon the experimental conditions, e.g., under conditions of high [HCHO] and low total pressure, the yields of HCOOH are relatively high. Further work is needed to ascertain if HCOOH is an important product under atmospheric conditions.

The quantum yield data for the free radical fragmentation process are now in satisfactory agreement.

It might be useful to have confirmation of the single set of cross-section data for HCHO.

1.2.(b) CH_3CHO

It would be useful to carry out further work to confirm the existing photochemical data on CH_3CHO.

1.2.(c) Higher Aldehydes

Photochemical studies of the higher aldehydes would be useful, but are not of prime importance to atmospheric chemistry.

2. Role of Ketones

2.1 Kinetics

2.1.(a) Hydroxyl Radical Reactions

It would be useful to confirm the existing data by further study and and at the same time to obtain information on the mechanisms of the photooxidation of the lower ketones.

2.2 Photochemistry

Confirmation is needed both for the existing quantum yield measurements and for the photoabsorption cross-sections, preferably under atmospheric conditions.

3. Role of other Oxygenated Species

Alcohols, ethers and esters appear to be of little importance in the lower atmosphere.

Session III

Organic Free Radicals

ORGANIC FREE RADICALS

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The role of free radicals in the chemistry of the lower troposphere is reviewed. Methods of predicting and estimating kinetic parameters are discussed with particular reference to alkoxyl radical decomposition, isomerization, and reaction with oxygen. Data needs, accuracy and priorities are considered.

Key words: Alkoxyl; kinetics; radicals; review; troposphere.

Introduction

This paper, specifically prepared for the Workshop on Chemical Kinetic Data Needs for Modeling the Lower Troposphere, is built around several key questions proposed to the speakers by the organizers.

1. Why is this topic important with respect to the chemistry of the lower troposphere?

A simplified general scheme for understanding the chemistry of the lower troposphere is given in figure 1. We see the role of organic free radical chemsitry in those mechanisms, and we are quickly led to understand that modeling of this complex chemistry will require knowledge of many rate constants involving organic radical species, both aliphatic and aromatic. In fact, we can readily see that the numbers of individual rate constants which will be needed is enormous. Thus, we need to be able to make reliable predictions and estimations based on a carefully selected data base.

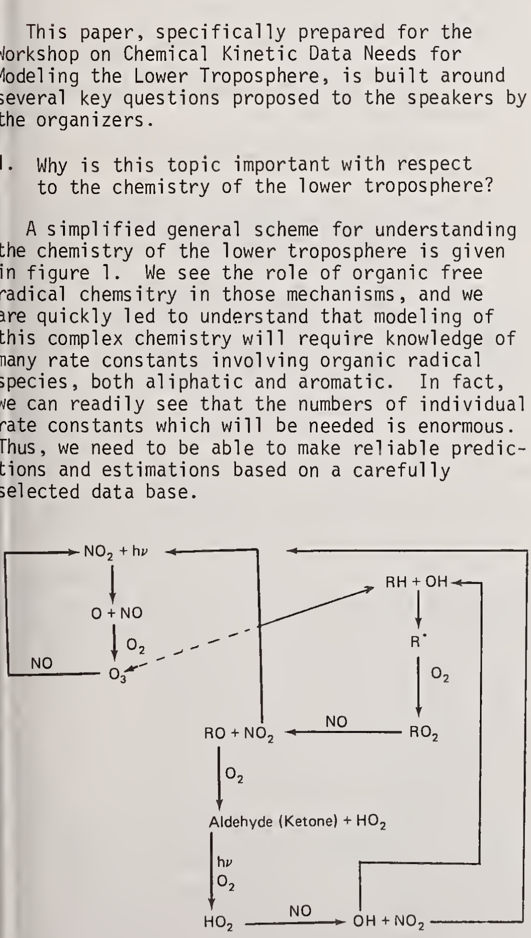

Fig. 1. A simplified scheme for the chemistry of the lower troposphere.

2. What is the current status of our knowledge?

This question is best addressed in terms of a framework for codification and extrapolation of kinetic data which allows us to choose the pursuit of specific data from which we can infer the maximum amount of new information.

A slight digression to remind us of the method involved seems in order here.

Thermochemistry. It is impossible to begin a discussion of the theoretical basis for critical evaluation and extrapolation of thermal rate data without first discussing methods for estimating thermochemical quantities, such as $\Delta H^\circ_{f,T}$, ΔS°_T, and $C^\circ_{p,T}$ for molecules.

Group Additivity. When a sufficient data base exists, we have found [1][1] the method of group additivity to best fit the need for accuracy and ease of operation. The basic concept and assumptions involved in the group additivity method are as follows:

For the disproportionation reaction

$$RNN'R + SNN'S \rightleftarrows RNN'S + SNN'R$$

any additivity approximation assumes that $\Delta\Phi = \Delta\Phi_\sigma$, where Φ is any molecular property, and $\Delta\Phi_\sigma$ is the contribution to that property due to symmetry changes and optical isomerism. For the molecular properties of interest here, $\Delta H_T \rightarrow 0$, $\Delta C_{p,T} \rightarrow 0$, and $\Delta S_T \rightarrow S_\sigma = R \ln K_\sigma$, where $K_\sigma = \sigma(RRNN'R)\sigma(SNN'S)/\sigma(RNN'S)\sigma,SNN'R)$, $\sigma(X)$ being the symmetry number including both internal and external symmetry. An additional term for entropy of mixing, due to the existence of optical isomers, must also be included.

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[1] Figures in brackets indicate literature references at the end of this paper.

If the molecular framework NN' is two atoms or greater, these relationships imply the additivity of group properties, which include all nearest-neighbor interactions, since a group is defined as an atom together with its ligands (e.g., in the group C-$(H)_3$(C), the central C atom is bonded to three H atoms and one C atom). Thus, the equation

$$CH_3OH + CH_3CH_2OCH_3 \rightleftarrows CH_3CH_2OH + CH_3OCH_3$$

implies the additivity of the properties of the groups C-$(H)_3$(C), C-$(H)_3$(O), O-(C)(H), C-$(H)_2$(C)(O), and O-$(C)_2$, if the appropriate $\Delta\Phi = \Delta\Phi_\sigma$.

We have developed group additivity methods that permit the estimation, for many organic chemicals in the gas phase, of heats of formation ± 1 kcal/mol, and of entropies and heat capacities to ± 1 cal/(mol-K), from which free energies of formation can be derived to better than ± 2 kcal/mol.

It should be noted that entropy and heat capacity are molecular properties that can be accurately estimated under much less stringent conditions than energy (or enthalpy). Thus, the method of bond additivity seems to work quite well (± 1 cal/(mol-K)) for estimating the former properties, but not at all well (± 4 kcal/mol) for the latter.

Structural Considerations and Model Compounds. If sufficient thermochemical data is lacking for the estimation of group properties, entropy, and heat capacity can often be adequately estimated from structural parameters of the molecule. (Enthalpy estimates are more difficult, requiring a better knowledge of potential functions than are usually available). The methods of statistical thermodynamics may be used to calculate C_p° and S° directly for those molecules where a complete vibrational assignment can be made or estimated.

Also, "reasonable" structural and vibrational frequency "corrections" to the corresponding established thermodynamic properties of "reference" compounds may be made. A suitable choice of reference compound, i.e., one similar in mass size and structure to the unknown, assures that the external rotational and translational entropies and heat capacities of the reference and unknown compounds will be the same and that many of the vibrational frequencies will be similar. The basic assumption is that S^0 and C_p^0 difference can be closely estimated by considering only low-frequency motions thought to be significantly changed in the unknown. Fortunately, entropies and heat capacities are not excessively sensitive to the exact choice of these vibrational frequencies, and estimates of moderate accuracy may be made with relative ease.

Kinetics. The extension of thermochemical estimation techniques to the evaluation of kinetic data rests largely on the validity of transition state theory.

The transition state theory expression for a thermal rate constant is:

$$k = (kT/h)\exp[-\Delta G_T^{0\ddagger}/RT]$$

(The units are s^{-1} for first order and $atm^{-1}\ s^{-1}$ for second order). And

$$\Delta G_T^0 = \Delta H_{300}^\ddagger - T\Delta S_{300}^{0\ddagger}$$

$$+ <\Delta C_p^\ddagger> [(T-300) - T\ln(T/300)].$$

(In the ideal gas approximation we can drop the standard state notation of $\Delta H^\ddagger$ and $\Delta C_p^\ddagger$). If the empirical temperature dependence is represented by

$$k = AT^B \exp(-C/T)$$

$$A = k/h(300)^{<\Delta C_p^\ddagger/R>} \exp[(\Delta S_{300}^\ddagger - <\Delta C_p^\ddagger>)/R]$$

$$B = (<\Delta C_p^\ddagger> + R)/R$$

$$C = (\Delta H_{300}^\ddagger - <\Delta C_p^\ddagger>(300))/R$$

k = Boltzmann's constant

h = Planck's constant

$\Delta S_{300}^{0\ddagger}$ = entropy of activation at 300 K, standard state of 1 atm.

$\Delta H_{300}^\ddagger$ = enthalpy of activation at 300 K.

$<\Delta C_p^\ddagger>$ = average value of the heat capacity at constant pressure of activation over the temperature range 300 T K.

If we wish to express second-order rate constants in concentration units instead of pressure units, we must multiply by RT in the appropriate units. This has the effect of writing:

$$k = A'T^{B'} \exp(-C/T)$$

where $A' = AR$ and $B' = B + 1 = (<\Delta C_p^\ddagger> + 2R)/R$

Thus, simple "Arrhenius behavior" which will be sufficient for lower tropospheric temperature is characterized for first-order reaction by $\Delta C^\ddagger = -R$; ($\Delta C_p^\ddagger = \Delta C_v^\ddagger = \Delta C^\ddagger$), and for second-order reactions using concentration units by $\Delta C_p^\ddagger = -2R$ (or $\Delta C_v^\ddagger = -R$).

In the case of simple Arrhenius behavior:

$$k = A\exp(-B/T)$$

$$\log A = \log(ek<T>/h) + \Delta S^\ddagger/R;$$

$$B = (\Delta H^\ddagger + R<T>)/R$$

Thus, the quantities $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta C^\ddagger$ are of interest. We apply similar methods to those already discussed with respect to thermochemistry to view rate data in a reactional framework. These rechniques are discussed in some detail by Benson [2], but certain points are worthy of re-emphasis here.

We begin by classifying reactions as unimolecular or bimolecular. (The only termolecular processes of interest to us will be energy transfer controlled bimolecular processes).

Unimolecular Processes.

Simple Fission: AB → A + B

Complex Fission: Molecule → Molecule + Molecule (or radical)

Isomerization: Intramolecular atom rearrangement

Bimolecular Processes.

Direct Metathesis: A + BX → AX + B

Addition: A + Molecule → Stable Adduct (reverse of complex fission)

Association: A + B → A - B (reverse of simple fission)

The first thing to notice is that of all these reactions, only direct metathesis reactions are not subject to becoming energy transfer limited at high temperatures and low pressures (i.e., in the "fall-off" region!). This means that not only does the so-called high pressure rate constant need to be estimated or known, but the extent of fall-off, as well. Methods are available for making fall-off correction [3].

In hydrocarbon reactions in the troposphere, including those of aromatic compounds, we may expect that most direct metathesis reactions will involve the exchange of a hydrogen atom between larger groups. A simple, semi-empirical prescription exists for estimating the value of $\Delta S^{\ddagger}$ for these types of reactions. First, one realizes that these values are limited between the "loosest" possible model (A-factor equals gas kinetic collision frequency) and the "tightest" possible model in which R•••H•••R' is represented by the molecular R-R'. Experience using data in the $300 < T/K < 700$ has taught us that generally the $\Delta S^{\ddagger}$ value corresponds to a transition state only slightly looser than the tightest possible value.

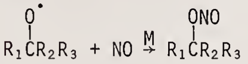
Since the other two classes of bimolecular processes are the reverse of unimolecular reactions, we may consider them in that direction. (The equilibrium constant is either known or estimable). Once again using experimental results as our guide, we note that model transition state which correspond to the values of $\Delta S^{\ddagger}$ are generally "tight". That is, we may visualize them as minor modifications of the reactant molecule, usually involving some increase in rotational entropy due to slight enlargement of certain bonds. The dominant entropic feature is usually the stiffening of internal rotations as a result of multiple bond formation or ring formation [2].

Bond scission reactions present a particular problem, since it is particularly difficult to locate a transition state. Recent work [2,4], both experimental and theoretical, indicates that these reactions can be modeled with a transition state which becomes tighter as the temperature rises.

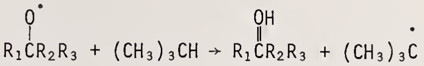
An example of the use of these methods to evaluate rate constants for modeling the lower troposphere is taken from Barker et al. [5]:

Alkoxyl Radical Decomposition Reactions. The decomposition reactions of alkoxyl radicals provide a good example of a family of reactions for which an adequate number of accurate studies have been made. Most of the studies have been made on t-butoxyl radicals, but several other radicals have been studied as well. All the studies were determinations of relative rate constants and so we returned to the original data and recomputed it on the basis of current values for the reference reaction rate constants.

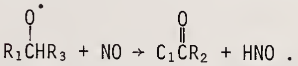
Three different reference reactions have been used:



$$R_1\overset{O^{\bullet}}{C}R_2R_3 + NO \xrightarrow{M} R_1\overset{ONO}{C}R_2R_3 \qquad (1)$$



$$R_1\overset{O^{\bullet}}{C}R_2R_3 + (CH_3)_3CH \rightarrow R_1\overset{OH}{C}R_2R_3 + (CH_3)_3\dot{C} \qquad (2)$$



$$R_1\overset{O^{\bullet}}{C}HR_3 + NO \rightarrow C_1\overset{O}{\overset{\|}{C}}R_2 + HNO\ . \qquad (3)$$

Values chosen for k_1 were those obtained by Batt et al. [6], and are in good agreement with those obtained by Golden et al. [7], the value of k_2 chosen was that determined by Berces and Trotman-Dickenson [8]; the values chosen for k_3 were derived from disproportionation/combination ratios and values of k_1 [6,9]. Other reported data were not used because their reference reaction rates are not sufficiently well known.

The recalculated data are presented in figures 2 through 5, and the corresponding Arrhenius parameters are presented in table 1. The data for t-BuO are the most extensive (fig. 2), covering nearly four orders of magnitude. The individual sets of experimental data taken independently show a rather wide range of Arrhenius parameters and appear to be inconsistent, but taken together, the actual data give a reasonably good straight line with parameters, $\log k/s^{-1} = 15.1 - 16.2/\Theta$. Given the entropy change of the reaction, $\Delta H^0_R =$ 41.2 Gibbs/mole, the A-factor for the reverse reaction is $A_r = 10^{7.9}\ M^{-1}\ s^{-1}$, a value very close to that for the reaction of methyl radicals with isobutene ($\log A = 8.0$) [10]. This suggests a self-consistent method for evaluating and codifying the limited data available for the other alkoxyl radical reaction: choose an A-factor for the reverse reaction and find the corresponding activation energy. If this unified scheme is used, the alkoxyl decompositions can be considered together as a class, rather than individually.

The decomposition of an alkoxyl radical is the reverse of the addition of an alkyl radical to the carbon atom of a carbonyl group, which is analogous to alkyl radicals adding to the 2-position of a primary olefin. Since data are only available for alkyl radicals adding to the 1-position of primary olefins, the assumption was

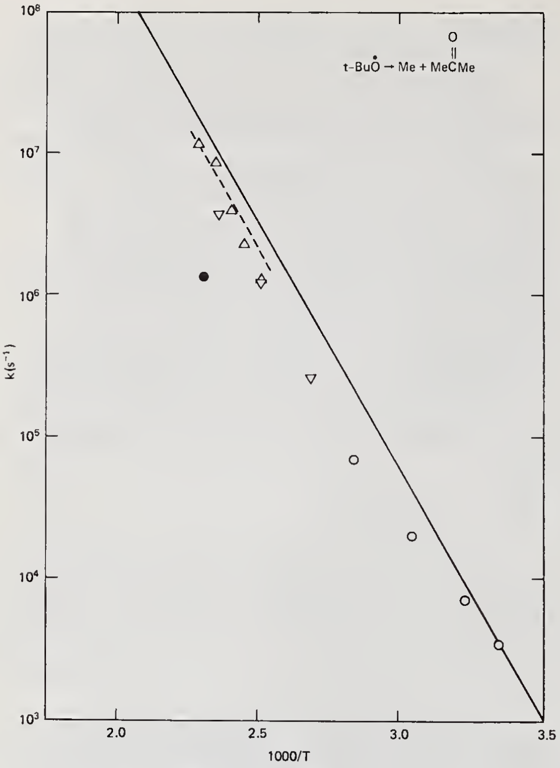


Fig. 2. t-BuO$^\cdot$ $\overset{M}{\rightarrow}$ Me + acetone. ▽, ref. [11]; o, ref. [12]; Δ, ref. [13]; o, ref. [14]; dashed line, ref. [6(c)]; solid line given by log k(s^{-1}) = 15.2 - 15.9/θ.

Table 1. Experimental values for RO$^\cdot$ decomposition rates.[a]

Radical	log A	log E	ΔS_R^0	log A_r	log A_{est}	E'	Ref.
EtO$^\cdot$	13.7	22.1	33.4	8.2	13.7	22.1	[67]
i-PrO$^\cdot$	16.1	20.6	37.8	8.2	14.6	17.4	[68,69]
s-8uO$^\cdot$	16.4 14.9	18.0 15.3	37.7	8.0	14.4	13.9 14.2	[70] [65d]
t-BuO$^\cdot$	15.1	16.2	41.2	8.0	15.2	16.3	[71-74]

[a] Units: E in kcal/mol; A_r in $M^{-1}s^{-1}$; A in s^{-1}.

made that the A-factors for addition to both ends of an olefin double bond are the same and only the activation energies differ. Thus, A-factors for analogous alkyl radical plus olefin reactions were chosen from the tables of Kerr and Parsonage [10], corrected for any difference in reaction path degeneracy, and applied to the alkoxyl reactions.

Assumed A-factors for the reverse reaction, A_r, are summarized along with ΔS_R, log A_{est}, and corresponding activation energies E in table 1. A plot of E vs ΔH_R^0 is presented in figure 6 and gives a good straight line:

$$E = 12.8 + 0.71\,\Delta H_R^0 \qquad \Delta H_R^0 > 0 \qquad (4)$$

$$= 12.8 \qquad \Delta H_R^0 \leq 0\ .$$

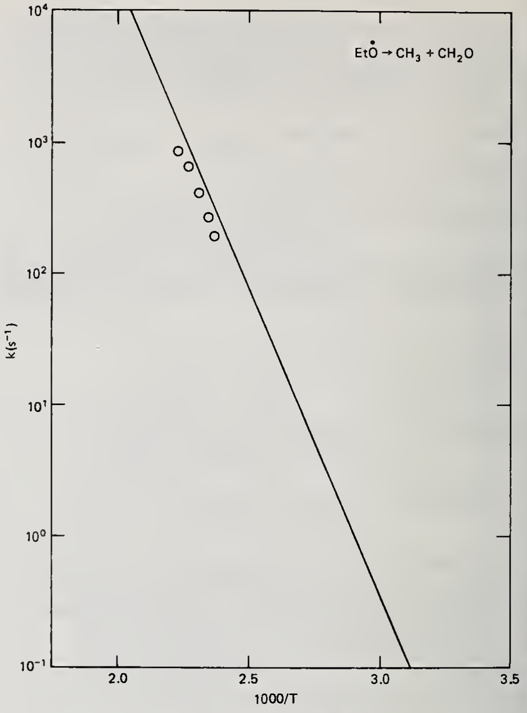


Fig. 3. EtO$^\cdot$ $\overset{M}{\rightarrow}$ Me + CHO. o, ref. [15], line given by log k(s^{-1}) = 13.7 - 21.6/θ.

This equation predicts activation energies with an uncertainty of about ± 0.5 kcal/mol. It predicts that the reverse reaction has an activation energy given by

$$E_r = E - \Delta H_R^0 + RT = 13.6 - 0.29\,\Delta H_R^0\ . \qquad (5)$$

Although these equations apply to ∿ 400 K where most of the experiments were carried out, the estimated activation energies will be negligibly different at ∿ 300 K.

Estimated decomposition rate constants for a number of alkoxyl radicals at 300 K and atmospheric pressure are presented in table 2. Fall-off corrections were obtained by use of the Emanual RRK Integral tables [3,19]. For the experimental data available, the estimated rates are accurate to about a factor of two, as demonstrated by comparing estimated and observed rate constants (figs. 2-5). The differences apparent between the estimated and experimental rate constants are due to the ± 0.5 kcal/mol uncertainty in estimating the reaction activation energy and round-off errors on the A-factors.

Estimates made when no experimental data are available can be appraised by using the propagation of errors equation. Since A-factor and activation energy are usually estimated independently, the uncertainty in log k can be written

$$\sigma^2_{\log k} = \sigma^2_{\log A} + \sigma^2_E/\theta_2 \qquad (6)$$

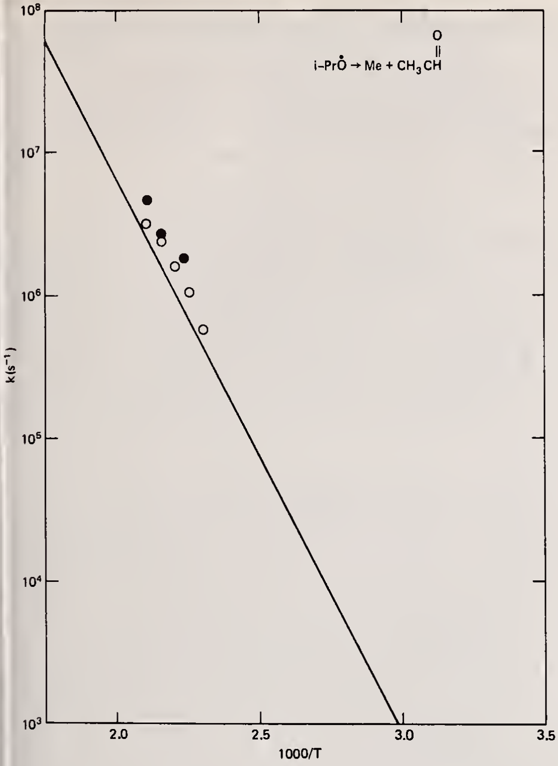


Fig. 4. i-PrO$^\cdot$ $\overset{M}{\rightarrow}$ Me + MeCHO. o, ref. [16]; o, ref. [17]; line given by log k(s^{-1}) = 14.6 - 17.8/θ.

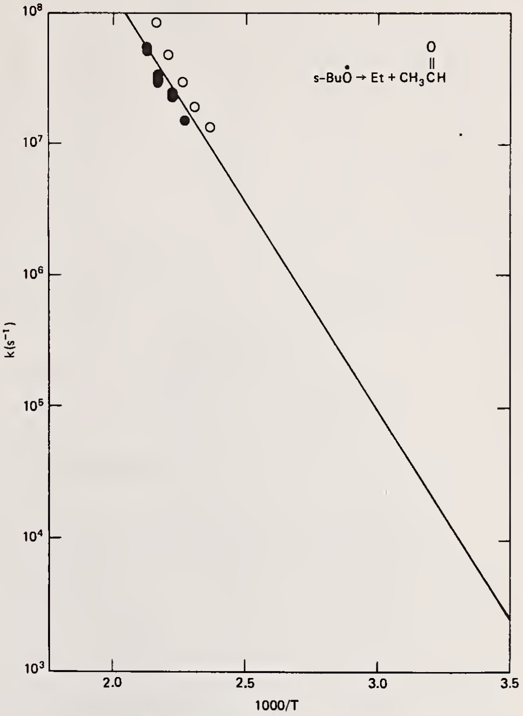


Fig. 5. s-BuO$^\cdot$ $\overset{M}{\rightarrow}$ Et + MeCHO. o, ref. [18]; ref. [6(d)]; line given by log k(s^{-}) = 14.4 - 14.6/θ.

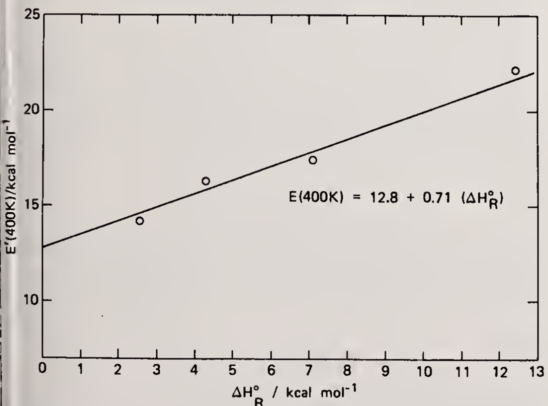


Fig. 6. Correlation between activation energy E and enthalpy of reaction ΔH^0_R.

where $\sigma_{\log k}$, $\sigma_{\log A}$, and σ_E are standard deviations in log k, log A, and activation energy respectively, and Θ = 2.303 RT. Since log A is probably uncertain by ± 0.5, and the activation energy is uncertain by about ± 1 kcal/mol, the value for $\sigma_{\log k} \approx 0.88$ at 300 K, and k is uncertain by about a factor of eight. This represents a relatively favorable case for estimations, since an adequate amount of kinetic data is available, and it is fairly consistent. For the reactions discussed below, very little data is available, and the realiability of the estimates is much lower.

Alkoxyl Radical Reactions with Oxygen. The only reliable Arrhenius parameters [21] known for this class of reactions are:

$$CH_3O + O_2 \rightarrow CH_3O + HO_2$$

$$\log k/M^{-1}s^{-1} = 8.5 - 4.0/\Theta \ . \qquad (7)$$

Rates for other members of this class can only be estimated after making assumptions regarding variations in A-factors and activation energies. The concomitant uncertainties in estimating rate constants will be relatively large since little is known about such variations.

The A-factors for this group of reactions are expected to be similar to that for methoxy radicals, aside from the reaction path degeneracy (n) factor; therefore, log A can be estimated as follows:

$$\log A_{est}/M^{-1}\ s^{-1} = 8.0 + \log n \ . \qquad (8)$$

Estimates for activation energy variations are rather problematical, especially when E_a is low. Two alternative methods can be used:

Table 2. Estimated RO˙ decomposition rates.

Radical[a]	ΔH_R	ΔS_R	log A_r[b]	log A(s^{-1})	E_{est}[c]	k/k_∞[d]	k(min^{-1})[e]
$\mathrm{C{-}CO\cdot}$	12.4	33.4	8.2	13.7	21.6	0.003	2.1×10^{-3}
$\mathrm{CC{-}CO\cdot}$	9.4	35.0	8.0	13.8	19.5	0.6	1.7×10^{1}
$\mathrm{C{-}\overset{\dot{O}}{C}C}$	7.1	37.8	8.2	14.6	17.8	0.5	1.6×10^{2}
$\mathrm{CCC{-}CO\cdot}$	8.9	36.3	7.5	13.6	19.1	0.8	2.9×10^{1}
$\mathrm{CC{-}\overset{\dot{O}}{C}C}$	2.6	37.7	8.0	14.4	14.6	0.7	2.9×10^{5}
$\mathrm{C{-}\overset{C}{\underset{C}{C}}O\cdot}$	4.3	41.2	8.0	15.2	15.9	0.5	1.5×10^{5}
$\mathrm{HOC{-}\overset{\dot{O}}{C}C}$	6.8 (3.5)[f]	38.0	8.0	14.5	17.6 (15.3)[f]	0.8	2.8×10^{3} (2.2×10^{5})[f]
$\mathrm{HOCCC{-}CO\cdot}$	8.7	36.6	7.1	13.3	19.0	1	2.1×10^{2}
$\mathrm{HOCCC{-}\overset{\dot{O}}{C}OH}$	-9.7	39.2	7.1	13.8	12.8	1	2.1×10^{6}
$\mathrm{(HO)_2CCC{-}\overset{\dot{O}}{C}OH}$	-9.6	39.2	6.8	13.5	12.8	1	1.0×10^{6}
$\mathrm{(HO)_2CCC{-}\overset{\dot{O}}{C}(OH)_2}$	-30.9	37.7	6.8	13.2	12.8	1	5.2×10^{5}
$\mathrm{(HO)_3CCC{-}\overset{\dot{O}}{C}(OH)_2}$	-24.5	37.7	6.5	12.9	12.8	1	2.6×10^{5}
$\mathrm{HO\overset{C}{C}{-}CO\cdot}$	11.4 (8.2)[f]	37.7	7.5	13.9	20.9 (18.6)[f]	0.9	3.6×10^{0} (2.2×10^{2})[f]
$\mathrm{C\overset{O}{\overset{\|}{C}}{-}\overset{\dot{O}}{C}C}$	-5.1	40.3	7.5	14.5	12.8	0.8	8.2×10^{6}

---

[a] Notation: $\mathrm{HOC{-}\overset{\dot{O}}{C}C}$ represents $\mathrm{HOCH_2\overset{\dot{O}}{C}HCH_3 \rightarrow HOCH + H\overset{O}{\overset{\|}{C}}CH_3}$, etc.
[b] A-factor for analogous alkyl radical + alkene association reaction.
[c] E_{est} - 12.8 + 0.71 H^0_R (kcal/mol).
[d] Fall-off estimated from RRK tables for 1 atm, 300 k.
[e] Rate constants for 300 K and atm air.
[f] Based on Group Additivity [2], not on experimental ΔH^0_f for propane-1, 2-diol [20].

(1) Assume E_a is constant for the entire homologous series.

(2) Assume that an empirical relationship that holds for other radical reactions applies to this series as well.

A simple empirical relationship [22] that gives E_a with an uncertainty of about ± 3 kcal mol^{-1} for exothermic H, OH, and CH_3 reactions is given by equation (9):

$$E_a = 11.5 + 0.25\ (\Delta H_R), \tag{9}$$

where ΔH_R is the enthalpy of reaction. For reaction (7), equation (9) predicts E_a = 5 kcal mol^{-1}, about 1 kcal mol^{-1} too high. Equation (9) has two different ways to give the proper E_a for reaction (1);

$$E_a = 10.5 + 0.25\ (\Delta H_R) \tag{10}$$

$$E_a = 11.5 + 0.29\ (\Delta H_R)\ . \tag{11}$$

Rate constants for a number of alkoxyl radical reactions were estimated by the three methods and are presented in table 3. Considering the large uncertainty associated with equation (2) and the low activation energies, the estimates in column III of the table are highly uncertain and may well be upper limits to the correct rate constants. Similarly, rate constants in column I of the table may be near the lower limits.

Table 3. Estimates: RO· + O_2 reactions[a].

Reaction	log $(A)_{est}$	I E_a = 4.0 k (min^{-1})	II E_a = 10.6 + 0.25 x (ΔH^0_R) k (min^{-1})	III E_a = 11.5 + 0. x (ΔH^0_R) k (min^{-1})
$CH_3O + O_2$	8.5	2.0×10^5	2.0×10^5	2.0×10^5
$EtO + O_2$	8.3	1.3×10^5	8.2×10^5	1.3×10^6
$n\text{-}PrO + O_2$	8.3	1.3×10^5	8.2×10^5	1.3×10^6
$i\text{-}PrO + O_2$	8.0	6.7×10^4	1.5×10^6	3.7×10^6
$n\text{-}8uO + O_2$	8.3	1.3×10^5	3.5×10^5	5.8×10^5
$s\text{-}BuO + O_2$	8.0	6.7×10^4	1.1×10^6	2.2×10^6

---

[a] Effective first-order rate constants at 300 K in air (2.1×10^5 ppm 0

The overall uncertainties for this family of reactions may be estimated as before. Log A is probably uncertain by ± 0.5 and the activation energy is probably uncertain by an average of ± 1.5 kcal/mol. Thus, $\sigma_{\log k} \approx 1.2$, and the estimated rate constant is uncertain by about a factor of 16. If the activation energy is uncertain by an average of ∿ ± 2.5 kcal/mol, the estimated rate constant is uncertain by a factor of ∿ 80.

Alkoxyl Radical Isomerization Reactions. The importance of alkoxyl radical isomerization reactions has been inferred from smog chamber data [23], as well as from more qualitative consideration [24]. The estimation of the isomerization rates is relatively straightforward but the estimates are somewhat uncertain, as discussed below.

A-factors for 5-membered ring (5R) and 6-membered ring (6R) isomerizations were estimated to be $10^{11.2}s^{-1}$ and $10^{10.9}s^{-1}$ (per H-atom), respectively. The estimate for the 5R transition state was made by noting that in tying up the methyl and ethyl internal rotations, the change in entropy is about -6.6 Gibbs/mole; subtracting another 0.3 Gibbs/mole for the reaction coordinate, we obtain $\log A_{5R} = 11.7$ for three abstractable H-atoms. Thus, for each abstractable H-atom, $\log A_{5R}$ (per-H) = 11.2.

For the 6R transition state, a model transition state was used. For the decomposition of ethyl vinyl ether (EVE), log A = 11.4 at 700 K. If log A is about the same at 300 K and S^{0}(EVE) = 82.6 Gibbs/mole [2], then the entropy of the transition state is 74.3 Gibbs/mole. In comparing the EVE transition state and that of n-butoxyl radical, EVE has some doube bond character, and that of n-butoxyl will be looser by about 0.6 Gibbs/mole. n-Butoxyl has one more hydrogen atom, worth about 0.2 Gibbs/mole, and has spin, contributing 1.4 Gibbs/mole. Adding all of these corrections gives $S^{0\ddagger} = 76.5$ and log A = 11.4 for three abstractable H-atoms; thus $\log A_{6R}$ (per H) = 10.9. The uncertainties in these estimates are probably ± 4 Gibbs/mole and log A is uncertain by ± 1.

Activation energies may be estimated from the activation energies for H-abstraction by alkoxyl radicals [25] by adding a "strain" energy of 0.5 kcal/mol for 6R reactions and 5.9 kcal/mol for 5R reactions [2]. These activation energies are rather uncertain, probably ± 2 kcal/mol. The combination of the two sources of error by the propagation of errors formula gives an estimated uncertainty in log k of ± 1.8 at room temperature. Thus, the rates are estimated to be uncertain by about a factor of 60.

The method for estimating these rates is summarized in table 4 and estimated rates for several alkoxyl radicals are presented in table 5. All reactions are assumed to be at the high-pressure limit.

3. What do we need to know?

First of all, we need to test some of the preceding ideas with experiments conceived for just that purpose. Since the ideas are based on the transition state theory formalism, it is important to address the question of limits of validity of transition state theory. In general, these testing reactions should be measured under conditions where isolated reactions can be observed, as the extraction of individual rate constants from complex reacting systems is fraught with difficulty.

Table 4. RO· isomerization reactions--estimation procedure.

E = E (abstraction) + E (strain)

Hydrogen Abstracted	E (abstraction), kcal/mol
RCH_2-H	7.2
RCH(OH)-H	6.0
R_1R_2CH-H	4.1
$R_1R_2R_3C$-H	4.1
$RC(OH)_2$-H	4.1[a]

Strain Energy	
5-membered ring	5.9 kcal/mol
6-membered ring	0.5 kcal/mol

A-Factor (per abstractable H)	
5-membered ring	$A = 10^{11.2}\ s^{-1}$
6-membered ring	$A = 10^{10.9}\ s^{-1}$

[a] Estimated.

Table 5. Estimated RO· isomerization reaction rates.

Reaction[a]	log A(s^{-1})	E(kcal/mol)	k(min^{-1})
$\dot{\mathrm{O}}\mathrm{CCCC} \rightarrow \mathrm{HOCCC}\dot{\mathrm{C}}$	11.4	7.7	3.7×10^{7}
$\mathrm{C}\overset{\dot{\mathrm{O}}}{\mathrm{C}}\mathrm{CC} \rightarrow \mathrm{C}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{CC}\cdot$	11.7	13.1	8.6×10^{3}
$\mathrm{HOCCCC}\dot{\mathrm{O}} \rightarrow \mathrm{HO}\dot{\mathrm{C}}\mathrm{CCCOH}$	11.2	6.5	1.9×10^{8}
$\mathrm{HO}\overset{\mathrm{O}^{\cdot}}{\mathrm{C}}\mathrm{CCCOH} \rightarrow \mathrm{(HO)_2CCC}\dot{\mathrm{C}}\mathrm{OH}$	11.2	6.5	1.9×10^{8}
$\mathrm{(HO)_2CCC}\overset{\mathrm{O}\cdot}{\mathrm{C}}\mathrm{OH} \rightarrow \mathrm{(HO)_2}\dot{\mathrm{C}}\mathrm{CCC(OH)_2}$	10.9	4.6	2.2×10^{9}
$\mathrm{(HO)_2}\overset{\dot{\mathrm{O}}}{\mathrm{C}}\mathrm{CCC(OH)_2} \rightarrow \mathrm{(HO)_3CCC}\dot{\mathrm{C}}\mathrm{(OH)_2}$	10.9	4.6	2.2×10^{9}
$\mathrm{C}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{CCO}\cdot \rightarrow \dot{\mathrm{C}}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{CCOH}$	11.4	7.7	3.0×10^{8}

[a] Notation: $\mathrm{C}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{CCO}\cdot \rightarrow \dot{\mathrm{C}}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{CCOH}$ represents $\mathrm{CH_3}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2CH_2O}\cdot \rightarrow \dot{\mathrm{C}}\mathrm{H_2}\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2CH_2OH}$

Preliminary results from our own laboratory indicate that the isomerization reaction of primary alkoxyl radicals predicted by Barker et al. [5], does indeed take place at the rate expected. In this experiment, nbuO$^{\cdot}$ radicals were generated from the VLPP of nbnONO in the presence of DI. The mass spectrum of products indicated the production of both nbuOD and $DCH_2CH_2CH_2OH$.

There are many examples of reactions for which rate constants have been studied, but product studies are lacking. Thus, in reactions of OH with olefins current models must arbitrarily decide on branching ratios. This is equally true in aromatic systems.

In all of the above discussion of estimation of rate data, the importance of thermochemical values for all species has been emphasized. It is particularly important to have a good set of values for the entropy and heat of formation of organic free radicals.

Very few spectroscopic assignments exist for modest-to-large size organic free radicals and entropies (and heat capacities) have generally been estimated by methods discussed earlier. Uncertainties arise from changes in hindered rotation barriers and changes in skeletal bending frequencies.

Heats of formation of organic free radicals have been measured by a variety of techniques. All have been extensively presented in the literature. Common techniques and problems associated with them are:

1. Bond scission activation energy assigned as bond strength:

$$R\text{-}R' \xrightarrow{k_1} R + R'$$

   (a) E_1 is a function of T.

   (b) k_{-1} is a function of T.

   (c) Small fractional errors in slope of Arrhenius line lead to large absolute errors in E_1. (This problem is overcome to a large extent by use of relative rate techniques).

   (d) k_1 and k_{-1} are functions of P.

2. Mass spectrometric techniques requiring cycles involving ion thermochemistry:

$$R \rightarrow R^+ + e \qquad \text{IP}$$

$$S \rightarrow R^+ + e \qquad \text{AP}$$

$$\text{AP-IP} = \Delta H^0_{f,0}(R) - \Delta H^0_{f,0}(S)$$

   (a) Difficulties measuring IP and AP (a whole literature)

$$R + e^- \rightarrow R^- \qquad \text{EA}$$

$$RH \rightleftarrows R^- + H^+ \qquad pK_a \rightarrow \Delta H^0_a$$

$$\Delta H_a - EA = \Delta H^0_f(H^+) - \Delta H^0_f(RH) + \Delta H^0_f(R)$$

   (a) Difficulties measuring EA and pK_a.

3. Halogenation kinetics (principally iodination):

   Measurement of the rate constant k_1 for

$$RH + I \xrightarrow{k_1} R + HI$$

and the assumption that $E_{-1} = 1 \pm 1$ kcal mol^{-1}

   (a) Validity of the assumption

Recently several workers have suggested that the value of $\Delta H_f(R)$ determined by iodination techniques are two low. This says, in effect, that if k_1 is correctly measured E_{-1} must be lower than 1 ± 1 kcal/mol^{-1}.

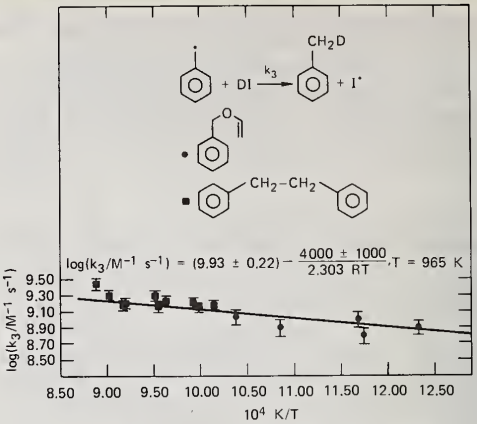


Fig. 7. Arrhenius plot. ■ bibenzyl as precursor; □ benzylvinylether as precursor for benzyl radicals.

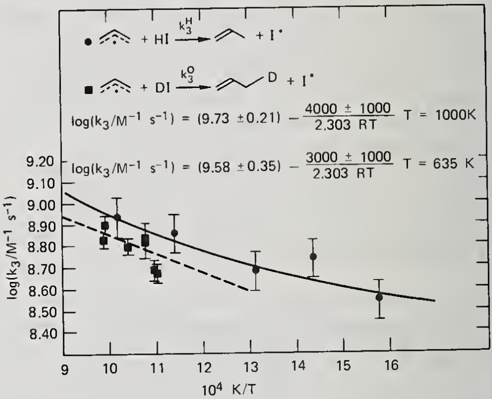


Fig. 8. Arrhenius plot. --- methathesis reaction involving DI; — metathesis reaction involving HI.

We have recently tested this possibility with several experiments where R is allyl or benzyl radical. Figs. 7 and 8 show the results. These Arrhenius parameters are shown to be compatible when a suitable transition state model is chosen with values of $\Delta H_{f,298}$ (allyl) = 39.1 ± 1.0 (corresponding to E_{-1} - 2.3 kcal mol^{-1}) and $\Delta H_{f,298}$ (benzyl) = 46.6 ± 1.5 (corresponding to E_{-1} = 2.5 kcal mol^{-1}). Thus we see no indication of any major problem with the halogenation technique. Work on t-butyl radical is in progress.

There are other specific elementary processes for which the rate constants (and products) requi study. It is not my intention to try to develop a list in this paper, but this workshop as a whol might consider doing so.

4. How Accurately (do we need to know whatever it is that we need to know?

This question cannot be answered in a general way. It is optimistic to think that we can know thermochemical values for the free radicals to better than ± 1 kcal mol^{-1} in ΔH_f and ± 1 cal mol^{-1} deg^{-1} for S^0. Errors of this size will limit possible accuracy of estimates of rate constants to an order of magnitude. If the data being modeled justify higher accuracy, individual rate constants will have to be measured. In general, rate constants can be expected to be measured to accuracies on the order of a factor of two but some are hard to obtain at all.

As far as I can tell, the limiting problem in current smog modeling is as much with the data to be modeled as the kinetic and/or thermochemical data.

5. With respect to this particular topic what do you see as the research priorities?

I have really addressed these previously, but to summarize:

General

Tests of predictions using thermochemical kinetics

Thermochemistry of free radicals

Product studies

Reactions in aromatic systems

Specific (incomplete)

Branching ratios in OH reactions with unsaturates

Heats of formation of prototype alkyl radicals

This Workshop should develop a list like this combining all topics to eliminate overlap.

6. Are there speculative problem areas that should be given some attention?

In the general area of organic free radical kinetics, the question of perturbation of "elementary" reactions by the formation of weakly bound complexes is one that I find perturbing. Thus, if:

$$A + BC \underset{-1}{\overset{1}{\rightleftarrows}} A{\cdot}BC \xrightarrow{2} \text{products}$$

nd $k_{-1} > k_2$

$$k_{exp't} = K_1 k_2$$

his allows for low and/or negative activation nergies, since $E_{expt} = \Delta E_1 + R_2$ and $\Delta E_1 < 0$. If $_{-1} > E_2$, $A_{-1} > A_2$ for $k_{-1} > k_2$, thus: $A_{expt} =$ $A_1/A_{-1})A_2 < A$.

If this type of mechanism is common, it must be taken into account and what will be needed is a method for recognizing and predicting such occurrences.

Acknowledgment. I have profited greatly from the work of my colleagues, Dr. John R. Barker and Dr. Alan C. Baldwin. Conversations with these coworkers and Dr. Dale G. Hendry have been very valuable.

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Some parts of this paper are taken from previous reports and publications.

References

[1] Benson, S. W., Cruickshank, F. R., Golden, D. M., Haugen, G. R., O'Neal, H. E., Rodgers, A. S., Shaw, R., and Walsh, R., Chem. Rev. 69, 279 (1969).

[2] Benson, S. W., Thermochemical Kinetics, 2nd Ed. (John Wiley and Sons, Inc., New York, 1976).

[3] Golden, D. M., Solly, R. K., and Benson, S. W., J. Phys. Chem. 75, 1333 (1971).

[4] Smith, G. P. and Golden, D. M., Int. J. Chem. Kinetics (to be published).

[5] Barker, J. R., Benson, S. W., Mendenhall, G. D., and Golden, D. M., EPA-600/3-77-10, Grant No. R802288, October 1977.

[6] (a) Batt, L., McCulloch, R. D., and Milne, R. T., Int. J. Chem. Kinetics 6, 945 (1974).

(b) Batt, L., McCulloch, R. D., and Milne, R. T., Int. J. Chem. Kinetics Symposium No. 1, 441 (1975).

(c) Batt, L. and Milne, R. T. Int. J. Chem. Kinetics 8, 59 (1976).

(d) Batt, L. and McCulloch, R. D., Int. J. Chem. Kinetics 8, 911 (1976).

[7] Mendenhall, G. D., Golden, D. M., and Benson, S. W., Int. J. Chem. Kinetics 7, 725 (1975).

[8] Berces, T. and Trotman-Dickenson, A. F., J. Chem. Soc. 83, 348 (1961).

[9] Heicklen, J. and Johnston, H. S., J. Amer. Chem. Soc. 84, 4030 (1962).

[10] Kerr, J. A. and Parsonage, M. J., Evaluated Kinetic Data on Gas-Phase Addition Reactions (CRC Press, Cleveland, Ohio, 1972).

[11] Cadman, P., Trotman-Dickenson, A. F., and White, A. J., J. Chem. Soc. (A), 2296 (1971).

88B, 88(B),

89A, 89(a),

[12] Bires, F. W., Danby, C. J., and Hinshelwood, C. M., Proc. Roy. Soc. (London) A239, 154 (1957).

[13] Quee, N. J. and Thynne, J. C. J., Trans. Faraday Soc. 63, 2970 (1967).

[14] McMillan, G. R., J. Amer. Chem. Soc. 82, 2422 (1960).

[15] Leggett, C. and Thynne, J. C. J., J. Chem. Soc. (A), 1188 (1970).

[16] Ferguson, J. M. and Phillips, L., J. Chem. Soc. 87, 4416 (1965).

[17] Cox, D. L., Livermore, R. A., and Phillips, L., J. Chem. Soc. (B), 245 (1966).

[18] East R. L. and Phillips, L., J. Chem. Soc. (A), 1939 (1967).

[19] Emanuel, G., Aerospace Report No. TR-0200(4240-20)-5.

[20] Stull, D. R., Westrum, E. F., Jr., and Sinke, G. C., The Chemical Thermodynamics of Organic Compounds (John Wiley and Sons, Inc., New York, 1969); Thermochemistry of Organic and Organometallic Compounds (Academic Press, Inc., New York, 1970).

[21] Barker, J. R., Benson, S. W., and Golden, D. M., Int. J. Chem. Kinetics 9, 31 (1977).

[22] "Semenov Rule," see Laidler, K. J., Chemical Kinetics, p. 132 (McGraw-Hill, Inc., New York, 1965).

[23] Carter, W. P. L., Darnall, K. R., Lloyd, A. C., Winer, A. M., and Pitts, J. N., Jr., Chem. Phys. Letters 42, 22 (1976).

[24] Whitten, G. Z. and Hugo, H. H., SAI Report EF76-126, Draft Final Report (1976).

[25] Benson, S. W. O'Neal, H. E., Kinetics Data on Gas-Phase Unimolecular Reactions, NSRDS-NBS 21 (U. S. Government Printing Office, Washington, D.C., 1970).

Appendix

Application of Thermochemical Kinetics to the Analysis of Some Recent Data

Niki et al. (J. Phys. Chem. 82, 135 (1978)) present data involving the analysis of a complex mechanism which leads them to the conclusion that in the HO radical-initiated oxidation of the ethylene-NO system the radical $HOCH_2CH_2\dot{O}$ cleaves in preference to reacting with tropospheric O_2 concentrations. This conclusion is difficult to justify, viz:

$$HOCH_2CH_2\dot{O} \underset{-1}{\overset{1}{\rightleftarrows}} CH_2OH + CH_2O$$

$\Delta H° = -42 \pm 2 \quad -6.1 \pm 2 \quad -26.0 \qquad \Delta H^\circ_R = 9.9 \pm 3$

$S° = 76.4 \quad 59.0 \quad 53.3 \qquad \Delta S^\circ_R = 34.9$

$C_p = 21.7$

$E_1 = 12.8 + 0.71\ (9.9 \pm 3) = 19.8 \pm 2$

For k_{-1}, similar to $C_2H_5 + C_2H_4$ and $\log A_{-1} = 8.0$

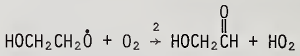
$\therefore \log A_1 = 8.0 + (34.9 - 8.35)/4.58 = 13.8$

$\log k_{1_\infty} = 13.8 - 19.8/\Theta$

RRK correction for fall-off $s = \frac{C_p - 8}{2} \stackrel{\sim}{=} 7$

$$\frac{k}{k_\infty} \stackrel{\sim}{\sim} 0.75 \text{ 1 atm, 300 K}$$

$\therefore k_1$(1 atm, 300 K) = 0.2 s^{-1}, within a factor of 50.



$$HOCH_2CH_2\dot{O} + O_2 \xrightarrow{2} HOCH_2\overset{\overset{O}{\|}}{C}H + HO_2$$

$\Delta H° = -42 \quad 0 \quad -75 \quad 5 \qquad \Delta H^\circ_R = -28$

$\log A_2 = 8.3$

Three methods for estimating E_2:

(a) $E_{2_a} = 4.0$

(b) $E_{2_b} = 10.5 + 0.25(\Delta H^\circ_R) = 3.5$

(c) $E_{2_c} = 11.5 + 0.29(\Delta H^\circ_R) = 4.0$

Three estimates for k :

(a) $k_{2_a} = 2.4 \times 10\ M^{-1}s^{-1}$

(b) $k_{2_b} = 5.8 \times 10\ M^{-1}s^{-1}$

(c) $k_{2_c} = 7.0 \times 10\ M^{-1}s^{-1}$

For a 20 percent mixture of O_2 at 700 torr, the effective first-order rate constants are:

$$\left.\begin{array}{ll} \text{(a)} & k'_{2_a} = 1.8 \times 10^3 \\ \text{(b)} & k'_{2_b} = 4.3 \times 10^3 s^{-1} \\ \text{(c)} & k'_{2_c} = 5.2 \times 10^3 s^{-1} \end{array}\right\} \text{average} = 3.8 \times 10^3 s^{-1}$$

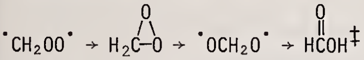
Thus, k^1 (1 atm, 300 K) $\stackrel{\sim}{\sim}$ 0.2 s^{-1} and k_2 (300 K) $\stackrel{\sim}{\sim}$ 4 x 10 s^{-1} indicate that the decomposition pathway is expected to be totally negligible, if our estimation techniques are okay. For k_1, there is an uncertainty of a factor of 50, and that for k_2 is probably a factor of 20. Thus, the ratio of k'_2/k_1 can range as shown:

$$\log\left(\frac{k_2'}{k_1}\right) = 4.3 \pm 3$$

Another interesting question is raised by the work of Herron and Huie (J. Amer. Chem. Soc. 99, 5430 (1977)). They found from a study of ozone-alkene reactions that they could explain their data best by invoking the production of vibrationally excited formic acid which decomposes by several steps, the principal one of which is

$$HCOOH^{+} \rightarrow CO + H_2O$$

If the pathway for creating of HCOOH involves the rearrangement of the intermediate CH_2OO via



$$^{\bullet}CH_2OO^{\bullet} \rightarrow H_2\overset{O}{\overset{/\ \backslash}{C-O}} \rightarrow {}^{\bullet}OCH_2O^{\bullet} \rightarrow H\overset{O}{\overset{\|}{C}}OH^{\ddagger}$$

we can calculate that the internal energy in formic acid must be ca. 150 kcal mol^{-1}. [$\cdot CH_2OO\cdot$] is the least stable of the above species ($\Delta H_f \sim 48$ kcal mol^{-1} calculated from BDE(H-$CH_2OO\cdot$) = 93 kcal mol^{-1}. Since the ring closing this species undergoes has about 10 kcal mol^{-1} activation energy, the excitation relative to HCOOH ($\Delta H_f = -90.5$ kcal mol^{-1}) is $\sim$ 150 kcal mol^{-1}].

It is possible to use quantum RRK theory to estimate the rate constant for all pathways providing that we can write the Arrhenius parameters:

$$k \sim A\ \frac{n!\ (n-m+s-1)!}{(n-m)!\ (n+s-1)!}$$

$n = E/h\nu$; $m = E_{act}/h\nu$; s = number of oscillators for HCOOH; $s = 9$; and ν (geometric mean) = 1345 cm^{-1}.

These calculations favor the production of OH and HCO radicals, but all the rate constants are so fast that this simple calculation may not be able to discriminate properly between the first and last reaction above. However, similar calculations for larger species do not have this difficulty. Furthermore, in the case of larger species deactivation by collision must be taken into account.

$n \cong \frac{150}{h\nu} \sim 40$	ΔH/kcal mol^{-1}	E_a/kcal mol^{-1}	log A/s^{-1}	log[k/s^{-1}]
$HCOOH \rightarrow H_2 + CO_2$	- 3.6	> 50	13	< 11.7
$\rightarrow H_2O + CO$	6.3	> 30	12	< 10.3
$\rightarrow H\overset{O}{\overset{\|}{C}}O + H$	106.6	107	14	10.3
$\rightarrow H + \overset{O}{\overset{\|}{C}}OH$	92.6	93	14	11.1
$\rightarrow H\overset{O}{\overset{\|}{C}} + OH$	108.9	109	16	12.3

Summary of Session

Parkes opened the discussion by re-iterating Golden's contention that there is no use trying to understand the reactions of one radical in a class in isolation from the other members of that class.

Batt followed with extensive comments on his work on alkoxy radical reactions (see contributed comments). In response to a question by Benson as to whether the production of hot radicals by photolysis could explain the various divergent results, Batt replied that his experiments were carried out in an atmosphere of CF_4 using 366 nm radiation for the photolysis, so that any excess energy in the radicals should be quenced rapidly. Cox pointed out that they had done some photolysis experiments using methyl nitrate at low concentration ($\sim$ 10 ppm) and get similar results to those of Batt and those of Heicklen, both carried out at higher concentrations. This suggests that hot radical production in the photolysis is not the reason for the discrepancy.

Ravishankara stated that when methyl nitrate is photolyzed in the banded region, the excess energy is predicted to go to NO, whereas in the continuum, CH_3O comes off with excess energy and NO is in the ground state.

In discussion on the rate constant for the reaction $CH_3O + O_2 \rightarrow CH_2O + HO_2$, it was apparent that not only was the value not completely agreed upon, even the extent of the discrepancy was subject to some controversy. Much of this appeared to be due to different conceptions of what is reasonable agreement. Cox felt that, compared to other reactions of this type, it is known rather badly. There is a discrepancy of at least a factor of three in the room temperature value. Batt is reporting $10^{9.5}$ l $mol^{-1}s^{-1}$ for the A factor, while Golden spoke of $10^{8.5}$, which appeared to agree with the other data. Batt pointed out that, due to the pressure dependence of $CH_3O + NO$, Heicklen's value at room temperature could be high, bringing the A factors into better agreement.

Tsang pointed out that, for a given class of reactions, the pre-exponential factor for decomposition is a constant, which is a valid base point for comparison.

The discussion of alkyl peroxy radicals was initiated by Benson (see contributed discussion) who proposed a complete new mechanism for their self reaction. Briefly, for alkyl peroxy radicals with an α-hydrogen, the reaction proceeds through a radical disproportionation to produce a carbene peroxide radical and a hydroperoxide: $2RCH_2O_2 \rightarrow RCH_2O_2H + RCHOO$. Heicklen asked how peroxides (ROOR), which he has observed in these systems, are formed. Huie asked if secondary ozonides had been observed in any of these systems. Benson replied that the reaction of an aldehyde and the carbene peroxy radical to form a secondary ozonide is slow, so it might not compete. Huie questioned this, pointing out that work from both his laboratory and Niki's showed secondary ozonide formation at low aldehyde concentrations.

The focus of the discussion was shifted to HO_2, as the simplest peroxy radical. Golden, noted that two unpublished papers suggest that its heat of formation is 5 kcal/mol lower than presently accepted.

Calvert brought up the question of hydration with reference to HO_2 reactions. Recent work on the recombination of HO_2 suggested that HO_2 was hydrated. Calvert asked if other peroxy radicals could be hydrated, or even if other classes of radicals, like alkoxy and hydroxyl, could also be hydrated.

Cox (see contributed comments) discussed his work on HO_2 recombination, which suggests the involvement of an H_2O_4 intermediate. His results are consistent with hydration of HO_2.

Tsang asked how much peroxy recombination reactions affected photochemical smog. Apparently, they are not important since as Calvert pointed out, in an urban environment, NO was always being pumped in. The importance of these reactions in the clean troposphere was noted by Warneck.

Tsang discussed the discrepancy in alkyl radical studies (see contributed remarks). In addition, he emphasized that the systematic approach to radical chemistry outlined by Golden is the only way to solve these problems.

Basco presented results on ethyl radical recombination by flash photolysis, which is in agreement with the value reported by Parkes. Also, rate constants measured for the methyl peroxy and ethyl peroxy radicals agree with the values of Parkes. Calvert noted that this rate constants also agreed with those of Parkes and Hochanadel, but the extinction coefficients appear to differ, which suggest the agreement in rate constants may ben fortuitious.

Basco and Parkes both stated that they have obtained a spectrum for the acetyl radical, which should allow them to carry out kinetic measurements.

In closing, Tsang asked if spectroscopic techniques might be useful in studying the properties of large organic radicals. It was agreed that uv spectroscopy would not separate these species, but infrared spectroscopy looked promising.

Comments

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Our work on the decomposition of alkyl nitrites (RONO) has resulted in the determination of values for k_2 and k_6 (tables 1 and 2 respectively):

$$\mathrm{RONO} \longrightarrow \mathrm{RO} + \mathrm{NO} \qquad (1)$$

$$\mathrm{RO} + \mathrm{NO} \longrightarrow \mathrm{RONO} \qquad (2)$$

$$\mathrm{RO} \longrightarrow \mathrm{Products} \qquad (3)$$

$$\mathrm{RO} + O_2 \longrightarrow \mathrm{RO}_{-H} + HO_2 \qquad (4)$$

$$\mathrm{RONO} \longrightarrow \mathrm{RO}_{-H} + \mathrm{HNO} \qquad (5)$$

$$\mathrm{RO} + \mathrm{NO} \longrightarrow \mathrm{RO}_{-H} + \mathrm{HNO} \qquad (6)$$

These studies show that reaction (6) accounts for the production of nitroxyl (HNO) rather than reaction (5).

Table 1. Rate constants for the reaction $\mathrm{RO} + \mathrm{NO} \rightarrow \mathrm{RONO}$ (2).

R	log k_2 (M^{-1} s^{-1})
Me	10.1 ± 0.6
Et	10.3 ± 0.4
i - Pr	10.5 ± 0.4
s - Bu	10.4 ± 0.4
t - Bu	10.5 ± 0.2

Table 2. Rate constants for the reaction $\mathrm{RO} + \mathrm{NO} \rightarrow \mathrm{RO}_{-H} + \mathrm{HNO}$ (6).

R	log k_6 (M^{-1} s^{-1})
Me	9.3 ± 0.6
Et	9.8 ± 0.4
i - Pr	9.8 ± 0.4
s - Bu	9.8 ± 0.4

Table 3. Arrhenius parameter for reaction (3).

Reaction	log A (s^{-1}) ± 0.5	E(kcal mol^{-1}) ± 1
t-AmO → M_2K^a + Et	14.8	13.8
s-BuO → ACH^b + Et	14.9	15.3
t-BuO → M_2K^a + Me	15.5	17.0
i-Pro → ACH^b + Et	14.6	17.2
EtO → CH_2O + Me	15.0	19.8
MeO → CH_2O + H	14.2	27.5

[a] M_2K = acetone.
[b] ACH = acetaldehyde.

Values of k_3 have been obtained by allowing reactions (2) and (3) to compete (table 3) except for R = Me. Here the value of k_3 has been obtained via a thermochemical kinetic argument. These values may be contrasted with Golden's estimated values. Figure 1 shows the first, proper and unequivocal evidence for the pressure dependence of k_3(t-BuO). (This means that table represents limiting values). Table 4 indicates the variation of k_3 at 160 °C as a function of pressure and shows that k_3 is within a factor of 2 of its limiting value at a pressure of 1 atmosphere of carbon tetrafluoride. Suitable

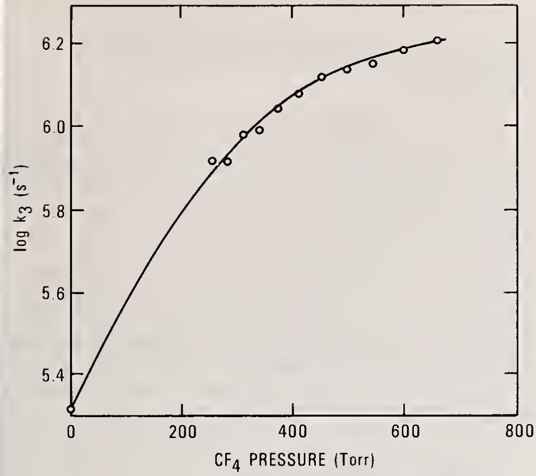

Fig. 1. Pressure dependence of k_3 (130 °C).

Table 4. Arrhenius parameters for k_3(t-BuO) as a function of CF_4 pressure.

log A_3 (s^{-1})	E_3 (kcal mol^{-1})	log k_3 (s^{-1})	
11.45	11.4	5.7	no CF_4
14.7	15.5	6.8	1 atm CH_4
15.5	17.0	7.0	P → ∞

conclusions may be drawn for smaller and larger alkoxyl radicals!

Using essentially Group Additivity Rules, we have calculated values of ΔH_3^0 for alkoxyl radicals that appeared in Niki's schemes. We used figure 2 to determined values of E_3 (table 5). By a consideration of the reverse step we calculate that A_3 for these radicals is ∿ 10^{14} s^{-1}. Golden came to a similar conclusion.

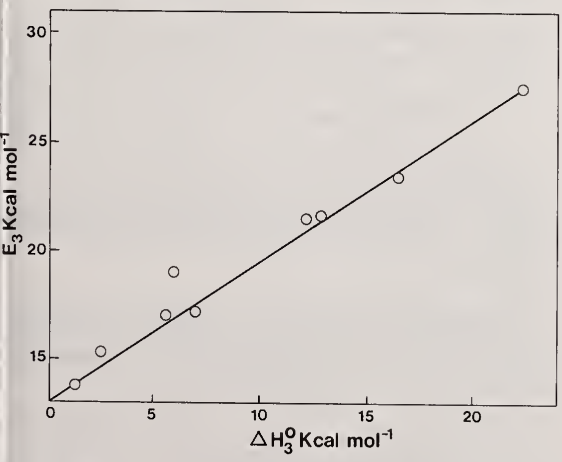

Fig. 2. E_3 values determined from table 5.

Table 5. Thermochemistry for some alkoxyl radicals.

			E_3	ΔH_3^0
			(kcal mol^{-1})	
OH				
CH_2CH_2O → CH_2OH + CH_2O				
- 39.9	-4	-27.7	18	8.2
OH CH_3				
CH_3CH CHO → CH_3CH OH + CH_3CHO				
- 57.7	-13.3	-39.7	16	4.7
OH				
CH_2O → CH_2O + HO				
- 31.8	-27.7	9.4	28.5	23.5
OH				
$CH_2O + O_2$ → HCOOH + HO_2				
- 31.8	-90.5	5.0	?	-53.7

Our values for k_2 have allowed us to determined values for k_2' (table 6):

$$RO + NO_2 \longrightarrow RONO \qquad (2')$$

We allowed reactions (2') and (4) to compete in order to determine a value for k_4 where R = Me.

Table 6. Rate constants for the reaction $RO + NO_2 \rightarrow RONO_2$ (2').

R	log $k_{2'}$ (M^{-1} s^{-1})
Me	9.8 ± 0.4
Et	9.9 ± 0.4
t-Bu	10.2 ± 0.4

By using dimethyl peroxide as a thermal source and methyl nitrite as a photochemical source of methoxyl radicals, we were able to cover a temperature range from 200 °C to (Scottish) room temperature. All methoxyl radical sources now give essentially the same result that $k_4 = 10^{9.5} \cdot 10^{-5}/\theta$ $M^{-1}s^{-1}$. It is too premature to qualify these results with error limits. This result may also be contrasted to that of Golden's. One other result from this study is the ratio $k_{6'}/k_{2'} \leq 0.1$:

$$MeO + NO_2 \longrightarrow CH_2O + HONO \qquad (6')$$

We conclude that for the alkoxyl radicals that occur in Niki's scheme, decomposition will compete with difficulty if at all with their reaction with oxygen at room temperature. In the series R = Me, Et, i-Pr, and t-Bu where we consider the two possible competing reactions of decomposition and reaction with oxygen at room temperatures:

(a) MeO reacts exclusively with oxygen

(b) t-BuO decomposes exclusively

(c) EtO and i-Pro react via both paths.

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Dr. Golden has demonstrated the important role that the thermochemistry unstable organic intermediate can play in providing a basis for the estimation of the rates of a variety of reactions of importance in air pollution. It is necessary to point out that for proper application under ambient conditions highly accurate enthalpies are necessary. A change of 1.4 kcals in activation energy is equivalent to a factor of 10 in rate constant. In this respect some of our recent results are especially disturbing (W. Tsang, Int'l. Journal of Chemical Kinetics, 10, 821 (1978)). These investigations demonstrated the concordance of all existing results on the symmetrical decomposition and combination of the alkanes: n-butane $\rightleftarrows$ 2 ethyl, 2,3-dimethylbutane $\rightleftarrows$ 2 isopropyl and hexamethylethane $\rightleftarrows$ 2 t-butyl, over a temperature range of 350-1200 K. Unfortunately, this very satisfactory agreement between four completely disparate type of experiments (comparative rate single pulse shock tube, radical buffer, very low pressure pyrolysis and modulation spectroscopy) also leads to the conclusion that the commonly accepted heats of formation of ethyl, isopropyl and t-butyl radical are ~10, 10 and 20 kJ higher than currently accepted numbers from metathesis reactions. The implication of these results is that if there are serious questions for such simple radical species, then, what degree of confidence can one have for more complex systems? Thus the utilization of estimation schemes may be badly flawed by the uncertainty in the data base.

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Although bimolecular reactions of the two $RO_2^\cdot$ radicals do not seem to be of importance in the modeling of the tropospheric photochemistry, their self-reactions provide an important clue about an intermediate which is assuming more and more importance, namely the carbene dioxide $R'R''\overline{COO}$ more commonly referred to as the Criegee zwitterion.

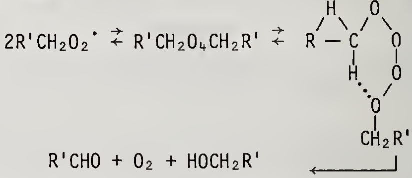
During the past two years, under Army sponsorship, we have been reexploring in our laboratories at USC the reactions of interest in ignition and combustion. In these systems the self-reactions of $RO_2^\cdot$ radicals assumes great importance. It has been known for some time that when R represents a tertiary carbon grouping such as Me_3C or F_3C, these self-reactions follow the path:

$$2RO_2 \rightarrow 2RO + O_2$$

this overall reaction proceeds through the formation of a weakly bonded tetraoxide: ($\Delta H_r \sim 9$ kcal):

$$2RO_2 \rightleftarrows ROOOOR + 9 \text{ kcal}$$

R_2O_4 is stable only at T < -70 °C but at least two groups of workers have studied the reversible equilibrium in solution below 200 K and made measurements of ΔH and ΔS. For RO_2 radicals where R does not contain a tertiary C atom but has instead α-H atoms such as $R'CH_2OO^\cdot$ or $R'R''CHOO^\cdot$, the equilibrium has not been observed but only a very rapid reaction leading to termination. The major products observed for such terminations are the conjugate alcohol-ketone (or aldehyde) pair. G. Russell some time ago proposed the following mechanism for it:



This is a 1,5 H transfer reaction which has never been observed in saturated molecules but only in molecules containing at least one multiple (pi) bond. There are many objections to it and in previous publications I have discussed some of them. Its longevity may be attributed chiefly to its apparent ability to predict the major termination products.

In our recent reexamination of these and related ozone systems, my colleague Dr. P. Nangia and I have come to the conclusion that this reaction proceeds instead through an atypical radical disproportionation to produce the Criegee zwitterion and a hydroperoxide:

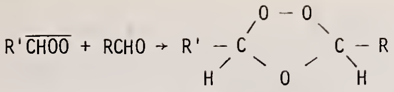
$$2R'CH_2O_2^\cdot \xrightarrow{2} R'CH_2O_2H + R'\overline{CHOO}$$

We estimate that $\Delta H_2 \approx -26$ kcal/mol with an activation energy of about 1 to 2 kcal/mol. This estimate is in excellent agreement with the ab initio calculations recently made by Goddard et al. on the stability of the zwitterion. The reaction

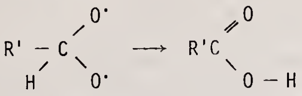
$$R'\overline{CHOO} \rightarrow RCHO + O(^3P)$$

is endothermic by only 6 to 8 kcal but must have an appreciable barrier of perhaps 15 kcal in excess of this because it is a spin forbidden process. Thus the zwitterion may have a reasonable life time at ambient temperatures in excess of 1 second.

The zwitterion is expected to react relatively rapidly with aldehyde to form secondary ozonides and we estimate the mechanism to be a concerted one with a low activation energy.



This ozonide will slowly decompose into an aldehyde R'CHO or RCHO and the isomeric, biradical $R'CHO_2$, which can rapidly and exothermically isomerize to the carboxylic acid.



It is our feeling that this is the mechanism for formic acid production which has been observed in both smog chamber experiments as well as in the ambient atmosphere during smog periods. There is no kinetically acceptable way in which the precursor HCO radicals which have been supposed to be the source of formic acid in the ambient atmosphere can do anything but produce peroxyformic acid and that only slowly relative to $HO_2 + CO$ production. HCO_3H on decomposition will not produce HCOOH.

We also estimate that $R\overline{CHOO}$ can donate its weakly-bonded oxygen atom to many species such as NO, NO_2, RO, RO_2, SO_2, and possibly SO_3. It can also in principle react with O_2 to form O_3 and RCHO. However, this reaction is spin forbidden and may have an appreciable activation energy. Despite this it may play a role in O_3 production in a number of oxidation experiments which have been reported some time ago.

The only pathways suggested so far for the zwitterions in smog episodes is from the relatively slow secondary reactions of O_3 with olefins. However, it does not seem unreasonable to suppose that the exothermic reactions of α-H containing peroxy radicals with NO_2 or with NO_3 may also occur:

$$R'CH_2O_2^{\cdot} + \left\{\begin{matrix} NO_2 \\ \\ NO_3 \end{matrix}\right. \rightarrow R'\overline{CHO_2} + \left\{\begin{matrix} HONO + 14\ \text{kcal} \\ \\ HONO_2 + 41\ \text{kcal} \end{matrix}\right.$$

In the later portions of the smog reaction when NO has decreased and NO_2 and O_3 have begun to peak, such reactions may become significant. In this period of the overall reaction HO_2 reactions with $RO_2^{\cdot}$ can also produce zwitterion as well as the more familiar ROOH.

It is our intention to publish all of these considerations and their related antecedents in a forthcoming publication now in preparation.

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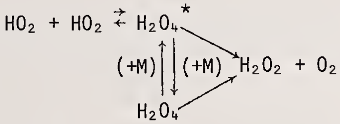
In connection with the problem of disproportion/combination of peroxy-radicals we have some experimental information which may suggest the involvement of an H_2O_4 intermediate in the reaction $HO_2 + HO_2 = H_2O_2 + O_2(1)$. The overall rate constant k_1 exhibits a substantial negative temperature dependence ($\exp(+1250/T)$) and a small pressure effect (30 percent decrease between 760 and 40 Torr). Other unpublished results from Burrows and Thrush (Cambridge, U.K.) suggests an even lower rate constant at ∿ 5 Torr. These effects may possible be understood in terms of the formation, by the combination of 2 HO_2 radicals, of an H_2O_4 molecule which can be vibrationally relaxed by energy transfer:



If formation of products $H_2O_2 + O_2$ (as opposed to redissociation to $2HO_2$) from the vibrationally relaxed H_2O_4 molecule is relatively more favored then from H_2O_4*, factors favoring population of the lower vibrational levels of H_2O_4 will tend to increase the overall rate constant.

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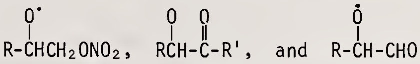
There is inadequate data concerning the effect of non-hydrocarbon substituents on the decompositions of alkoxy radicals. Substituted alkoxy radicals of many types are formed in polluted tropospheric systems, and in some cases, it is uncertain whether decomposition of reaction with O_2 predominates. As discussed in the previous section uncertainties in the decomposition rates of β-hydroxy-alkoxy radicals present serious problems in developing models for the OH-olefin-NO_x system. In addition to β-hydroxy-alkoxy radicals, our detailed propene + n-butane-NO_x-air model[1] predicts formation of species of the types



$$R\text{-}\overset{O^{\cdot}}{\overset{|}{C}}HCH_2ONO_2,\quad RC\overset{O}{\overset{|}{H}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}R',\quad \text{and}\quad R\text{-}\overset{\dot{O}}{\overset{|}{C}}H\text{-}CHO$$

and it is probable that in a more complete detailed smog model, other types of substituted alkoxy radicals would be predicted to be formed. It is commonly assumed that decompositions of these species predominates, but this requires experimental verification.

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[1] Carter, W. P. L., Lloyd, A. C., Sprung, J. L., and Pitts, J. N., Jr., Computer modeling of smog chamber data: progress in validation of a detailed mechanism for the photooxidation of propene and n-butane in photochemical smog, <u>Int. J. Chem. Kinetics</u> <u>11</u>, 45 (1979).

Recommendations

An understanding of the chemical kinetic behaviour of large organic free radicals is necessary to describe the oxidation of hydrocarbons released into the troposphere. Before we describe specific areas where we consider research is necessary there are some general points that should be made - points that arise from the particular complexity of the problem.

1. The majority of the existing chemical kinetic data on the reactions of organic free radicals have been obtained from measurements of the ratios of the rates of competing processes - very often the ratio of a propagation rate constant to a termination. It is also true that in practice such ratios or combinations of rate constants are often the controlling parameters. It would be generally useful therefore if experimentalists published clearly the actual ratios that they have measured as well as the rate constants that they have deduced from them. Further, the users of rate data, particularly modelers, should state what is needed for given situation, absolute or relative rate constants.

2. There are too many hydrocarbons and too many resultant radicals to be able to hope to study all their potential reactions individually. This means that we fully support the thesis of Golden in his talk that we should consider the behaviour of classes of radicals. We should make sure that any new results are consistent with observations from other members of the same class and examine deviations carefully. At the present time, this means that the thermodynamic properties of the key radical classes such as alkyl, alkoxy and alkyl peroxy need to be firmyl reestablished after the recent upheavals. The kinetic parameters from the different types of processes have also to be measured. At the present time we are beginning to obtain absolute rate information for the first members of the different classes. We will have to extrapolate to larger radicals that we cannot easily produce in the laboratory to estimate firstly, rate constants for processes that are identical to those undergone by smaller radicals, e.g., abstraction from a substrate hydrocarbon, and secondly, to predict rate constants for processes such as alkoxy rearrangements or cleavages that the smaller species cannot themselves undergo. The results of recent product studies show such processes are important and the only way they will be consistently and rationally modeled will be by the establishment of a sound and consistent data base for the radicals that can be studied.

3. The techniques for making careful systematic measurements for individual organic free radicals in the gas phase at temperatures of atmospheric interest are now becoming available. The infrared and ultraviolet absorption spectra of several larger alkyl and alkyl peroxy radicals have been detected and used for kinetic studies. The agreement between flash photolytic and modulation methods has been good. So too, to a large degree, has been the similarity for, for example, peroxy radical combination in the gas and liquid phases. Kinetic studies using direct detection of alkoxy radicals would make a key contribution that would help complete the stody of aliphatic radical chemistry. Oxidation chemistry can now do more than just elucidate the admittedly complex mechanisms and can produce directly measured quantitativ data.

4. These developments in detecting transients have been accompanied by advances in the methods of detecting stable products. Long path ir has been extended by using Fourier transform technique and the chromatography of peroxides is becoming more reliable. Such studies tell the paths that the radical reactions must follow. New techniques such as laser pyrolysis when they are applied to larger molecules will confirm whether these suggested paths are reasonable.

5. Classical determinations of radical thermochemistry could perhaps be supplemented usefully by structural information from the spectroscopic information that is now appearing for larger organic radicals.

6. The existing theory of chemical kinetics, particularly transition-state theory and its deriatives provides a useful tool for rationalizin the kinetic information (see 2). It is important to emphasis however the degree of accuracy in energy measurements that is needed for prediction at ambient temperatures using rate expression in the Arrhenius form.

The following specific points were raised durin the discussion:

1. Alkyl Radicals. The thermochemistry of these key initial building blocks is the subject of controversy at the present time and must be clarified before we can proceed with confidence with more complex radicals. There is no longer an dispute about the order of magnitude of the rate constants of combination, but there is uncertainty about the heat of formation and the structural details of the radicals.

2. Alkoxy Radicals. Here there is a glaring need for a direct detection technique useful for kinetic studies. The cleavage reactions appear to be relatively satisfactorily described but the rates of reaction with O_2 need measurement. This means in turn consistency between measurements against different reference reactions e.g. alkoxy + hydrocarbon rate constants. The rate parameters for the recently proposed isomerizations of the large alkoxy radicals need testing preferably directly, or if not, against an improced data base of alkoxy measurements. Recently it has been claimed that alkoxy radicals have been detected by emission - if confirmed this could produce a breakthrough.

3. Alkyl Peroxy. The key reactor here with NO has so far proved too fast for direct measurement but in the light of the changed values for HO_2 + NO needs to be checked. The rates of radical combination that are important in lightly polluted situations are in the process of being firmly established but the mechanistic explanation of the results is speculative. Further information about the different channels in the combination is needed together with better product data.

4. Acetyl and Acetyl Peroxy. The absence of discussion here on what are precursors on the route to PAN illustrates an important area of ignorance. The recent detection of acetyl radicals should allow a start in this area and permit checking of the classical works in the field.

5. Information from Solution. There is a vast body of data on low temperature radical chemistry in solution. This could form a useful basis for ideas, comparisons with gas phase work and surface processes.

Session IV

NO_x Chemistry

TROPOSPHERIC CHEMISTRY OF NITROGEN OXIDES - A SUMMARY OF THE STATUS OF CHEMICAL KINETIC DATA

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This paper is a review of the tropospheric chemistry of nitrogen oxides. The important atmospheric reactions and the photolysis of these compounds are discussed and problem areas are emphasized.

Key words: Nitrates; nitrites; nitrogen oxides; photolysis; reactions; review; tropospheric chemistry.

1. Introduction

An important role for nitrogen oxides in the chemistry of the lower atmosphere, both from the point of view of urban atmospheres (Leighton, 1961) and natural trace gas budgets, (Junge 1963, Levy 1972) has been recognised for some time now. The term 'NO_x' in air chemistry has usually been synonymous with the commonly known oxides of nitrogen, NO and NO_2, but recent fashion in terminology refers to total 'odd nitrogen' species which includes, in addition to NO and NO_2, the higher oxides of nitrogen, N_2O_3, N_2O_4, NO_3, N_2O_5 and also the oxyacids of nitrogen, HONO (nitrous) and $HONO_2$ (nitric). A significant role is also now believed to be played by peroxynitric acid, HO_2NO_2.

In any model of the chemical transformations in urban air, the chemistry of the organic derivatives of the oxyacids, alkyl nitrites, alkyl nitrates and the peroxynitrates must be considered. Especially important are the peroxyacylnitrates (PAN's) which observational data show to be one of the most important compounds in photochemical smog.

An important atmospheric nitrogen oxide, not normally included under the terminology 'NO_x', is nitrous oxide N_2O. Present knowledge does not point to a role for this oxide in the tropospheric gaseous nitrogen cycle. However, observational data suggests that there is a sizeable unidentified sink for N_2O in the troposphere. It may be appropriate, therefore, to consider any chemical kinetic data which might relate to this problem.

Finally, reduced nitrogen compounds, NH_3 and its derivatives, should be mentioned, since the problem of coupling of the NH_3 and NO_x cycles has been raised from time to time (Robinson and Robbins, 1971). NH_3 undeniably plays an important role in the aerosol and precipitation chemistry of nitrates. Relating more to the current chemical kinetic data assessment, is the problem of oxidation of NH_3 to NO (or NO_2).

2. Importance of NO_x in Atmospheric Chemistry

Nitrogen oxides and related species are important atmospheric pollutants in their own right, e.g. the toxicity of NO_2 and the corrosive nature of NO_2 and nitric acid toward many types of materials. However for the atmospheric chemist it is the interaction of NO_x with other chemical species in the atmosphere and the resulting influence on the basic trace-gas cycles and the formation of secondary pollutants, which is of interest. It is in the solution of problems arising from these interactions where chemical kinetics can play a role. These problems are primarily related, both in the natural and the polluted troposphere, to the photochemical oxidation of hydrocarbons.

It is now well-established that the atmospheric oxidation of hydrocarbons and relative substances (i.e. oxygenated and halogenated organics), proceeds by a photochemically initiated free radical chain process. The chain carrying radicals are OH, HO_2 and their organic analogues RO and RO_2. Nitric oxide, NO, is involved in this chain process through its ability to convert the relatively inactive RO_2 radicals to active RO species via the general atom transfer reaction:

$$RO_2 + NO = RO + NO_2 \quad (R = H, \text{alkyl, etc.})$$

Nitrogen dioxide, on the other hand, acts as a chain terminating species through its recombination reactions with RO and RO_2 radicals, e.g.

$$HO + NO_2 \rightarrow HONO_2$$

$$RO_2 + NO_2 \rightleftarrows RO_2NO_2.$$

In the lower atmosphere $HONO_2$ formation provides an efficient sink for both NO_2 and HO_x species. Formation of peroxynitric acid and the peroxynitrates acts as a more or less temporary sink, since the products are thermally unstable and redissociate to RO_2 and NO_2.

The other important role of NO_2 arises from its rapid photo-dissociation to give ground state atomic oxygen and nitric oxide:

$$NO_2 + h\nu(\lambda \leq 400 \text{ nm}) = O(^3P) + NO$$

followed by

$$O + O_2 + M = O_3 + M \quad .$$

This provides the source of ozone in photochemical smog and also in the natural troposphere. Also the primary source of OH radicals in the lower atmosphere, is through production of excited atomic oxygen, $O\ ^1D$, from the photolysis of O_3 in the ultra-violet region at $\lambda \leq 310$ nm:

$$O_3 + h\nu = O(^1D) + O_2 \quad \lambda < 310 \text{ nm}$$

$$O(^1D) + H_2O = 2OH$$

Thus the involvement of NO_2 in the tropospheric ozone budget, has a direct bearing on the average concentration of OH in the lower atmosphere and consequently on the atmospheric residence times of a variety of trace-gases.

A model of atmospheric NO_x chemistry is therefore necessary to (a) formulate a realistic model of photochemical smog on which to base control strategy and (b) to provide an understanding of the global tropospheric trace-gas cycles. The objective of such a model is to predict the total budget of NO_x from source to sink, and the distribution of NO_x among the various chemical species in time and in space. This distribution depends on the nature and strength of the sources, the chemical interactions within the atmosphere and the role of the various sink mechanisms.

3. Cycle of NO_x Through the Lower Atmosphere

The currently accepted picture of the cycle of gaseous-nitrogen oxides through the lower atmosphere is similar to that formulated originally by Robinson and Robbins (1971). It was based on observations and measurements of the distribution of atmospheric NO_x, chemical reaction rate data, and meterological factors. Figure 1 shows a schematic illustration of the cycle.

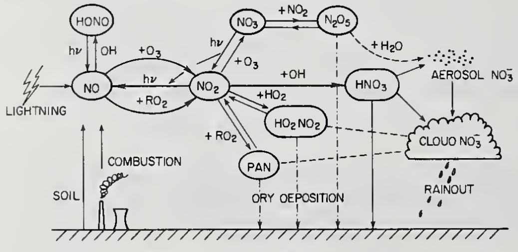

Fig. 1. Life-cycle of nitrogen oxides in the troposphere.

The main source of NO_x is believed to be emission of NO from the ground, either from man-made sources, mainly combustion, or from soil processes. An additional source of NO_x is fixed atmospheric N_2 from lightning. There is current argument about the magnitude, both relative and absolute, of these sources.

Once in the atmosphere, chemical oxidation of NO to NO_2 occurs rapidly, primarily through the reaction

$$O_3 + NO = NO_2 + O_2 .$$

In daylight NO is reformed by photolysis of NO_2, but is also oxidised by photochemically generated radicals, i.e.

$$RO_2 + NO \rightarrow RO + NO_2 .$$

Removal of NO_2 is primarily via formation of nitric acid, with alternative pathways via organic nitrates and pernitrates. Formation of peroxynitric acid and PANs is reversible but this can act as a sink if PANs are removed, for example, by absorption at the ground. Additional removal of NO_2 can occur by reaction with O_3 to give NO_3. NO_3 is rapidly photodissociated (in daylight) but also reacts with NO (to reform NO_2) or with NO_2 to give N_2O_5. The latter reaction is reversible and so NO_2, NO_3, N_2O_5 and O_3 can exist in equilibrium. N_2O_5 can also be converted to HNO_3 by heterogeneous reaction with water.

The nitric acid, N_2O_5 and organic nitrates can all be removed from the atmosphere by absorption at the ground (dry deposition) or by incorporation into the precipitation elements - aerosol particles, cloud and fog droplets, which eventually leads to rain-out.

4. Status of Chemical Kinetic Data

Accurate chemical kinetic data is clearly required for the primary chemical processes involved in the transformation of NO to nitric acid. Also of interest is data relating to all possible minor interactions which would influence the basic atmospheric NO_x cycles, or which produce unusual secondary pollutants in urban air. Due to the recent stimulus in the field of atmospheric kinetics, data for some of these processes is now rather well known. For some processes more and better data is badly needed, and these become self-evident during any detailed discussion of the data base. In the following paragraphs the status of the data base is very briefly indicated for some specific areas of NO_x chemistry mentioned above. The topics covered should not be considered exhaustive, but rather a minimum set necessary for modelling the basic NO_x cycle.

A. Photochemical data - for NO_2, NO_3, N_2O_5, HONO, $HONO_2$ and HO_2NO_2

In order to calculate photodissociation rates for a species in the atmosphere, a knowledge of the absorption cross-section σ as a function of wavelength and the quantum yield(s) of the photodissociation pathway(s), Φ_1, is required. This is then combined with suitably averaged data for the photon-flux in the atmosphere to obtain the

'J value' which is essentially a first order rate constant for photochemical removal of that species.

Reasonably reliable data are now available for σ and Φ_1 for the photodissociation of NO_2, HONO and $HONO_2$ over the important wavelength regions

$$NO_2 + h_\nu = O + NO$$
$$HONO + h_\nu = OH + NO$$
$$HONO_2 + h_\nu = OH + NO_2$$

Data on absorption cross-sections and on the various possible dissociation pathways of NO_3, N_2O_5 and HO_2NO_2 is much less satisfactory. Data for NO_3 is particularly important since recent work has indicated that photodissociation can follow two different pathways, depending on wavelength:

$$\begin{aligned} NO_3 + h_\nu &\rightarrow NO + O_2 \\ &\rightarrow NO_2 + O \end{aligned}$$

Only a limited amount of data is available on the absorption cross sections and dissociation quantum yields of the organic nitrites and nitrates.

B. Reactions of NO_x with odd-oxygen species

The reactions of NO and NO_2 with the odd oxygen species O and O_3 have long been recognized as important for aeronomy and reliable rate data is now available for the following reactions

$$O + NO(+M) = NO_2\ (+M)$$
$$O + NO_2 = NO + O_2$$
$$O + NO_2(+M) = NO_3(+M)$$
$$O_3 + NO = NO_2 + O_2$$
$$O_3 + NO_2 = NO_3 + O_2$$

Less well known is the chemistry of NO_3 and N_2O_5 and a number of investigations have sought to define the rate constants for the following processes, all of which are needed for modelling NO_x in the urban atmosphere:

$$NO_3 + NO = 2NO_2$$
$$NO_3 + NO_2 \overset{(M)}{=} N_2O_5$$

Due to the chemical complexity of these systems, there is some uncertainty in the kinetic parameters. NO_3 may also undergo H-abstraction reactions with organic molecules and some kinetic parameters for these reactions have been reported. The effective rate of the reaction of N_2O_5 with water which is probably heterogeneous, is rather uncertain at this time and could be of importance in the overall NO_x budget in the lower atmosphere. A quantitative treatment of the rate of heterogeneous removal of gaseous species on aerosol particles and cloud and fog droplets, which is acceptable to many modelers, has yet to be formulated.

C. Reaction of NO_x with odd-hydrogen species

The coupling of the NO_x and HO_x cycles is one of the most important aspects of atmospheric free-radical chemistry. The reactions of hydroxyl (HO) radicals with NO_x species has been widely studied in response to problems of aeronomy, and a reasonably good data base is available here. The important reactions are:

$$HO + NO\ (+M) = HONO\ (+M)$$
$$HO + NO_2(+M) = HONO_2(+M)$$
$$HO + HNO_3 = H_2O + NO_3$$
$$HO + HONO = H_2O + NO_2$$

Note that the M dependent reactions are in the transition region between third-order and second-order kinetics at the pressures encountered in the troposphere. If the actual measurements of the rate constants as a function of pressure for M = Air are not available, the rate constants in the transition region can be estimated from a knowledge of the third order low pressure rate constants, k_{III}, and the high pressure second-order rate constant k_∞. These two rate constants k_{III} and k_∞ therefore comprise a minimum data set for this type of reaction. The temperature dependence of these association reactions is also important since in the low pressure regime they usually exhibit a significant negative temperature coefficient. This can be important in modelling NO_x circulation in the global troposphere.

The reactions of the hydroperoxyl radical, HO_2 with NO and NO_2 are also very important. Kinetic information on HO_2 reactions is not as complete as that for HO reactions but application of new free radical detection techniques to kinetic studies of HO_2 has led to a significant improvement of the reliability of the data base. Recently new data has been reported for

$$HO_2 + NO \rightarrow HO + NO_2$$
$$HO_2 + NO_2(+M) \rightleftarrows HO_2NO_2 + M$$

which allows a more quantitative appraisal of the role of these reactions. These studies have shown in particular that the reaction of HO_2 (and probably other peroxy radicals) with NO are much more rapid than had hitherto been believed, and they then assumed much greater significance in atmospheric free radical chemistry. The formation of peroxynitric acid is reversible and associated data for its thermal decomposition which has recently been obtained allows the role of this 'new' species to be assessed with some confidence.

D. Reactions of NO_x with organic radicals

The possible reactions of NO and NO_2 with organic radicals are numerous. However reactions with organic peroxyradicals appear to be the most significant for atmospheric chemistry, and these are exemplified by the reactions of NO and NO_2 with peroxyacetyl radicals:

$$CH_3C(O)OO + NO \rightarrow CH_3 + CO_2 + NO_2$$
$$CH_3C(O)OO + NO_2 \rightleftarrows CH_3COO_2NO_2(PAN)$$

These reactions govern the formation of peroxyacetylnitrate in urban air and show clearly the competition between the chain carrying reaction involving NO and the chain terminating step involving NO_2. Also since PAN can decompose back to CH_3COO_2 and NO_2, it only acts as a temporary sink for radicals. Reasonably reliable kinetic data for the thermal decomposition of PAN are now available and the relative rates of reaction of the peroxyacetyl radicals with NO and NO_2 are moderately well-defined.

There is little or no kinetic information concerning the analogous reactions of other organic peroxy radicals with NO and NO_2, or the thermal stability of the peroxynitrate species produced in the reaction with NO_2. Several of the peroxynitrates have been identified in the laboratory by infra-red spectroscopy and they may therefore play a significant role in urban smog formation. Evaluation of the rate parameters for the analogous reactions of other organic peroxy radicals with NO and NO_2 is necessary to define the chemistry of the breakdown of individual organic species during atmospheric photooxidation.

References

Junge, C. E., Air Chemistry and Radioactivity (Academic Press, New York, 1963).

Leighton, P. A., Photochemistry of Air Pollution (Academic Press, New York, 1961).

Levy, H. II., Photochemistry of the lower troposphere, Planet. Space Sci. 20, 919-935, (1972).

Robinson, E. and Robbins, R. C., Sources, abundance and fate of Gaseous Atmospheric Pollutants-Supplement, American Petroleum Institute Publication No. 4015, April (1971).

Summary of Session

This session was concerned with the various simple reactions of NO, NO_2, NO_3 and N_2O_5, few of which are well understood. The conversion of NO_2 into N_2O_5 and its subsequent reaction with water to give nitric acid is of great importance. Levine noted that if the N_2O_5-H_2O rate constant were fast enough it would play a significant role in NO_2 removal. O'Brien discussed smog chamber data in which the fate of NO_3 depended on the substate present, suggesting aerosols may be involved in some cases in HNO_3 formation. Stedman noted that NO_2 disappearance rates at night corresponded to the NO_2-O_3 rate, but that the products were not able to regenerate the reactants, which suggested that HNO_3 might be a product. Benson suggested an additional possible product, pernitric acid, arising from the reaction of OH with NO_3.

The photolysis of NO_2 is still a subject of controversy since new data (reported by Whitten) suggest that the quantum yield is less that one around 380 to < 400 nm. It was also mentioned by Demerjian that the same workers measured different absorption coefficients than the NBS workers although the latter values are still to be preferred.

Basco commented on his earlier work on the flash photolysis of NO_2 in which the O_2 product, arising from the secondary O + NO_2 reaction, was monitored. The O_2 should be observed up to the 12th vibrational level corresponding to 46 kcal excess energy. In fact it was found up to the 16th level which is 12 kcal higher with radiation greater than 400 nm. Whether the photoexcited NO_2 implied by these results plays a role in atmospheric chemistry was not discussed.

The new high value of Howard for the rate constant of HO_2 + NO has been used by most modelers for the RO_2 + NO reaction. Golden pointe out that the HO_2 reaction has a negative temperature coefficient which implies a bound state. Th transfer of rate constants may thus be invalid. Heicklen raised the possible role of pernitrous acid in this reaction. Hendry presented data on the pyrolysis of nitrates which support the high values for RO_2 + NO. Parkes also noted that in flash photolysis systems the t-butyl peroxy and methyl peroxy radicals could never be seen in the presence of NO implying a very high rate constant ($\sim 10^{-11}$ cm^3 $molec^{-1}s^{-1}$). Another unresolved question was whether adducts are formed i.e., $RO_2 + NO \rightarrow ROONO$ which can rearrange and cleave. Carter presented smog-chamber results which suggest that the formation of alkyl nitrates is ar important reaction. Heicklen also suggested the possibility of a reaction $RO_2 + NO \rightarrow HONO$ + aldehyde involving a six member cyclic transition state.

The reactions of RO with NO and NO_2 were also considered. The reaction of RO with NO leading to the nitrate is not too important in the atmosphere (but could be in the laboratory) since the nitrate is rapidly photolyzed. However, as Heicklen noted, part of the reaction leads to HNO + aldehyde. It seems to be agreed that the principal fate of RO in the atmosphere is either isomerization, scission, or reaction with O_2 - as discussed in the Free Radical session.

The more general problems of modeling were discussed by Dodge in terms of current problems in NO_x chemistry. Questions as to whether the correc photolysis rates are used and how well the models should be expected to fit the observations were brought up but not resolved. Carter discussed radical initiation in smog chambers, emphasizing that it probably arises from contamination of the chamber. The real problem lies in its unpredictable nature. Solution of this problem must be given the highest priority.

Comments

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We have been analyzing several of the UCR smog chamber experiments for their nitrogen balance. The details of this analysis will be published in the near future and only the results will be discussed here.

For the case of a hydrocarbon which reacts only with hydroxyl radical and negligibly with other free radicals or ozone we may derive an equation for the NO_x balance based on the following mechanism:

1 $HC + OH \longrightarrow$ loss 1

2 $NO_2 + OH \xrightarrow{M} HNO_3$ 2

3 $NO_2 + O_3 \longrightarrow NO_3 + O_2$ 3

4 $NO_3 + NO_2 \longrightarrow N_2O_5$ 4

5 $N_2O_5 + H_2O \xrightarrow{\text{surface}} 2HNO_3$ 5

6 $NO_3 + NO \longrightarrow 2NO_2$ 6

Under the assumption that the OH concentration is given by

$$[OH] = \frac{-1}{k_1[HC]} \cdot \frac{d[HC]}{dt}$$

we may obtain the equation

$$[NO_x]_{initial} - [NO_x] - PAN] =$$

$$\frac{k_2}{k_1} \int \frac{[NO_2]}{[HC]} d[HC] + k_3 \int [NO_2][O_3]dt \qquad (1)$$

This equation assumes all NO_3 forms nitric acid, and that the total NO_x loss (except for PNA) is accounted for in HNO_3.

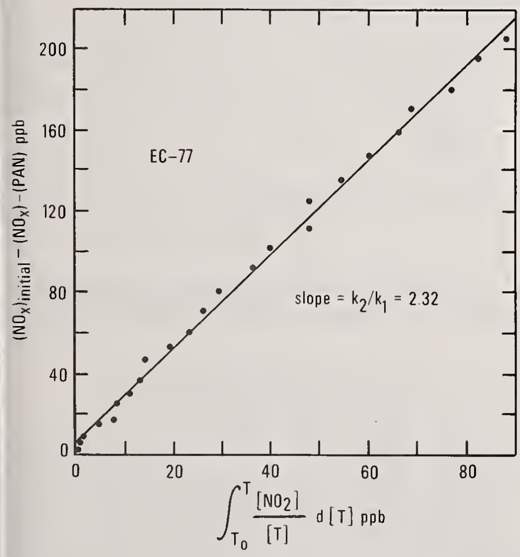

Fig. 1. Correlation of NO_x loss with reaction 2 for UCR run EC-77. T = toluene.

Figure 1 shows a plot of the left hand side of eq. (1) vs.:

$$\int_{T_0}^{T} \frac{[NO_2]}{[T]} d[T]$$

for UCR run EC-77 which is a toluene (T) run which made no ozone. The slope of this line, (k_2/k_1), is equal to 2.3 which is in good agreement with literature values for k_2 and k_1. Figure 2 shows a similar plot for EC-80, a toluene run which made ozone. The initial slop agrees with the previous run and the upward curvature coincides with the appearance of ozone. The deviation between the experimental data and the extrapolated straight line is correlated with the second term on the right hand side of eq. (1) in figure 3 which is a plot of

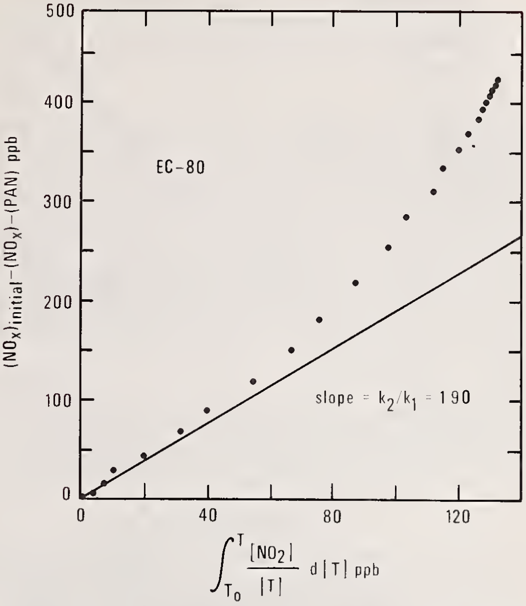

Fig. 2. Correlation of NO_x loss with reaction 2 for UCR run EC-80. T = toluene.

$$[NO_x]_i - [NO_x] - [PAN] - 1.9 \int \frac{[NO_2]}{[T]} d[T]$$

$$\text{vs.} \int [O_3][NO_2]\,dt \;.$$

An excellent linear relationship is obtained. If all NO_3 formed HNO_3 via the above mechanism we would expect the slope of figure 3 to be 2 k_3 or .100 ppm^{-1} min^{-1}. The actual slope is .032 ppm^{-1} min^{-1}.

Figure 4 gives a plot similar to figures 1 and 2 for EC-83, a run at zero relative humidity which made 0.42 ppm O_3 with 2 ppm initial NO_x. Note that there is an insignificant derivation from linearity indicating little conversion of NO_3 to HNO_3 in the absence of H_2O.

Table 1 gives a summary of 10 UCR toluene runs. The values of k_2/k_1 obtained agree well with literature values and have a standard deviation of 10 percent. The values obtained for the slope of the curves similar to figure 3 show greater scatter and indicate that about 1/4 to 1/3 of the NO_3 formed is converted to HNO_3. However, the kinetic analysis is not altogether clear as to the meaning of the linearity and value of the slope in these plots.

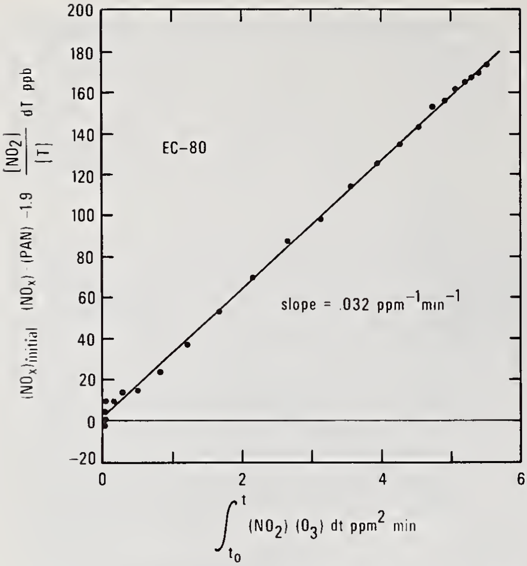

Fig. 3. Correlation of upward curvature from figure 2 with reaction 3. t = time.

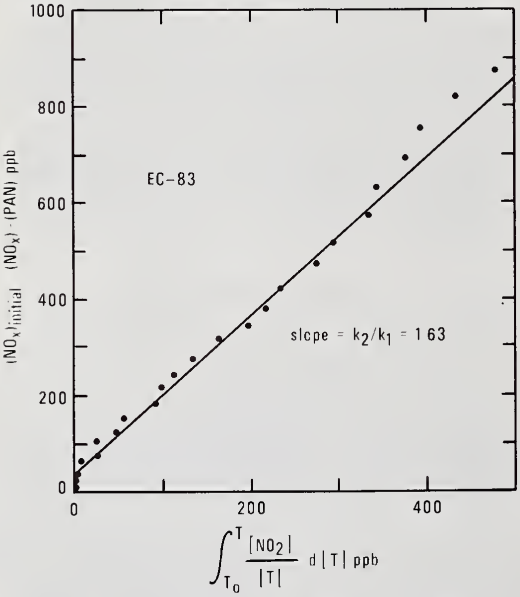

Fig. 4. Correlation of NO_x loss with reaction 2 for UCR run EC-83 a dry reaction. T = toluene.

Figure 5 shows a plot similar to figure 1 for a UCR butane run, EC-41. Although considerable ozone was formed, no upward curvature is observed in this or any other butane run, indicating no conversion of NO_3 to HNO_3. The slope of the plots for 10 UCR butane runs are summarized in table 2 and give a value of k_2/k_1 of 3.7 ± 9 percent (rel. std. deviation). This value is in good agreement with some literature values.

Table 1. Summary of experimental and computed data for UCR toluene reactions.

Rxn No. EC-	Initial NO/NO_2 ratio	Initial NO_x ppb	Initial toluene ppb	Maximum O_3 ppb	Maximum PAN ppb	Relative humidity %	k_2/k_1 ratio	Slope of figure 3 plots $ppm^{-1}min^{-1}$
77	8.9	574	276	12	2	40	2.3	
78	2.2	100	230	92	13	40	2.6	0.026
79	4.2	100	980	96	15	40	2.7	0.147
80	4.2	500	1000	27	47	40	1.9	0.032
81	4.3	500	2000	313	61	40	2.5	0.041
82	2.0	1000	1900	365	59	40	1.9	0.022
83	2.1	2000	5600	420	65	0	1.6	0.004
84	4.9	470	970	230	43	70	2.1	0.019
85	4.7	520	1900	290	50	48	2.2	0.046
86	5.1	490	1100	300	37	35	2.0	0.022
						Average	2.3	0.029
						Relative standard deviation	10%	40%

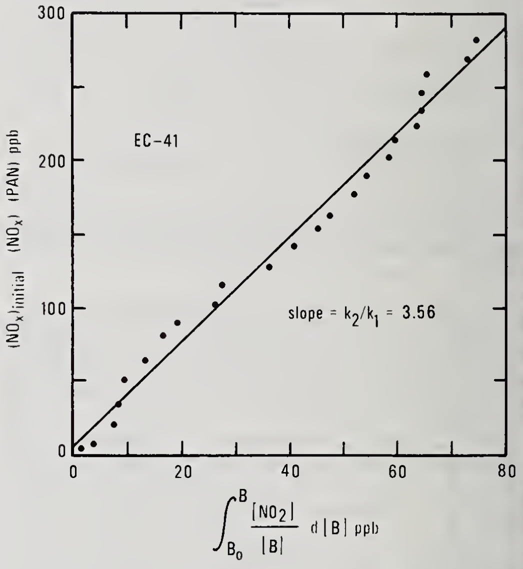

Fig. 5. Correlation of NO_x loss with reaction 2 for UCR run EC-41. B = butane.

Table 2. Summary of experimental and computed data for UCR butane reactions.

Rxn No. EC-	Initial NO_x ppb	Initial butane ppb	Maximum O_3 ppb	k_2/k_1 ratio
39	0.6	2.2	0.073	3.8
41	0.593	4.03	0.237	3.56
42	0.6	0.385	0.006	3.73
43	0.137	0.38	0.12	3.6
44	1.26	3.92	0.015	4.4
45	0.614	1.94	0.138	3.6
46	0.587	4.00	0.252	4.04
47	0.599	3.9	0.255	4.17
48	0.594	1.94	0.163	3.77
49	0.611	4.12	0.286	3.8
			Average	3.7
			Relative standard deviation	9%

The very interesting tentative conclusion we reach is that NO_3 in the presence of water is converted to HNO_3 in the toluene runs but not in the butane runs. The explanation may lie in aerosol formation which occurs with toluene but not with butane.

For runs which form no ozone, or before ozone buildup occurs in any run, we are able to use an analysis similar to the one in figure 1 to account for all NO_x loss by the reaction $OH + NO_2 + M \rightarrow HNO_3$. The slope of the line in this plot yields a rate constant ratio which shows only a 10 percent standard deviation in the two groups of ten experiments (toluene and butane) which we have analyzed. This rate constant ratio may then be used for computer modelling of the series of reactions with the confidence that the predicted HC and NO_x loss rates will agree within ± 10 percent (std. dev.) of the experimental values, provided the correct OH concentration profile is obtained. For the case of butane the relative HC and NO_x loss rates are not effected by O_3 or NO_3 formation and are controlled only by OH.

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It has been frequently observed in our data and in others from rural air that NO_2 decays at night and does not come back in the morning. The decay rate is roughly equal to the rate of $NO_2 + NO_3$. The product of the reaction is not observed so it is not stopping at NO_3, presumably going on to N_2O_5. When the sun comes up in the morning the NO_2 thus lost does not reappear so the sink cannot be photolyzed, thus it has to be going further to some product such as nitric acid.

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Alkyl nitrate yields observed in alkane-NO_x-air smog chamber runs suggest that the following reactions

$$RO_2 + NO \xrightarrow{M} RONO_2$$

are important sources of alkyl nitrates when the alkyl group, R, is sufficiently large [1]. No other mechanism for alkyl nitrate formation can explain the observed near-independence of the $RONO_2$ yield on initial NO_x levels, or the fact that the possibility of H shift isomerizations of some alkoxy radicals do not result in significantly reduced yields of the corresponding alkyl nitrate. We consider it unlikely that the high yields of alkyl nitrates observed in the smog chamber runs [1] could be due to heterogeneous reactions of NO_x with organic products, since the measured alkyl nitrate levels do not significantly decline following NO_x consumption.

If these reactions are as significant as our smog chamber results suggest, then they would have the effect of making larger alkanes act as radical inhibitors in photochemical smog systems, which has significant implications concerning their reactivity and effects on smog formation rates.

Unfortunately, the only evidence for these reactions comes from smog chamber data, and as far as I know, our model is the only current one which includes them. Direct laboratory studies, obtaining unambiguous mechanistic and kinetic data concerning the reactions of RO_2 radicals with NO, are clearly required. It is particularly important that a wide variety of RO_2 radicals be studied, in order to clearly establish substituent and size effects.

Reference

[1] Darnall, K. R., Carter, W. P. L., Winer, A. C., and Pitts, J. N., Jr., J. Phys. Chem. 80, 1948 (1976).

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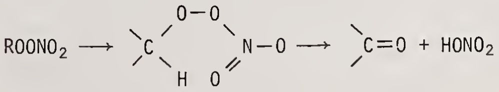
Peroxyacly nitrates (PANs) play an important part in influencing the OH radical concentration in the atmosphere. Under conditions where PANs increase in concentration they act as radical sources. This effect is associated with the facile equilibrium

$$ROONO_2 \rightleftarrows ROO\cdot + NO_2$$

where $R = CH_3C(O)O_2$, $CH_3CH_2C(O)O_2$, etc.

Peroxyalkyl nitrates are a second type of peroxynitrate (where $R = CH_3$, CH_3CH_2, etc.) that could also be important in affecting the OH concentration. Richard Kenley and I are currently studying the decomposition of these types of compounds and, in the case of peroxy-t-butyl nitrate, find evidence for a 20-23 kcal mol O-N bond strength, which is considerably weaker than found for peroxyacetyl nitrate (27 kcal/mol).

When reactions 1 and -1 for peroxyalkyl nitrates are included in atmospheric models for propene, n-butane, and toluene, we find they have no significant effect on the overall chemistry if it is assumed that $\log A_1 = 16.5\ s^{-1}$, $E_1 = 23$ kcal/mol, $\log A_{-1} = 9.0\ s^{-1}$, and $E_{-1} = 0$ kcal/mol. However other reactions of peroxyalkyl nitrates beside reactions 1 and -1 may be important. For example if the reaction



competed with reaction -1 then the formation of peroxyalkyl nitrates could be important radical sinks. Additional information is needed on the chemistry of peroxyalkyl nitrates to develop reliable atmospheric chemistry models.

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Research Triangle Park, North Carolina 27711

We are encountering difficulties in our modeling efforts that appear to be related to NO_x chemistry. In our modeling of smog chemaber data for the propylene-NO_x system, we are able to obtain respectable fits for all species except O_3. As an example, in one particular run conducted in the UCR evacuable chamber, we achieved excellent fits for NO, NO_2, PAN, and propylene. The predicted concentrations of formaldehyde and acetaldehyde were a little low in this run, but well within the experimental uncertainty of the measurements. Despite the good agreement obtained for these six species, the peak O_3 concentration for this particular simulation was 42 percent too high. The experimental peak occurred at 0.38 ppm whereas the simulated O_3 max occurred at 0.54 ppm. Similar results are found for the other propylene/NO_x runs and for several other hydrocarbon/NO_x systems as well.

In our modeling we are using Howard's value of $8.1 \times 10^{-12} cm^3$/molecule-second for the rate of reaction of HO_2 with NO. Prior to Howard's determination, we were using a rate constant of $1.4 \times 10^{-12} cm^3$/molecule-second for this reaction. If we repeat the propylene-NO_x run described above using the old, much slower rate constant for the HO_2 + NO reaction, we obtain a predicted O_3 maximum of 0.39 ppm, in excellent agreement with the experimental value of 0.38 ppm.

We have tried to off-set the effect of the new, fast rate constant for the HO_2 + NO reaction. Although we have varied all rate constants in the mechanism within their limits of uncertainty, we have not been able to reduce the simulated O_3 levels without destroying the fits for the other species. With the new HO_2-NO rate constant, too much NO is consumed by HO_2 late in the reaction and O_3 continues to build in the simulations long after the time O_3 was observed to level off in the smog chamber. We are tempted to conclude from this that there may be competing reactions for HO_2 in addition to the HO_2-NO reaction or Howard's rate constant for the HO_2-NO reaction does not apply at atmospheric pressure. Perhaps the rate constants for the reaction of HO_2 with itself or with O_3, at atmospheric pressure and in the presence of water vapor, are higher than the values currently accepted for these reactions. It is also conceivable that some of the HOONO intermediate formed in the HO_2 + NO reaction may be stabilized at atmospheric pressure so that the effective rate of formation of OH and NO_2 is less than that measured by Howard at low pressure. It is difficult to say what the source of discrepancy is, but the fact that many modelers are not able to handle the new, fast HO_2-NO rate constant suggests that the role of NO_x in smog chemistry is not yet fully understood.

William P. L. Carter, Statewide Air Pollution Research Center, University of California, Riverside, California 92521

Perhaps the most important single uncertainty in NO_x chemistry affecting the problem of developing unambiguously validated models for tropospheric chemistry concerns initiation in smog chamber systems. As is now well known, model simulations which assume radical initiation only from known processes predict overall transformation rates in hydrocarbon-NO_x-air systems far slower than those experimentally observed in smog chambers. It is highly probable that this excess radical initiation observed in smog chamber is due to some aspect of heterogeneous NO_x chemistry, since of the known species formed in these systems which can photolyze to give radicals, only nitrogen-containing species, specifically nitrous acid or alkyl nitrites, photolize sufficiently rapidly that contamination by currently undetectable amounts could give the necessary rates of radical input [1]. At least in the UCR chambers, oxygenate contamination is far lower than the levels required to give the necessary radical initiation.

This excess radical initiation in smog chamber systems is probably due to a chamber contamination effect, and not to some unknown omission in the homogeneous mechanisms, or to HONO being inadvertently injected along with NO_x. Evidence for this was obtained in experiments performed at UCR employing large Teflon bags inside the black-light irradiate all glass chamber. It was observed that the overall reactivity of hydrocarbon-NO_x-air photolyses in a new, clean bag was far less than the reactivity subsequently observed in the same bag after only a few smog simulation experiments were performed in it [2]. If the excess radical initiation were due to HONO injection or to some deficiency in the model, and not to chamber contamination, then high reactivity should have been observed in the clean, as well as in the dirty bag.

In terms of model validation, the most serious problem caused by this chamber radical source is due to the fact that it is unpredictable, and must be represented in models by some type of adjustable parameter. This means that aspects of the model concerning radical initiation or termination cannot be unambiguously validated. A mechanism with erroneously high radical input in the homogeneous chemistry (such as those assuming 100 percent fragmentation to radicals in the O_3-olefin system), or with erroneously low radical termination rates, can be made to fit the smog chamber data by suitably reducing the adjustable chamber radical input parameter, and vice-versa. These erroneous mechanisms, which appear to be "validated" by smog chamber experiments, will then give erroneous predictions in ambient air simulations, where the compensating chamber radical parameter is removed from the model. Thus, the occurrence of this chamber radical input phenomenon is clearly a very serious problem, and studies aimed at resolving it should be given very high priority.

References

[1] Carter, W. P. L., Lloyd, A. C., Sprung, J. L., and Pitts, J. N., Jr., Computer modeling of smog chamber data: Progress in validation of a detailed mechanism for the photooxidation of propene and n-butane in photochemical smog, Int. J. Chem. Kinetics 11, 45 (1979).

[2] Darnall, K. R., Winer, A. M., and Pitts, J. N., Jr., unpublished results.

W. Tsang, Center for Thermodynamics and Molecular Science, National Bureau of Standards, Washington, D.C. 20234

It is clear that within the forseeable future EPA will place a great deal of dependence on smog chamber data with regard to pollution regulations and abatement strategies. It is therefore extremely disturbing to learn of the large uncertainties and irreproducibilities in such experiments. One hopes that if environmental decisions are to have any basis in science that a vigorous program for the proper validation of smog chamber data would be instituted as soon as possible. In particular, investigations on the nature of the surface processes, occurring on smog chamber walls should have first priority.

Recommendations

Although significant advancements have been made recently in understanding the role of nitrogen oxides in photochemical smog, there are a number of key processes in the NO_x cycle for which reliable rate data do not exist. In the session on NO_x chemistry, six major areas for further research were identified. In order of decreasing priority, the recommended areas for investigation are the following:

(1) Reactions of Alkylperoxy Radicals

The oxidation of NO by alkylperoxy radicals,

$$RO_2 + NO \rightarrow RO + NO_2,$$

is an important process in photochemical smog formation. Rate constnats, however, have not been measured for this family of reactions. It is generally assumed that the rate of reaction of RO_2 radicals with NO is comparable to the rate of reaction of HO_2 radicals with NO. This assumption may not be valid. Because of the importance of RO_2-NO reactions, the temperature and pressure dependency of these reactions should be determined. As a first priority, it is recommended that the rate of oxidation of NO by methylperoxy radicals be investigated. Methylperoxy radicals are the most prevalent of the RO_2 radicals and the fate of the CH_3O_2 radical is important to an understanding of the background troposphere.

In addition to the oxidation of NO by RO_2 radicals, it has been postulated that longer chain alkylperoxy radicals may add to NO to form excited complexes that decompose to alkyl nitrates:

$$RO_2 + NO \rightarrow (RO_2NO)^* \rightarrow RONO_2$$

Since alkyl nitrate formation is radical terminating, the rearrangement shown in the above equation could have a significant impact on smog chemistry. It is important, therefore, to determine the extent to which this chain-terminating reaction can occur.

Another process of potential importance in the polluted atmosphere is the reaction of alkylperoxy radicals with NO_2 to form peroxynitrates,

$$RO_2 + NO \rightleftarrows RO_2NO_2,$$

and the subsequent decomposition of the nitrates. If this class of reactions is analogous to the $HO_2 + NO_2$ reaction, the alkyl peroxynitrates would be too short-lived to be of importance in smog chemistry. They could, however, play a role at higher altitudes and at low temperatures and are worthy of study for this reason.

The possibility of the alternative channel of decomposition,

$$RO_2NO_2 \rightarrow RCHO + HONO_2,$$

should also be investigated. Decomposition to nitric acid could be important even if this route occurs to only a small extent.

To model the behavior of the alkyl peroxynitrates (and HO_2NO_2 as well), information is needed on the absorption cross-sections and the products arising from the photodissociation of these nitrates. The photochemistry of these species, however, is expected to be of greater importance in the stratosphere than in the lower troposphere.

(2) Chemistry of Peroxyacyl Nitrates

It was recently determined that PAN undergoes rapid thermal decomposition:

$$PAN \rightarrow CH_3C(O)O_2 + NO_2.$$

The rate of this decomposition as a function of temperature is reasonably well-known. Reliable kinetic data are also available on the relative rates of reaction of the peroxyacetyl radical with NO and NO_2,

$$CH_3C(O)O_2 + NO \rightarrow CH_3 + CO_2 + NO_2$$

$$CH_3C(O)O_2 + NO \rightarrow PAN$$

Rate data, however, do not exist for the analogous reactions of the other peroxyacyl radicals. Atmospheric observations indicate that the PAN-type compounds are the most stable of the organic peroxynitrates and, therefore, merit study. As a first order of priority, the thermal stability of the higher analogs of PAN should be determined. If these compounds are sufficiently stable, the relative rates of the reactions of the corresponding peroxyacyl radicals with NO and NO_2 should be measured. The PAN-type compounds recommended for study are peroxypropionylnitrate (PPN) and peroxybenzoyl nitrate (PBzN), important for understanding the fate of aromatics in smog.

(3) Reactions of OH and HO_2 Radicals with NO and NO_2

The reactions of hydroxyl radicals with NO and NO_2,

$$OH + NO + (M) \rightarrow HONO + (M)$$

$$OH + NO_2 + (M) \rightarrow HONO_2 + (M),$$

have been studied by a number of investigators. Uncertainties, however, in the rates of these reactions under atmospheric conditions still exist. These pressure-dependent reactions are in the changeover region between third-order and second-order kinetics at atmospheric pressure. Because of this pressure effect, additional studies of these reactions are warranted.

New rate data have been reported recently for the reaction

$$HO_2 + NO \rightarrow OH + NO_2$$

The new rate constant is significantly higher than previously determined values for the rate of this reaction. The faster rate constant has a substantial impact on the predictions of photochemical models.

Direct determinations of the HO_2-NO rate constant have been made only at reduced pressure. Because of the significant impact of this reaction on model calculations of smog formation, the effect of pressure on the reaction rate should be determined. In addition, the effect of water vapor on the rate of this important reaction should be elucidated.

(4) NO_3 Chemistry

The reactions of NO_3 have been extensively studied by Johnston. Recently he corrected his previous rate data for the reactions,

$$NO_3 + NO \rightarrow 2NO_2$$

$$NO_3 + NO_2 \rightarrow N_2O_5$$

An independent confirmation of the pressure and temperature dependency of these reactions is recommended.

A confirmation of the recently published absorption cross-section and quantum yields for NO_3 photolysis is also desirable. Two pathways have been identified for this photodissociation:

$$NO_3 + h\nu \rightarrow NO + O_2$$

$$NO_3 + h\nu \rightarrow NO_2 + O$$

The significance of these processes in the perturbed troposphere appears to be minimal; however, NO_3 dissociation could be of importance to an understanding of the natural troposphere.

(5) Reactions of Alkoxy Radicals

Alkoxy radicals in the lower troposphere undergo bimolecular reaction with O_2, NO, and NO_2 To assess the importance of the alkoxy-NO_x reactions, it is necessary to know the rate of reaction of RO radicals with NO and NO_2 relative to the rate of reaction with O_2. Such relative rate data do not exist.

Reaction of alkoxy radicals with NO_2 can procee by two pathways:

$$RO + NO_2 \rightarrow RONO_2$$

$$RO + NO_2 \rightarrow RCHO + HONO$$

The rates of the addition and abstraction reactio for the various alkoxy radicals are reasonably well-known. Rate constants for the alkoxy-NO_2 reactions relative to O_2, however, are less well-defined.

Reaction of alkoxy radicals with NO also can proceed by two pathways:

$$RO + NO \rightarrow RONO$$

$$RO + NO \rightarrow RCHO + HNO$$

It is generally assumed that the alkyl nitrites rapidly photolyze and, therefore, do not serve as effective sinks for alkoxy radicals. The rate of photolysis, however, is uncertain and merits study

Only one determination has been made of the relative rate of the addition reaction versus the abstraction reaction to form an aldehyde (or a ketone) and HNO. An independent confirmation of the importance of the abstraction pathway is recommended.

(6) Heterogeneous Reactions

The assumption is generally made that heterogeneous processes are unimportant in the atmosphere. Little quantitative information is available to support this statement. As an example, the rate of removal of N_2O_5 by water in the lower troposphere,

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

is uncertain. This heterogeneous reaction could b significant and deserves additional study. The rate of heterogeneous removal of other gaseous species by aerosols or fog droplets could also be significant and merits attention. An estimate of the dry deposition velocities of various reactive NO_x species is also needed to assess the significance of such removal processes in the lower troposphere.

In addition to characterizing the role of heterogeneous processes in the atmosphere, it is also necessary to determine the degree to which heterogeneous processes affect the results of smog chamber studies. Kinetic mechanisms for photochemical smog are tested primarily using data collected in smog chambers and, therefore, it is important to fully characterize surface effects and other chamber-related phenomena. These phenomena include the heterogeneous formation of HNO_3 and HONO within chambers and the absorption and desorption of reaction species from the chamber walls. One common problem encountered in modeling chamber data is that it is difficult to reproduce the observed initial rate of hydrocarbon and NO disappearance. The very rapid initial decay of these species in smog chambers suggests that there is a nonhomogeneous source of free radicals present at the onset of irradiation. It is possible that radicals may be produced from contaminants on the chamber walls or they may arise from the photolysis of nitrous acid. (There is evidence to suggest that HONO may form during loading of smog chambers). It is important to the modeling effort to characterize this radical initiation process.

Summary: A number of the key processes suggested for study involve organic peroxy radicals. It is not recommended that kinetic studies be conducted on every member of each family of reactions. Only enough members of each class of reactions should be studied to establish a representative data base. This data base should then be used to generalize rates for the other members of the series using established thermochemical estimation techniques.

Session V

Aromatics

REACTIONS OF AROMATIC COMPOUNDS IN THE ATMOSPHERE

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This paper is a review of the tropospheric chemistry of aromatic compounds. The reactivity of aromatic compounds is discussed and rate constants for their reactions with OH are tabulated. The reaction mechanisms are discussed in detail.

Key words: Aromatics; free radicals; mechanism; reactions; tropospheric chemistry.

1. Introduction

Single-ring aromatic compounds make up a high proportion of the carbon found in the urban atmosphere. Table 1 summarizes data reported on the composition of the atmosphere in Los Angeles, California [1][1], and Manhattan, New York [2]. From these studies we see that benzene and alkyl-substituted benzene compose roughly 24 carbon percent of the total hydrocarbon in Los Angeles and about 37 carbon percent in Manhattan.

Table 1. Atmospheric concentrations of single-ring aromatic hydrocarbons.

Compound	Concentration, ppm (ppmC)			
	Los Angeles (1973)		Manhattan (1969)	
C_6H_6	0.008	(0.048)	0.004[a]	(0.022)[a]
CH_3-C_6H_5	0.020	(0.140)	0.013	(0.094)
$(CH_3)_2$-C_6H_4	0.020	(0.160)	0.012	(0.094)
CH_3CH_2-C_6H_5	0.004	(0.032)		
n-C_3H_5-C_6H_5	0.001	(0.009)		0.083
s-C_4H_9-C_6H_5	0.005	(0.050)		
Σ Aromatic	0.058	(0.439)		(0.294)
Σ Alkane-CH_4	0.259	(1.15)		(0.371)[b]
Σ Alkene	0.087	(0.271)		(0.096)
CH_4	2.1	(2.1)		
C_2H_2	0.038	(0.076)	0.022	(0.044)
ΣΣ	0.404	(1.86)		(0.761)[b]

[a] Estimated.

[b] Not included: ca. 0.038 ppmC ethane, ca. 0.043 ppmC propane and ca. 0.022 ppmC benzene.

The aromatic compounds in the atmosphere come from gasoline [3], in which they are used to enhance the octane rating. Gasoline itself is composed of 30 to 40 percent aromatic hydrocarbons and apparoximately 6 to 8 percent toluene. Hydrocarbons emitted in automobile exhaust are composed of 6 to 8 percent toluene.

We have known for some time from smog chamber reactivity studies that the alkyl-substituted benzenes are reactive in promoting oxidation of NO to NO_2 and formation of ozone [4]. However, only in the last few years has an effort been made to understand specifically how these compounds react. This effort has been very productive, largely because it builds on an existing background of moderately well understood smog chemistry of the alkanes and alkenes. The total conversion of the aromatics to H_2O, CO, and CO_2 is a complex process, of which we understand only the initial steps.

2. Initial Reactions of Alkylbenzenes

Table 2 summarizes the possible reactions of toluene, a representative aromatic hydrocarbon, with the oxidizing species known to be present in the atmosphere. Best values of rate constants and approximate concentrations are included for estimating the rate of loss of toluene by the various processes. The data in table 2 show clearly that the only important reaction of toluene in the atmosphere is with OH. The contribution of the reactions with O atom and O_3 are about 10^{-4} and 10^{-3} of that of OH reaction. The reactions of $RO_2\cdot$ proceed extremely slowly and can account for only 10^{-8} of the total consumption of toluene.

Rate constants for the reaction of OH with various alkyl benzenes are summarized in table 3. We are fortunate to have several techniques for measuring the rate constants for reaction of OH with aromatic hydrocarbons. The agreement between

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[1] Figures in brackets indicate literature references at the end of this paper.

Table 2. Reactions of toluene in the atmosphere.

Reactant	Concentration molec cm^{-3} (ppm)	k, cm^{3}molec^{-1}s^{-1}	τ_{tol}, s
OH [5-7]	5.0×10^6 (2×10^{-7})	6.4×10^{-12}	3.1×10^4
O [8]	2.5×10^4 (1×10^{-9})	7.5×10^{-14}	5.3×10^8
O_3 [9]	1.5×10^{12} (6×10^{-2})	3.4×10^{-22}	2.0×10^9
$RO_2\cdot$ ($HO_2\cdot$) [10]	2.5×10^9 (1×10^{-4})	1.7×10^{-22}	2.3×10^{12}

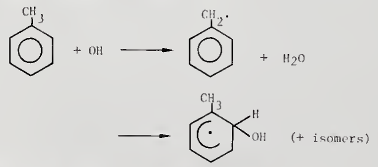
Table 3. Reported rate constants for reaction of OH plus aromatic hydrocarbon.

Compound	Perry [7]	Hansen [6]	Doyle [11]	Davis [5]
Benzene	1.20	1.24	$\leq$ 3.8	1.59
Toluene	6.40	5.78	4.2	6.11
o-Xylene	14.3	15.3	12.8	12.4
m-Xylene	24.0	23.6	23.2	20.5
p-Xylene	15.3	12.2	12.3	10.5
1,2,3-Mesitylene	33.3	26.4	23.0	
1,2,4-Mesitylene	40.0	33.5	33.0	
1,3,5-Mesitylene	62.4	47.2	52.0	

the reported values is very good, and we have confidence in these numbers. Two basic techniques have been used: measurement of the decay of a pulse-generated OH concentration by resonance fluorescence [5-7] and determination of the rate of disappearance of the hydrocarbon relative to a standard hydrocarbon under conditions where OH is the sole reactive species [11].

3. Products of OH-Aromatic Reactions

Two reactive pathways are expected for the reaction of aromatics with OH radical. For toluene, these two pathways are H-atom transfer from the methyl group (reaction 1) and addition to the ring (reaction 2).



(1)

(2)

From the pressure dependence at 25 °C, Davis et al. [5] suggested that $k_1/(k_1 + k_2)$ was less than 0.5. Perry et al. [7] found that the toluene-OH reaction, as well as other aromatic-OH reactions, was strongly temperature dependent. In fact, at higher temperatures the apparent first-order rate constants were found to be lower than the room temperature value because of the reversibility of reaction (2). From extrapolation of the data at high temperature (where only reaction 1 is important) to lower temperatures, the ratio $k_1/(k_1 + k_2)$ at 25 °C could be estimated. For toluene, Perry et al. postulate $k_1/k_1 + k_2) = 0.16^{+0.07}_{-0.05}$. The relatively large uncertainty arises from the uncertainties associated with extrapolating the high temperature data to determine the value of k_1 at 25 °C.

In our laboratory we have been investigating the products of reaction of aromatic hydrocarbons and OH in a discharge flow system [12,13]. The products were collected in cold traps and on solid adsorbents. The product distributions were determined as a function of hydrocarbon, NO_2, and O_2 pressures. Table 4 summarizes some of the data obtained as a function of NO_2 pressures. The fraction of products resulting from reaction (1) is a measure of $k_1/(k_1 + k_2)$ and remains constant over the range of conditions. For toluene we obtain 0.15 ± 0.02, which agrees very well with the best value reported by Perry et al. [7]. The $k_1/(k_1 + k_2)$ values for various aromatic hydrocarbons obtained by these two methods are summarized in table 5.

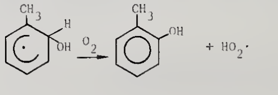
Table 4. Product distribution for the reaction of toluene plus OH[a].

	NO_2, 10^{-14} molec/cm^3			
Products	0.71	1.04	1.39	1.75
C_6H_5CHO	11.7	9.9	9.7	10.4
$C_6H_5CH_2OH$	3.5	3.3	4.4	4.6
m-$NO_2C_6H_4CH_3$	33.3	37.6	39.9	47.3
o-$HOC_6H_4CH_3$	40.3	37.3	35.8	29.0
p-$HOC_6H_4CH_3$	6.4	6.8	6.7	5.5
m-$HOC_6H_4CH_3$	4.3	4.8	3.2	2.9
$HOC_6H_4CH_3$	51.0	48.9	45.7	37.4
$CH_3C_6H_3O_2$	0.4	0.3	0.3	0.7
C_6H_5CHO + $C_6H_5CH_2OH$/ Total products	15.2	13.2	14.1	14.6

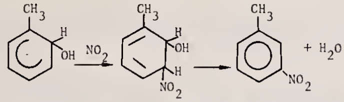
---

[a] Oxygen: 9.7×10^{16} molec/cm^3; toluene: 3×10^{1} molec/cm^3; total pressure: 8.8 Torr.

We find m-nitrotoluene to be a major product; however, the concentration varies with the O_2/NO_2 ratio. Thus the intermediate formed in reaction (2) appears to react by two parallel pathways.



(3



(4)

According to this mechanism, the relative amounts of the sum of the cresols compared with m-nitrotoluene are:

$$\frac{[\underline{m}\text{-nitrotoluene}]}{[\text{cresols}]} = \frac{k_4}{k_3} \cdot \frac{[NO_2]}{[NO]}$$

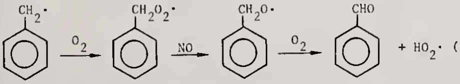
Analyzing our data according to this expression gives $k_4/k_3 = 4 \times 10^3$.

Using this value of k_4/k_3, we estimated the percent yield of m-toluene as a function of NO_2 in the atmosphere, as shown in table 6. Thus, at the NO_2 concentrations generally used in smog chamber experiments, m-nitrotoluene can account for 1 to 20 percent of the toluene. At concentrations of NO_2 found in the atmosphere, however, significantly less than 1 percent toluene will give m-nitrotoluene.

Table 5. Reaction of aromatic hydrocarbons with OH.

	$k_1/(k_1 + k_2)$		Atmospheric products
Hydrocarbon	This work	Perry [7]	$NO_2 < 1$ ppm
Benzene	< 0.05	0.01-0.13	100% Phenol
Toluene	0.15 ± 0.02	0.01-0.23	15% Benzaldehyde, 85% cresol isomers
p-Xylene	0.15 ± 0.02	0.04-0.14	15% Methylbenzaldehyde, 85% 2,5-dimethylphenol
Mesitylene	0.021 ± 0.006	0.01-0.04	2% Dimethylbenzaldehyde, 98% trimethylphenol

Table 5 also lists the products expected to be formed under atmospheric conditions. These estimates are corrected for the NO_2/O_2 ratio and the high radical concentration. Thus, for the intermediates formed in reactions (1) and (2), the reactions important in the atmosphere are reactions (3) and (5).



(5)

In addition to the meta-nitrotoluene ortho- and para-isomers have also been reported in smog chamber experiments [14,15]. These isomers could potentially be formed from the meta-OH-adduct of toluene in sequences similar to reaction (4). However, since very little m-cresol is formed, this route does not seem reasonable. In many cases, we have observed NO_x to be an effective nitrating agent upon condensing our reaction mixtures, and we believe that many nitro products observed in smog chambers may reflect heterogeneous reactions either during the actual chamber reaction or during trapping out of the products. Since phenolic compounds are especially susceptible to heterogeneous nitration, the origin of nitrophenols must be interpreted with extreme caution.

Table 6. Calculated yields of m-nitroluene as a function NO_2 concentration in the atmosphere.

NO_2		
10^{-12} cm^{3}molec^{-1}	(ppm)	m-Nitrotoluene, %
1.0	(0.04)	0.07
3.0	(0.12)	0.2
10.0	(0.40)	0.7
30.0	(1.2)	2.4
100.0	(4.0)	6.6
300.0	(12.0)	24.0

4. Reactions of Initial Products

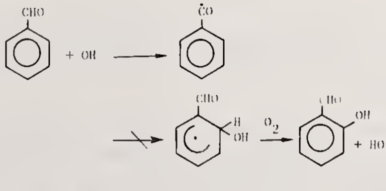
Benzaldehyde Reactions. Two processes appear to be important for the reaction of the benzaldehyde formed from toluene in the atmosphere: the reaction with OH and photolysis.

Niki et al. [16] recently reported the rate constant for the reaction

$$PhCHO + OH \longrightarrow \qquad (6)$$

as $k = 1.3 \times 10^{-11}$ cm^3 molec^{-1}s^{-1}, which is identical within the experimental uncertainties to rate constant for other aldehyde-OH reactions. Addition of OH to the ring as observed for toluene (reaction (2))is expected to occur no faster than addition to benzene, where $k_{OH} = 1.2 \times 10^{-12}$ cm^3 molec^{-1}s^{-1}. Thus the attack of OH is expected to be largely at the aldehydic position.

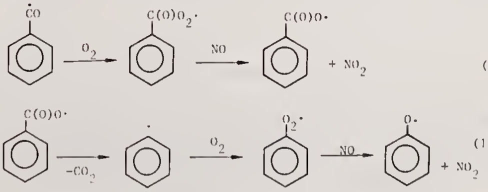
Using our discharge flow systems, we have found that the reaction produces phenol as the only gas phase product [17]. Thus the initial reactions of the benzaldehyde with OH is



(7)

(8)

followed by the reactions



(9)

(10)

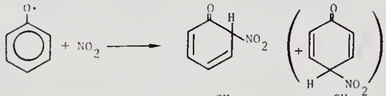
In our flow system phenoxy is converted to phenol, presumably by a wall reaction with benzaldehyde [17]. Considerable amounts of wall products are also found, but field ionization mass spectrometry indicates that the products are largely various states of oxidized phenol including as much as 10 percent nitrophenol.

Niki et al. [18] found o- and p-nitrophenol in the Cl_2-catalyzed reaction of benzaldehyde in presence of air and NO_2. The benzoyl radical is first formed by the reactions of Cl atom

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot \qquad (11)$$

$$PhCHO + Cl\cdot \longrightarrow PhCO + HCl \qquad (12)$$

which is followed by reactions (9) and (10). A significant fraction of the benzaldehyde appears as nitrophenols, presumably by reaction of phenoxy radical with NO_2.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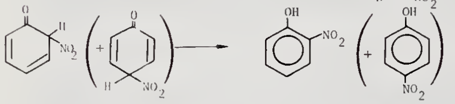

(14)

The second important reaction of benzaldehyde, photolysis, has been studied by Berger et al. [19] in the gas phase and in the absence of oxygen. Three photolytic reactions are possible.

$$PhCHO \longrightarrow PhH + CO \qquad (15)$$

$$\longrightarrow Ph\cdot + H\dot{C}O \qquad (16)$$

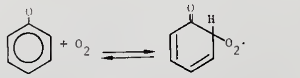
$$\longrightarrow Ph\dot{C}O + H\cdot \qquad (17)$$

Although reaction (15) is energetically favorable at all wavelengths of the visible spectrum, its measured quantum yield is significant only at wavelengths less than 300 nm [19]. Reaction (16) is energetically possible only below 300 nm. Thus, only reaction (17), which has an energy cut-off at 330 nm, appears to be important in the solar spectrum. However, the possibility of the generation of a triplet excited state that reacts with oxygen above 330 nm cannot be ruled out.

$$PhCHO \xrightarrow[O_2]{h\nu} PhC(O)O_2\cdot + HO_2 \qquad (18)$$

Such a reaction would be an important source of radicals and therefore critical for modeling purposes.

In both the reaction paths for benzaldehyde, the phenoxy radical is eventually formed. In the atmosphere, the fate of phenoxy, we believe, is determined by the reaction with oxygen as well as by reaction (13).


(19)

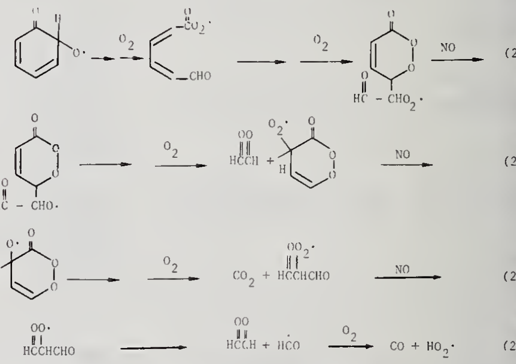
However, thermochemical calculations indicate that the DH°($C-O_2$) in the resulting peroxy radical is small and that the reaction will be reversible. The importance of reaction (19) therefore depends on how fast the peroxy radical is trapped by reaction with NO.


(20)

The competition between the formation of nitrophenol (reaction 13) and reaction (20) is

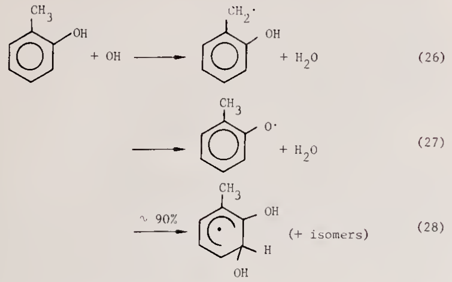
$$\frac{Rate_{13}}{Rate_{20}} = \frac{k_{13}\,[PhO\cdot][NO_2]}{k_{20}\,[Ph(O)O_2\cdot][NO]} = \frac{k_{13}k_{-19}}{k_{20}k_{19}[O_2]} \cdot \frac{[NO_2]}{[NO]} \qquad (21)$$

The following estimates are applicable: $k_{13} = 1.7 \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}, $k_{20} = 5.0 \times 10^{-12}$ cm $molec^{-1}$ s^{-1}, $k_{19} = 6.0 \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1} and $[O_2] = 0.01$ M in air at 1 atm. If $k_{-19} = 10^7$ s^{-1} which is consistent with our estimate of DH°($C-O_2$) = 10 kcal/mol, the two processes will compete equally at $NO_2/NO = 1$. At very high ratios of NO_2/NO, however, the formation of nitrophenol will predominate. If the DH°($C-O_2$) is much weaker than 10 kcal/mol ($k_{-19} >> 10^7$ s^{-1}), reactio (13) will predominate under most atmospheric conditions, but if it is much stronger than 10 kcal/mol ($k_{-19} >> 10^7$ s^{-1}), reaction (13) will be unimportant and reactions (19) and (20) will predominate. The relative importance of reactions (13) and (19)-(20) is very critical because reaction (13) is a termination reaction whereas (19)-(20) will lead to ring degradation and further oxidation of NO by reactions of the following type.

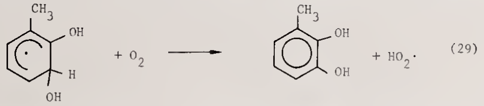


This reaction sequence is speculative, although each step can be justified in most cases by analysis of competing reactions. It does suggest that α-dicarbonyl compounds should be important secondary products. These compounds absorb light very strongly in the solar spectrum and can be significant source of radicals [20,21].

Cresol Reactions. The reaction of OH plus o-cresol was studied by Perry et al. [22] over the temperature range 300 to 435 K (reactions for p- and m-cresols are expected to be similar). Rate constants were reported for two processes: (1) a nonreversible reaction believed to be hydrogen abstraction ($k = 2.6 \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}) and (2) a reversible reaction believed to be addition to the ring ($k = 3.1 \times 10^{-11}$ cm^3 $molec^{-1}$ s^{-1}). We postulate the following reaction pathways.



Reaction (26) should lead to hydroxybenzaldehyde, reaction (27) should be followed by reactions of the type proposed for the simple phenoxy radical, and reaction (28) will lead to dihydroxytoluenes.



We are beginning to investigate the products of reaction of o-cresol plus OH in our discharge flow system to determine if the above reaction routes are valid.

Other homoegeneous reactions of cresols to be considered are the reactions with O_3 and O atoms. For p-cresol we have obtained a second-order rate constant for reaction with ozone equal to about 1.4×10^{-18} cm^3 $molec^{-1}$ s^{-1}. At 0.05 ppm O_3, this reaction is about 1 percent of the OH-cresol reaction, assuming the o- and p-cresol have the same reactivities. While the reaction may prove unimportant as a loss mechanism for cresols, it can be a dominant source of free radicals at high ozone concentrations if it produces radicals efficienctly. We hope to determine if this is the case in our studies of cresol-O_3 reactions.

Atkinson and Pitts [23] studied the reaction of O atom plus o-cresol and found it to have a rate constant of 5.8×10^{-13} cm^3 $molec^{-1}$ s^{-1}. Since the OH reaction is 100 times faster and since OH is 100 times more abundant than O atom, this reaction with o-cresol is insignificant.

5. Modeling of Toluene Smog Chamber Data

The Statewide Air Pollution Research Center (SAPRC) at the University of California, Riverside has carried out a series of runs with toluene in their smog chamber facility. Concentrations of toluene range from 0.2 to 2.0 ppm while the NO_x concentration was varied from 0.1 to 1.0 ppm. We have developed a mechanism to simulate these data. The mechanism includes the standard inorganic reactions and those organic reactions which have been discussed in previous sections. We have also included reactions for formation and decomposition of the major peroxynitrates as well as the termination reactions of $HO_2\cdot$ with $RO\cdot$ and $RO_2\cdot$ radicals.

Figures 1 and 2 show simulation and experimental data for SAPRC Runs EC-77 and EC-86. Run EC-77 was with 0.28 ppm toluene and 0.58 ppm NO_x, which run EC-86 was with 1.09 ppm toluene, 0.49 ppm NO_x and 0.16 ppm formaldehyde. The agreement between the simulation and experiment data is very good.

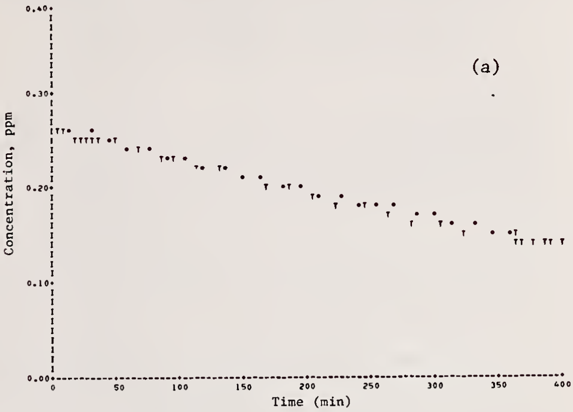


Fig. 1. (a) Simulation of SAPRC EC-86: Toluene (* = experimental, T = simulation).

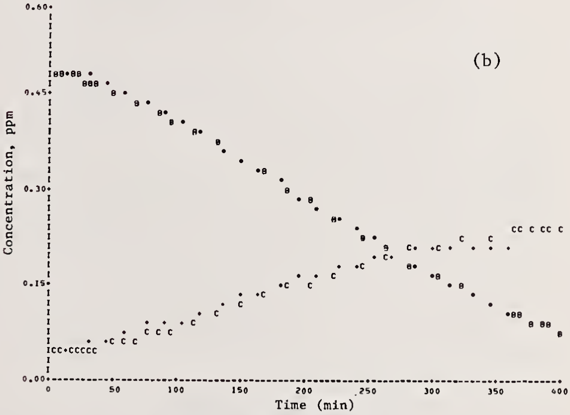


Fig. 1. (b) Simulation of SAPRC EC-86: NO (* = experimental, I = simulation) and NO_2 (+ = experimental, 2 = simulation).

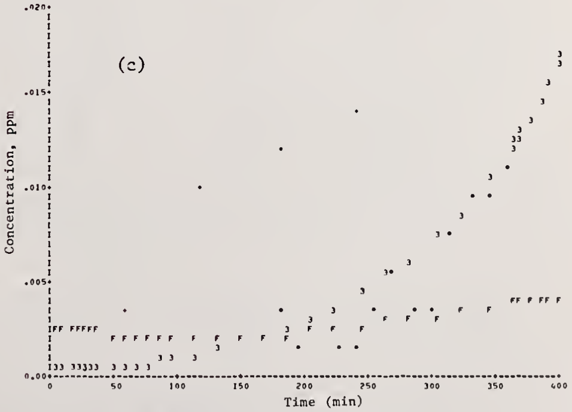


Fig. 1. (c) Simulation of SAPRC EC-77: Ozone (* = experimental, 3 = simulation) and Formaldehyde (+ = experimental, F = simulation).

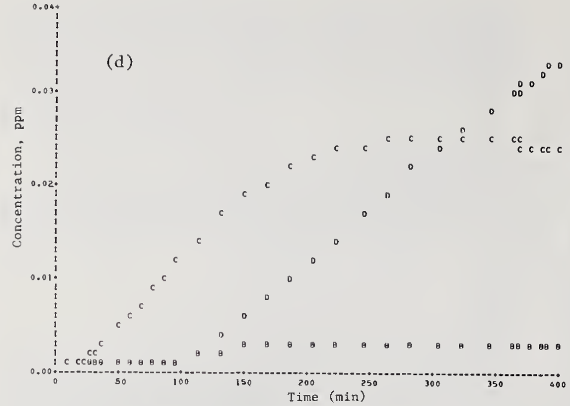


Fig. 1. (d) Simulation of SAPRC EC-77: Cresol-total (C = simulation), Dihydroxy toluene (D = simulation, and Benzaldehyde (B = simulation).

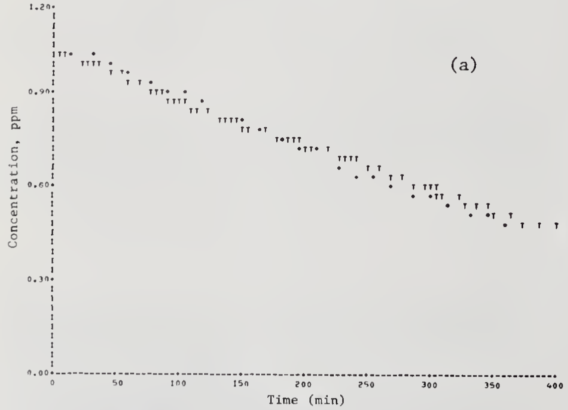


Fig. 2. (a) Simulation of SAPRC EC-86: Toluene (* = experimental, T = simulation).

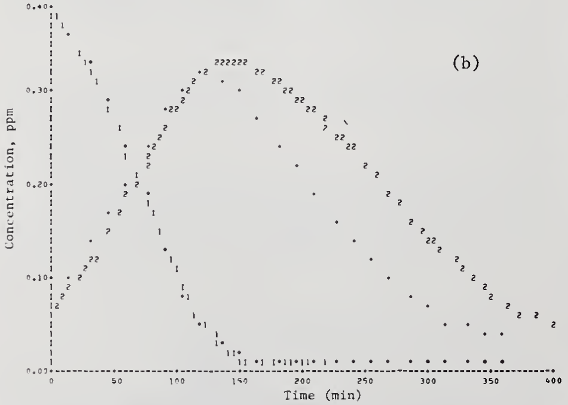


Fig. 2. (b) Simulation of SAPRC EC-86: NO (* = experimental, 1 = simulation) and NO_2 (+ = experimental, 2 = simulation).

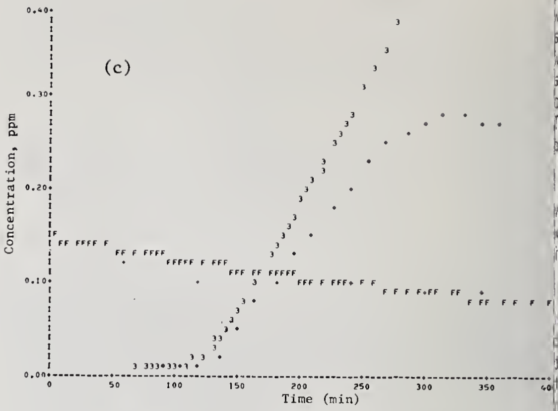


Fig. 2. (c) Simulation of SAPRC EC-86: Ozone (* = experimental, 3 = simulation) and Formaldehyde (+ = experimental, F = simulation).

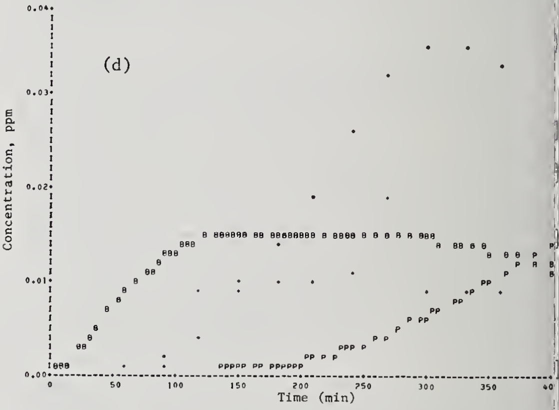


Fig. 2. (d) Simulation of SAPRC EC-86: Benzaldehyde (+ = experimental, B = simulation) and PAN (* = experimental, P = simulation).

There are discrepancies in the formaldehyde and PAN values which in part may be due to experimental uncertainties. The reason for the over prediction in EC-86 of the ozone near its maximum is not clear. However, the effect is also seen in the simulation of smog chamber data for other hydrocarbons, and thus may or may not be due to the actual toluene mechanism.

6. Conclusions

The reaction of toluene in the atmosphere is very complex. We have a good understanding of the initial reactions, but we still need to determine the fate of the primary and secondary products. We can model the toluene smog chamber reasonably well, but out mechanism includes speculation regarding many of the intermediates.

More smog chamber studies are needed to identify the products of toluene reaction and their yields.

Currently, data show very low material balances which may be indicative of the formation of aerosols or deposition of products on the chamber walls. The chamber data should be obtained over a wide range of conditions because the sensitivity of individual reactions varies with the conditions. Thus, by using a wide range of conditions, different parts of the model can be tested.

The current study of individual reactions of various intermediates should be continued. This work has been one of the most helpful sources of information in developing the toluene mechanism.

Finally, the inability to simulate the ozone data in smog chamber runs, indicate a need for a better understanding of the chemistry that controls the ozone concentration. Since this effect appears to be common to the simulation of data for other hydrocarbons, the problem may not be solely with the organic part of the mechanism.

References

[1] Calvert, J. G., Environ. Sci. Tech. 10, 256 (1976).

[2] Lonneman, W. A., Kopczynski, S. L., Danley, P. E., and Sutterfield, F. D., Environ. Sci. Tech. 8, 229 (1974).

[3] Crabtree, J. H., private communication.

[4] Heuss, J. M. and Glasson, W. A., Environ. Sci. Tech. 2, 1109 (1968).

[5] Davis, D. D., Bollinger, W., and Fischer, S., J. Phys. Chem. 79, 293 (1975); Davis, D. D., Investigation of Important Hydroxyl Radical Reactions in the Perturbed Troposphere, EPA-600/3-77-11 (October 1977).

[6] Hansen, D. A., Atkinson, R. and Pitts, J. N., Jr., J. Phys. Chem. 79, 1763 (1975).

[7] Perry, R. A., Atkinson, R. and Pitts, J. N., Jr., J. Phys. Chem. 81, 296 (1977).

[8] Atkinson, R. and Pitts, Jr., J. N., J. Phys. Chem. 79, 295 (1975).

[9] Nakagawa, T. W., Andrews, L. J., and Keefer, R. M., J. Amer. Chem. Soc. 82, 269 (1960).

[10] Hendry, D. G., Mill, T., Piszkiewicz, L., Howard, J. A., and Eigenmann, H. K., J. Phys. Chem. Ref. Data 3, 937 (1974).

[11] Doyle, G. J., Lloyd, A. C., Darnall, K. R., Winer, A. M., and Pitts, J. N., Jr., Environ. Sci. Tech. 9, 237 (1975).

[12] Kenley, R. A., Davenport, J. E., and Hendry, D. G., J. Phys. Chem. 82, 1095-1096 (1978).

[13] Kenley, R. A. and Hendry, D. G., manuscript in preparation.

[14] O'Brien, R. J., Green, P. J., and Doty, R. A., Interaction of Oxides of Nitrogen with Aromatic Hydrocarbons, 175th National Meeting, of the American Chemical Society, March 1978.

[15] Fitz, D. R., Grosjean, D., Van Cauwenberghe, K., and Pitts, J. N., Jr., Photo-oxidation Products of Toluene-NO_x Mixtures Under Simulated Atmospheric Conditions, 175th Meeting of the American Chemical Society, March 1978.

[16] Niki, H., Maker, P. D., Savage, C. M., and Breitenbach, L. P., J. Phys. Chem. 82, 132 (1978).

[17] Kenley, R. A., Lan, B., and Herdry, D. G., unpublished data.

[18] Niki, H., Maker, P. F., Savage, C. M., and Breitenbach, L. P., Fourier Transform IR Studies of Gaseous and Particulate Nitrogeneous Compounds of Atmospheric Interest, 175th National Meeting of the American Chemical Society, March 1978.

[19] Berger, M., Goldblatt, I. L., and Steel, C., J. Amer. Chem. Soc. 95, 1717 (1973).

[20] Porter, G. B., J. Chem. Phys. 32, 1587 (1960).

[21] Bouchy, M. and Andre, J. C., Molec. Photochem. 8, 345 (1977).

[22] Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., J. Phys. Chem. 81, 1607 (1977).

[23] Atkinson, R. and Pitts, J. N., Jr., J. Phys. Chem. 79, 541 (1975).

Summary of Session

The presentation by Hendry emphasized the importance of aromatic compounds in the chemistry of urban air pollution. Single ring aromatic compounds account for 25-40 percent of the carbon species found in urban air. From chamber studies these compounds are known to be reactive in the production of ozone (O_3). Therefore a knowledge of the atmospheric chemistry of simple aromatics is required for inclusion of these compounds in tropospheric models to predict their role and contribution to photochemical smog formation. The importance of a better understanding of the chemistry was illustrated in comments by Atkinson and Hendry on the uniqueness of the O_3 formation curve and the current inability to simulate O_3 smog chamber data.

The major theme of the discussion and the majority of the uncertainties centered around mechanisms of reactions of primary and secondary aromatics in the atmosphere. There was general agreement that the initial reaction can be accounted for almost solely by attack of the hydroxyl (OH) radical. For methyl substituted benzenes, the accepted mechanisms are hydrogen abstraction at the methyl group and OH addition at the ortho position. However, there was a degree of uncertainty regarding the branching ratio for the two pathways, with the only significant work being done on toluene. In addition Atkinson pointed out the thermodynamic favorability of OH addition at the methyl position. Inclusion of this pathway could alter mechanistic consideration of other investigators.

There was considerable discussion and some lack of agreement on product yields. For toluene, O'Brien reported lower product yields than Hendry for benzaldehyde and o-cresol by factors of approximately 4 and 10 respectively. There was some speculation that Hendry's results were higher because he based his yields on the total amount of gas-phase carbon analyzed. In any event none of the investigators have yet analyzed aerosol carbon or carbon on the walls of reaction chambers. Both O'Brien and Atkinson reported carbon balances well below 100 percent.

The question of the mechanism(s) of ring opening was raised several times. Tentative mechanisms were proposed in the papers by Hendry and Atkinson. Evidence for ring opening was given by the observation of peroxyacetyl nitrate and carbon monoxide by Atkinson. Ring opening could be of considerable importance as a source of free radicals and simple oxgenated products.

The status of the uncertainty on reaction mechanisms may be illustrated by the fact that the only work reported on basic mechanisms was the low pressure flow tube studies of Hendry. Most of the mechanistic work reported was on toluene. The reactions and fate of aromatic products was largely unconsidered. In his paper Hendry discussed the attack of OH on benzaldehyde and the cresols and subsequent reaction pathways.

With regard to reaction kinetics, relatively good agreement was reported for the OH reaction with the primary aromatics-benzene, toluene and xylenes. Little data are available on the higher homologues or on OH reaction with aromatic products. O'Brien reported ratio measurements, relative to toluene, for o-cresol and benzaldehyde. Atkinson presented reaction rate data for the cresols.

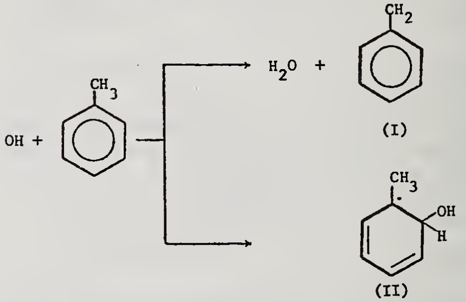
It was evident from the discussion that some problems exist with regard to analytical measurements of products. All of the analyses reported during the discussions were performed by gas chromatography (GC). O'Brien reported some difficulty with some product measurements at low concentrations, e.g. cresols. No analyses were reported by other techniques such as mass spectroscopy or Fourier transform infrared spectroscopy. Either of these techniques could give better time resolution and the possibility of observing intermediates. Finally there is the larger question of the amount and nature of products in the aerosol phase.

Comments

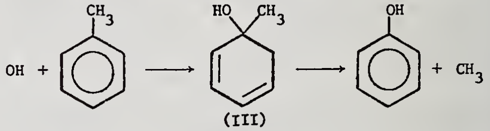
Roger Atkinson, Statewide Air Pollution Research Center, University of California, Riverside, California 92521

I would like to make three points:

1) Besides the two initial reactions of the O radical with the substituted aromatics (taking toluene as an example),



OH radical addition at the 1-position leads to the formation of phenol and CH_3 radicals

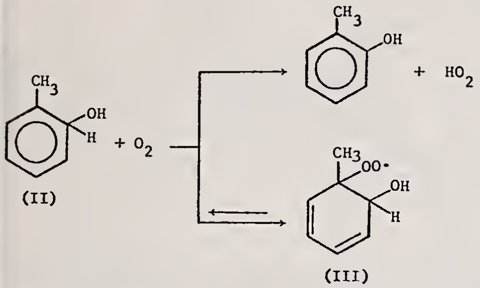


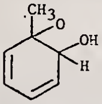
Elimination of CH_3 from radical III can be calculated to be ∿9 kcal mol^{-1} endothermic. This together with an activation energy for the addition of CH_3 radicals to toluene of ∿4 kcal mol^{-1} [1], leads to an activation energy of ∿ 13 kcal mol^{-1} for reaction (3). Hence reaction (3) will be favored over elimination of an OH radical (analogous to reaction (1)) from this OH-toluene adduct. The occurrence of this reaction pathway would hence mean that the values of k_1 and $k_1/(k_1 + k_2)$ obtained by Perry, Atkinso and Pitts [2,3] are upper limits. This may be especially true for o-xylene where, by analogy with the $O(^3P)$ atom reaction [4], OH radical addition at the methyl substituted positions is likely to be appreciable, and for which the reported value of $k_1/(k_1 + k_2)$ appears to be high, with a low value of E_{16}, compared to the other aromatic hydrocarbons.

2) At the Statewide Air Pollution Research Center, University of California, Riverside, we [5] have recently determined rate constants for the reaction of OH radicals with o-, m- and p-cresol from the rates of disappearance of the cresols and n-butane in irradiated NO_x-organic-ai mixtures of atmospheric pressure and 300 ± 1 K. Using a value of k(OH + n-butane) of 2.73×10^{-12} cm^3 $molec^{-1}$ s^{-1} at 300 K [6] rate constants k (cm^3 $molec^{-1}$ s^{-1}) of $(4.7 \pm 0.4) \times 10^{-12}$; $(6.7 \pm 0.7) \times 10^{-12}$ and $(5.2 \pm 0.5) \times 10^{-12}$ were obtained [5] for o-cresol, m-cresol and p-cresol. Further experiments [7] have shown that the NO_x photooxidations of the cresols form hydroxynitrotoluenes as the major observed gas phase

aromatic products, the 2,3- and 2,5-isomers from o-cresol, the 3,2- and 3,4-isomers from m-cresol, and the 4,3-isomer from p-cresol.

3) Ring cleavage in the OH-aromatic systems may occur, in part, through the reaction sequence



Radical (III) may then react with NO to form NO_2 and the radical , which would probably undergo ring opening, leading to a variety of oxygenated species. H atom abstraction from radical (II) by O_2 to form o-cresol is ∿ 26 kcal mol^{-1} exothermic, with the bond strength of the C-H bond at which abstraction takes place being ∿ 20 kcal mol^{-1}.

From group additivity calculations, using a COO-H bond energy of 90 kcal mol^{-1} (the same as that for HOO-H, ΔH_f(III) ∿ -6 kcal mol^{-1}. As ΔH_f(II) ∿ 1 kcal mol^{-1}, formation of (III) from (II) is ∿ 7 kcal mol^{-1} exothermic and hence radicals (III) and (II) will be in equilibrium. Hence this reaction pathway leading to ring opening is expected to become more important at lower temperature, and vice-versa.

References

[1] Cher, M., Hollingsworth, C. S., and Sicilio, F., J. Phys. Chem., 70, 877 (1966).

[2] Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., J. Phys. Chem., 81, 296 (1978).

[3] Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., J. Phys. Chem., 81, 1607 (1978).

[4] Grovenstein, E., Jr. and Mosher, A. J., J. Amer. Chem. Soc., 92, 3810 (1970).

[5] Atkinson, R., Darnall, K. R., and Pitts, J. N., Jr., J. Phys. Chem., submitted for publication (1978).

[6] Perry, R. A., Atkinson, R., and Pitts, J. N., Jr., J. Chem. Phys., 64, 5314 (1976).

[7] Darnall, K. R., Atkinson, R., Glangetas, A., Winer, A. M., and Pitts, J. N., Jr., unpublished data (1978).

Robert J. O'Brien, Patrick J. Green, and Richard M. Doty, Department of Chemistry, Portland State University, Portland, Oregon 97207

The product formation and dynamics for the toluene (T) system under ambient conditions are of great current interest. For the simple case where hydroxyl radical determines both formation and loss of "stable" products (P_i):

$$T + OH \xrightarrow{a} \alpha_i P_i \qquad a$$

$$P_i + OH \xrightarrow{b_i} \text{loss} \qquad b$$

the maximum production concentration will be given by

$$\frac{[P_i^{max}]}{[T]} = \frac{\alpha_i}{R_i} \qquad (1)$$

where α_i is the yield of product P_i in the primary reaction step and $R_i \equiv b_i/a$ is the ratio of the OH rate constant with the product, P_i, to the rate constant with toluene.

If we assume pseudo first order loss for toluene (constant OH concentration) we may integrate the rate expression to determine the length of time required to achieve maximum concentration (t_i^{max}) in terms of the toluene lifetime (τ_T). This is given by

$$\frac{t_i^{max}}{\tau_T} = \frac{1}{(R_i - 1)} \ln R_i \qquad (2)$$

A plot of this function is given in figure 1.

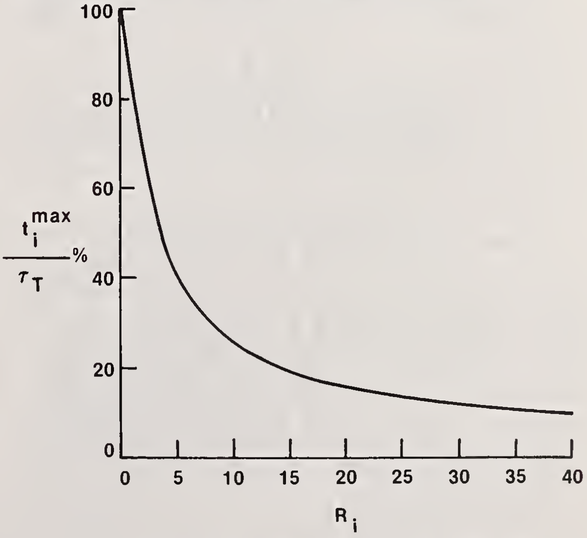


Fig. 1. Variation of the time for a product to reach maximum concentration relative to the toluene lifetime (t_i^{max}/τ_T) with the relative reactivity with OH radical (R_i) as given by eq. (2).

From this plot we may determine (for example) that for a typical atmospheric lifetime of toluene of 10 hours the concentration of o-cresol (which reacts six times faster than toluene with OH) should reach a maximum in 3.5 hours. If the yield of o-cresol is 5 percent (see below) and the ambient toluene concentration is .020 ppm, this maximum concentration calculated from eq. (1) is about 0.2 ppb.

Assuming pseudo first order toluene loss the variation of a product with toluene concentration is given by

$$P_i = \frac{\alpha_i T}{R-1} \quad 1-\left(\frac{T}{T_o}\right)^{R-1} \qquad (3)$$

The general form of this equation for various values of R_i is shown in figure 2.

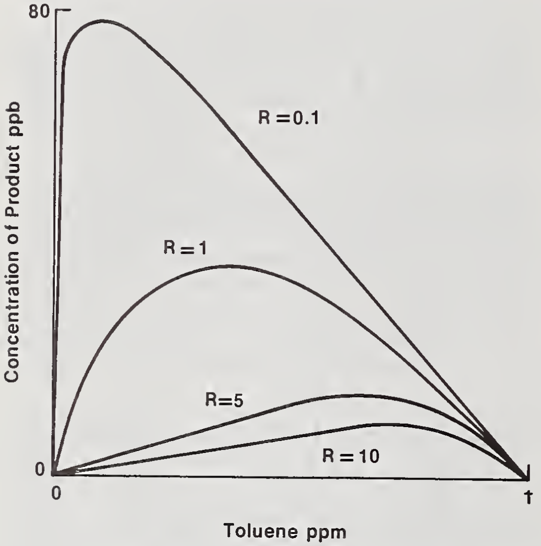


Fig. 2. Variation of a product concentration with toluene concentration for different values of R_i, assuming α = 10 percent.

The values of α_i may be obtained from the individual rate measurements of Atkinson and others. However, considering the errors present in each measurement a separate measurement of the ratio itself may be preferable. We have made such measurements by irradiating a mixture of P_i and toluene at about a 10 to 1 ratio (P_i/T). A plot of ln P_i vs. ln T gives the value of R_i as the slope. This analysis is not sufficient if the product photolyzes to any appreciable extent. For the case of o-cresol the photolytic lifetime in our reaction vessel is 10^4 minutes and is probably negligible.

For the more general case of non first order toluene loss (variable OH concentration) we may still derive an expression to analyze production formation and loss. For the same mechanism given above (reactions a and b) it can be shown that

$$\Delta[P_i] + R_i \int_{T_0}^{T} \frac{[P_i]}{[T]} d[T] = \alpha_i \Delta[T] \qquad (4)$$

For the simple case where a product is totally unreactive, R_i = 0 and a plot of P_i vs. T will give a straight line with slope = α. For the case where the product does react further, the second term on the left hand side of eq. (4) corrects for this loss of product. The variation of o-cresol and of benzaldehyde for one of our experiments are shown in figures 3 and 4. This experiment was carried out by irradiating toluene and NO_2 each at about 4 ppm in a 250 L evacuable glass vessel with a mixture of fluorescent black lights and sun lamps.

The yield of each product may be determined from the slope of these plots. For benzaldehyde we obtain a 2.5 percent yield and for o-cresol a 5 percent yield. These yields are much lower than those measured by Hendry in his low pressure flow system.

We have been initially skeptical of our low yields, especially for o-cresol since it is about ten times lower than the yield reported by Hendry. To double check this result we have carried out experiments in which we start with a mixture of toluene and o-cresol (4 ppm and 1 ppm) respectively). The decay of o-cresol is then modified by formation of o-cresol from toluene. Equation (3) holds for any initial product concentration so we have plotted the data for this experiment in the required form in figure 5. The yield of o-cresol is found from the slope to be 5 percent, in agreement with the other experiments. This experiment has the advantage of generating a large

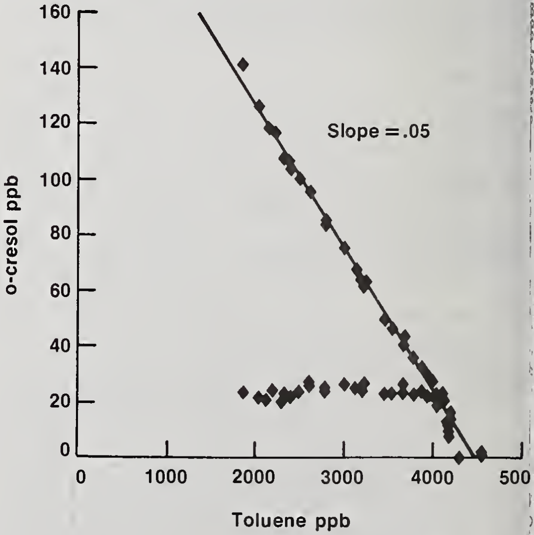


Fig. 3. Analysis of cresol formation from toluene. Lower data points are a plot of o-cresol vs. toluene. Upper data points with line are a plot of (C) + 6 ∫ (C)/(T) d(T) vs. (T) in accordance with eq. (s). (T = toluene; C = o-cresol).

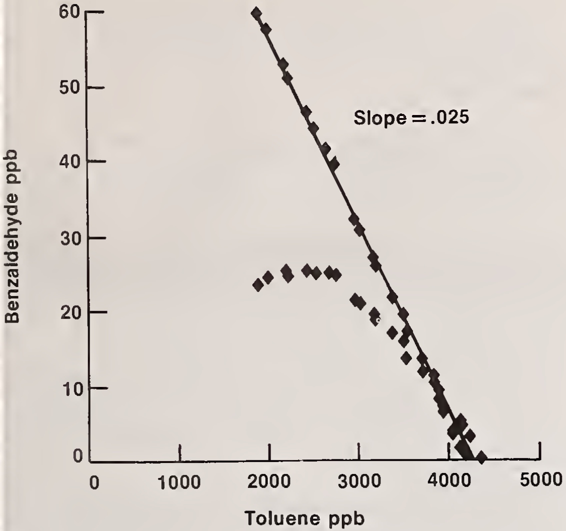


Fig. 4. Analysis of benzaldehyde formation from toluene. Lower data points are a plot of benzaldehyde vs. toluene. Upper data points with straight line are a plot of $(B) + 2.3 \int (B)/(T)\, d(T)$ in accordance with eq. (3). (T = toluene; B = benzaldehyde).

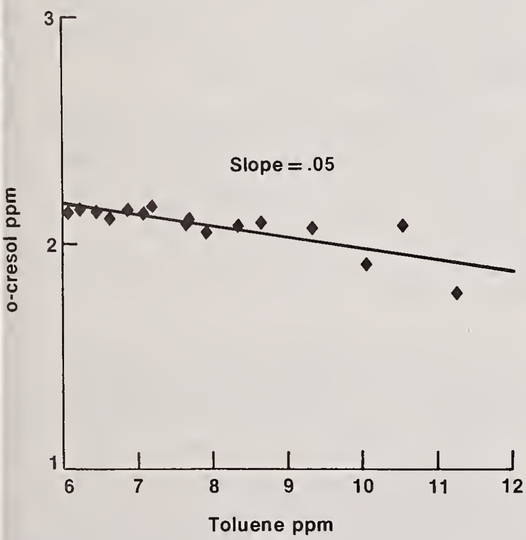


Fig. 5. Analysis of competitive disappearance of a mixture of 11 ppm toluene + 2 ppm o-cresol. Data plotted as $(C) + 6 \int (C)/(T)\, d(T)$ in accordance with eq. (3). (T = toluene; C = o-cresol).

unambiguous, initial cresol peak with the gas chromatograph.

We currently have no explanation for the lower product yields for toluene but the most obvious explanation would lie in the difference in pressure between the two measurements. Our yields of nitrotoluene are in agreement with those obtained from Hendry's work and would be negligible at sub ppm NO_2 concentrations. Our mass balance for gaseous toluene products is then well below 100 percent. The carbon balance may possibly be accounted for by aerosol analysis which we will do in the future.

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EES, Georgia Institute of Technology, Atlanta,
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We have noticed a decrease in the net rate constant for m-xylene (drops at lower pressures e.g. $\sim$ 3 Torr of Ar). In Hendry's experiments there could be an overemphasis on the abstraction route since his flow tube pressures are not very high.

Recommendations

Importance

Study of the atmospheric reaction processes of aromatic hydrocarbons is in its early stages. Our current knowledge about these compounds is rather primitive compared to the alkanes and alkenes. However, aromatics are major components of urban atmospheres and elucidation of their reaction pathways is essential for the following reasons.

1) Oxidant formation. As major urban hydrocarbons which react relatively rapidly with hydroxyl radical, aromatics will contribute directly to ozone formation and buildup and they seem to generate appreciable quantities of PAN, itself a harmful oxidant.

2) Direct health effects. Oxidant products of aromatic hydrocarbons are poorly characterized and present a potential health hazard of undetermined magnitude.

3) Aerosol formation. Gas phase mass balances for smog chamber experiments with aromatics are very poor and may indicate appreciable aerosol formation. If so, the aerosol so formed may contribute to a heterogeneous component of tropospheric chemistry which is currently unrecognized; this heterogeneous component may well impact other areas - in particular NO_x conversion to nitric acid or free radical loss processes.

Current Status

1) Rate constants. Considerable work has been done to determine the reaction rate constants for hydroxyl radicals with the chief aromatic constituents of the atmosphere. Agreement between various groups is quite good so this question is resolved. Ozone and other free radicals (HO_2, NO_3) are known to react slowly with aromatics and are therefore, at present of minor importance. Relative rates of ring addition versus side chain abstraction, while less certain than the overall rates, are also fairly well settled.

Rate constants for reaction of OH with some of the more important reaction products of aromatic hydrocarbons (cresols, benzaldehyde, etc.) have also been measured.

2) Product identification. Major products of the reaction of OH with toluene which have been identified are the following: cresols, nitrotoluenes, benzaldehyde, benzyl alcohol, benzyl nitrate, peroxybenzoyl nitrate, peroxyacetyl nitrate, and carbon monoxide. Yields of these compounds have been determined at low pressure and are becoming available at atmospheric pressure as well. Currently the low pressure yields are considerably higher on an absolute basis than those at high pressure, but on a relative basis are in good agreement. Products have been identified for the reactions of some other aromatics as well.

Products of the subsequent reactions of the primary products are known in a few cases.

The hydroxyl radical is a key component in controlling loss rates of the primary products but other processes, such as direct photolysis or reaction with O_3, RO_2, RO, NO_3, etc. may be important as well.

3) Ozone formation. Only a limited amount of work has been done on modeling the ozone profiles in aromatic/NO_x or mixed hydrocarbon/NO_x systems which include aromatics, because of the general lack of knowledge about the detailed reactions involved. However, the limited work done to date indicates that ozone profiles are different than those in nonaromatic systems and in some cases are difficult to model unless unique radical-radical reactions are invoked.

4) Analytical techniques. Current studies of aromatic hydrocarbon systems are severely hampered by a lack of versatile techniques for analyzing the high molecular weight products involved. Techniques which have been employed include gas chromatography, gas chromatography-mass spectrometry and to a limited extent Fourier transform infrared spectrometry. These techniques are difficult to employ when they are successful, and are often unsuccessful. Much time has been spent in adapting these techniques for use in the study of aromatic hydrocarbons, but they still suffer from some inherent problems.

Recommendations

1) Absolute yields of the major known primary products of aromatic-OH reactions should be determined at atmospheric pressure. These aromatics would include as a minimal set benzene, toluene, the xylenes, trimethyl benzene and some alkyl benzenes such as ethyl benzene.

2) Rate constants for the various processes these products undergo should be determined. Although a large number of compounds are involved, competitive kinetic studies employing several compounds simultaneously may suffice in some cases. This would reduce the total number of necessary experiments.

3) A carbon mass balance for the gaseous products including CO and CO_2 should be obtained for the major aromatics. The mass balance should include the carbon content of any aerosol formed.

4) New analytical techniques should be investigated for application to the study of aromatics. These techniques would be doubly useful because they would be equally applicable to the study of higher moleculas weight alkanes and alkenes. Techniques which might be investigated include improvement of gc sampling techniques and separation efficiency on the column, direct mass spectral analysis employing non-framentation ionization, liquid chromatography, and field desorption mass spectrometry.

In all these techniques every attempt should be made to work at realistic reactant concentrations and total pressures and to induce minimal sample alteration. However, some low pressure techniques may have to be employed (e.g., direct ms sampling) because of the lack of any other viable alternatives for direct analysis of intermediates. The current advancement of knowledge in this area is now limited by analytical methodology. Advancement of knowledge in the alkane and alkene systems will soon suffer the same fate, as the chemistry of the low molecular weight compounds becomes worked out, and higher members of the series are studied.

5) Heterogeneous processes may be of great importance in the aromatic hydrocarbon systems. The impact of these processes may well extend beyond the purely aromatic systems and influence the chemistry of NO_x and of free radicals generated from other classes of compounds. An attempt should be made to assess the significance of these processes on the overall chemistry of the troposphere.

6) Compouter modeling of the aromatic hydrocarbon system should be continued in order to assess the ozone forming potential of these hydrocarbons. It is expected that these modeling efforts will become more meaningful as more basic rate and product data become available.

Recommendations 1 to 3 may be expected to be completed with current funding in the next year or two. Recommendations 4 and 5 are much more ambitious and will require a long term committment and considerable additional funds for instrument development.

Session VI

SO_x Chemistry

SO_x CHEMISTRY

Jack G. Calvert

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An evaluation has been made of the existing kinetic data related to the elementary, homogeneous reactions of SO_2 within the troposphere. A set of recommended values of the rate constants for these reactions is presented. The results show that the direct photooxidation of SO_2 by way of the electronically excited states of SO_2 is relatively unimportant for most conditions which occur within the troposphere. The oxidation of SO_2 within the natural troposphere is expected to occur largely by way of reactions 39, 31, and 33, with reaction 39 being the dominant path: $HO + SO_2\ (+M) \rightarrow HOSO_2\ (+M)$ (39); $HO_2 + SO_2 \rightarrow HO + SO_3$ (31); $CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ (33). For certain special conditions within the troposphere the oxidation of SO_2 by way of the products of the ozone-olefin reaction may be significant. Also the reaction of $O(^3P)$ with SO_2 may contribute somewhat to the SO_2 removal in NO_2-rich, O_2-deficient stack gases in sunlight during the early stages of dilution of the plume.

The complete paper upon which most of the talk was based is: "Mechanism of the Homogeneous Oxidation of Sulfur Dioxide in the Troposphere", by Jack G. Calvert, Fu, Su, Jan W. Bottenheim, and Otto P. Strausz which appeared in the Preprint Volume I, Plenary Papers, International Symposium on Sulfur in the Atmosphere, July, 1977, and which was presented at the Symposium on September 7-14, 1977, Dubrovnik, Yugoslavia. The paper has been published in Atmospheric Environment, 12, 197 (1978).

Key words: Kinetics; photochemistry; review; sulfur dioxide; troposphere.

Summary of Session

The discussion was concerned with two basic problems - what is the mechanism of conversion of SO_2 in the atmosphere, and what do we know about aerosol formation arising from SO_x and NO_x reactions. There appeared to be a consensus that the reaction of SO_2 with OH is the most important homogeneous mechanism, but there is still great interest in quantifying the role of HO_2, RO_2, and the Criegee intermediate in this process. There is considerable experimental work underway on aerosol formation, the incorporation of NO_x in aerosols, and the role of specific radicals in aerosol formation.

Whitten opened the discussion with a descriptions of his modeling results for the Los Angeles basin. He pointed out that while OH levels could be reduced by reducing hydrocarbon or NO_x levels, they were relatively constant for a given HC/NO_x ratio. Thus if the reaction of OH with SO_2 controls the SO_2 level, control of the HC or NO_x levels will not necessarily have any affect on the OH levels if the HC/NO_x ratio remains fixed. A similar conclusion was reached in the case of HO_2 radical levels, although the new value for the rate of $NO_x + HO_2$ means that HO_2 levels are reduced to the point where the $HO_2 + SO_2$ reaction is probably unimportant.

Whitten also reported modeling studies which suggest that a fairly rapid conversion of SO_2 to sulfate takes place in fog droplets. The observations used in this study were based on one days sulfate collections from 14 monitor stations (24 hour averages). A photochemical model was not sufficient to account for the SO_2 conversion rate.

Miller reported on smog chamber results which supported Whittens observations. He also discussed measurements which show that the rate constant for $HO_2 + SO_2$ is no greater than 1 $ppm^{-1}\ min^{-1}$ and for $CH_3O_2 + SO_2$ is no greater than 2 $ppm^{-1}\ min^{-1}$. The role of NO_x in aerosol formation was also discussed.

Heicklen suggested that excited molecules such as NO_2, formed by irradiation at wavelengths above 400 nm, might react with SO_2. Also photo excited aldehydes and ketones might be important. Cox reported on the photolysis of HONO in the presence of SO_2. The end product was an aerosol. With added NO_x some of the NO_x was incorporated in the aerosol, but since NO_x can lead to aerosol formation without SO_2 being present, it was difficult to say how much of the lost NO_x was incorporated.

Jeffries reported smog chamber results on the effect of added CO on SO_2 conversion rates in natural background air, which indicate that OH is the only important oxidizing species for SO_2. Ravishankara noted that aerosols are readily formed in uv flashed H_2O-SO_2 mixtures, probably by photolysis of H_2O. Huie raised the question of the reactivity of the Criegee intermediate with respect to SO_2, pointing out that if the Criegee intermediate isomerized to a dioxirane intermediate it probably decomposes through a "hot" acid or ester before it has time to react with SO_2. However, Calvert noted, one would expect for larger olefins an increasing chance of stabilizing the Criegee intermediate and observing some direct chemistry.

Niki noted that generating HO_2 by reacting Cl with H_2 in the presence of O_2 and SO_2 led to H_2O_2 but no conversion of the SO_2. If NO was added (to drive the HO_2 to OH), then sulfuric acid aerosol is formed. In the case of CH_3O_2 some conversion of SO_2 is observed and there is evidence to suggest that sulfones are possibly formed. Jeffries asked if Niki has any evidence that water intercepted the Criegee intermediate to make acetic acid. Niki has not yet carried out an experiment with added H_2O. Jeffries noted that in earlier work they had not seen acetic but had seen formic acid in the reaction of ozone with propylene.

Comments

David F. Miller, Battelle-Columbus Laboratories, Columbus, Ohio 43201

Gary Whitten presented modeling results relating OH concentrations to initial concentrations of NMHC (nonmethane hydrocarbons) and NO_x. According to his model, OH concentrations are predicted to be nearly constant for any NMHC/NO_x ratio. I'd like to add that our smog chemaber results, reposted last year in Dubrovnik, led to the same conclusion. This finding has a very important implication regarding precursor controls designed for limiting ozone. Because SO_2 competes with NMHC and NO_x for OH, proportional control of NMHC and NO_x could result in an increase in the conversion of SO_2 to sulfate.

Secondly, I'd like to comment on some smog chamber experiments in which we've irradiated mixtures of nitrous acid with SO_2 and either CO or CH_4 to estimate the SO_2 oxidation rates attributable to HO_2 and CH_3O_2. Although our analyses of the data are less than satisfactory, primarily because of so much uncertainty about the nitrogen oxides chemistry, we estimate that the rate for $HO_2 + SO_2$ is not greater than 1 ppm^{-1} min^{-1} and the rate for $CH_3O_2 + SO_2$ is not greater than 2 ppm^{-1} min^{-1}

When we irradiate just SO_2 with nitrous acid we observe an NO_x loss in excess of that for the experiment without SO_2. The amount of the NO_x loss corresponds to the amount of H_2SO_4 formed. We suspected that either NO or NO_2 might be incorporated in the aerosol phase. It has been suggested, for example, that HSO_4 might react rapidly with NO_2 to give aerosol mixtures of sulfuric and nitric acids. However recent chemical analyses of filter collections from such reactions show very low nitrate levels relative to sulfate. Thus, if such reactions occur, the nitric acid apparently ends up in the gas phase.

The experiments were conducted with the following concentration ranges: SO_2 (400-500 ppb), HNO_2 (100-200 ppb), NO and NO_2 (20-200 ppb), CO (2-200 ppm) and CH_4 (200 to 900 ppm).

Richard A. Cox, U.K.A.E.A., Environmental and Medical Sciences, A.E.R.E, Harwell, Oxfordshire OX12 ORA, England

As part of an extensive research program on kinetics of reactions of SO_2 in the atmosphere, we have used the photolysis of HONO to produce OH radicals and allowed them to react with SO_2 at 25 °C and 1 atm pressure in air. We have drawn the following conclusions:

(a) Reaction of OH with SO_2 occurs with a rate constant of $\sim 6 \times 10^{-13}$ $cm^3 s^{-1}$

(b) This reaction proceeds by addition to give $HOSO_2$ and the subsequent radical chemistry leads to a short chain reaction in which NO is oxidized to NO_2. This chain reaction is inhibited by NO_2.

(c) The final reaction product is an aerosol, physically resembling model H_2SO_4 aerosols.

(d) In the NO_2 - inhibited system, the aerosol contains SO_x-NO_x species yielding equimolar proportions of SO_4^{2-} and NO_3^- on hydrolysis in water.

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In a series of experiments performed in UNC's outdoor aerosol chamber, SO_2 (at $\sim$ 0.3 ppm) oxidation in natural background air (< 20 ppb NO_x, < 50 ppb C organics) was followed by observing aerosol number (by CN), aerosol volume (by EAA), and aerosol sulfur content (by XRF analysis of filters). Runs were repeated with various additional amounts of CO added (5, 10, 15, 25 ppm). The additional CO resulted in delays in time of CN peak, small increases in O_3 produced, and reduced aerosol volume (by both EAA + XRF).

In one run, no CO was added initially, but when a steady rate of increase in aerosol volume had been established, 25 ppm of CO was injected; aerosol volume production (i.e. growth) was totally stopped within 4 minutes. CO's role in this otherwise low concentration system is to convert OH to HO_2. It seems clear that OH was by far the major oxidizing species. It is expected that under urban conditions, however, (i.e. higher NO concentrations) the effects of CO would not be observed because the higher NO converts HO_2 to OH.

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We have noticed formation of aerosols directly in our system when ∿ 300 mTorr of H_2O and SO_2 are photolyzed. This mechanism could be important where water concentrations are high i.e., very quick oxidation of sulfur dioxide leading directly to aerosol. (Even a mixture of SO_2, O_3 and H_2O gives aerosols). The water concentration needed to get this aerosol formation seemed rather magical - aerosols formed only after a critical amount of water was present.

Recommendations

It is recommended that kinetic and chemical data regarding SO_2 chemistry in the troposphere be obtained. The classes of reactions are of six types, with the first four of these being almost equally important.

1. Of most importance is obtaining both product and rate information of HO_xSO_2 and RO_xSO_2 with H_2O, NO_x, O_2, hydrocarbons, NH_3, and combinations of these gases.

2. Of essentially equal importance is obtaining information on the fate of SO_2 in O_3-olefin-O_2 reactions. There are three subsections of this problem which should be attacked in the following order:

    a) characterize the intermediates which which react with SO_2

    b) obtain products and rate coefficients for the reactions of these intermediates with SO_2

    c) study the effect of adducts such as H_2O, NO_x, hydrocarbons, NH_3, and combinations of these gases.

3. More data is needed on the rate coefficients (and products) for the reactions of HO_2, HO, and $O(^3P)$ with SO_2. These data should include pressure, temperature, and humidity studies. In the case of HO_2, there is a large uncertainty in the rate constant. With regard to HO and $O(^3P)$, fairly reliable values exist. However because of the importance of the HO radical, which appears to be the most important species for SO_2 removal, it is important to have as accurate a rate coefficient as possible.

4. The reactions of RO_2 radicals with SO_2 should be investigated to determine products and rate coefficients at a variety of pressures, temperatures, and humidities, and in the presence of NO_x, O_2, NH_3 and hydrocarbons. The reactions of RO radicals with SO_2 appear to be unimportant in the troposphere, and we do not give a high priority to their study. However it would be useful to actually have rate coefficients for RO reactions with SO_2 to know exactly what role these reactions do play.

5. A low priority recommendation is the study of the possible reaction of electronically excited NO_2 with SO_2. There is no evidence that a reaction occurs, but this should be confirmed.

6. The direct photoexcitation of SO_2 is not important in the removal of SO_2 in the troposphere, and we do not recommend studies in this area. However we do point out that such reactions may be important in the formation of sulfur-containing organic aerosols. If so then such reactions could be of significance in aerosol chemistry.

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This is a report of the proceedings of a workshop on chemical kinetic data needs for modeling the lower troposphere, held at Reston, Virginia, May 15-17, 19 The meeting, sponsored by the Environmental Protection Agency and the National Bureau of Standards, focussed on six key problem areas in tropospheric chemistry: reactions of olefins with hydroxyl radicals and ozone, reactions of aldehydes, free radical reactions, reactions of oxides of nitrogen, reactions of aromatic compounds, and reactions of oxides of sulfur.

The report includes a summary and list of major recommendations for further work, review papers, discussion summaries, contributed comments, recommendations, and an attendance list.

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