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NATIONAL BUREAU OF STANDARDS REPORT

6584

Heat of Formation of Tetrafluorohydrazine

by

George T. Armstrong, Sidney Marantz
and Charles F. Coyle

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Technical Report

to

U. S. Navy Bureau of Ordnance



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Thermodynamics Section
Heat Division

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Washington 25, D.C.

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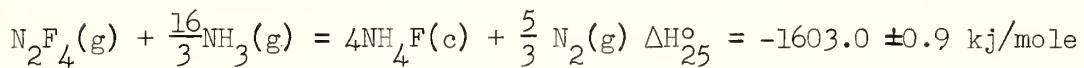
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Abstract

Heat of Formation of Tetrafluorohydrazine

By bomb Calorimetric experiments the heat of the reaction



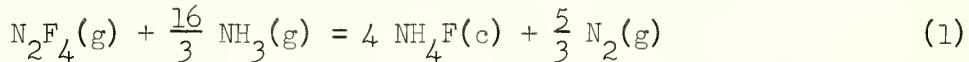
has been determined. When combined with known heats of formation and bond energies, this leads to $\Delta H_{25}^\circ [\text{N}_2\text{F}_4] = -2.0 \pm 2.5 \text{ kcal/mole}$ and $E(\text{N-F}) = 66.4 \pm 0.8 \text{ kcal/mole}$. The mean N-F bond energies in NF_3 and N_2F_4 are the same within experimental error.

1.0 Introduction

The heat of formation of N_2F_4 (Tetrafluorohydrazine) has not previously been determined. Small quantities of material of moderate purity have recently been prepared and, as part of a study of the N-F bond energy, have been made available for a determination of the heat of formation, by reactions which are discussed below. Because the purity of the material used is not high, the results reported here cannot be considered definitive. However, the results are still of interest because of the paucity of thermodynamic information on nitrogen fluorides and because of their applicability in the efforts of several groups working on the synthesis of compounds containing N-F bonds in one configuration or another. The work in the present report supplements recently reported work on the heat of formation of nitrogen trifluoride, carried out in this laboratory [1,2]¹. The present work is of more than ordinary interest because it demonstrates, with the use of reasonable assumptions, that there is little if any difference in the N-F bond energy in the two molecules which have been studied.

2.0 Experimental Procedures

The heat of reaction (1) between tetrafluorohydrazine and



ammonia, was carried out by bomb calorimetric experiments similar to those used for reaction (2) of the previous study on NF_3 [1,2]. No attempt was made to carry out reaction with hydrogen because of the limited amount of material available, because of the ambiguity of the results of the analogous reaction in the NF_3 experiments, and because the material had been reported to react spontaneously with hydrogen under some circumstances.

¹Numbers in brackets refer to references at the end of this report.

2.1 Calibration

The calorimeter was calibrated with benzoic acid (NBS Standard Sample 39h) in five experiments summarized in Table 1. The heating value used for the standardizing material was 26.4338 kj/gram mass (weight in vacuum). The final temperature to which the calibration is referred is 28°C. In Table 1, m_s is the mass of benzoic acid; ΔR_c is the corrected thermometer resistance change; and E_s is the energy equivalent of the standard calorimeter. The correction term, e , is the difference between the energy equivalent of the calorimeter as used in the calibration experiments and the standard calorimeter used for the combustion experiments. It includes heat capacity terms: 42 j/ohm for 1 ml of water, 15 j/ohm for the platinum crucible, 18 j/ohm for the benzoic acid pellet and 102 or 103 j/ohm for oxygen, all present in the calibration experiments, but not in the combustion experiments.

For each combustion experiment the energy equivalent of the actual calorimeter was obtained from the mean energy equivalent of the standard calorimeter by adding a term amounting to 34 j/ohm for the energy equivalent of the gases introduced into the bomb for the experiment. For this purpose the specific heat C_v of NH_3 was taken to be 28.47 j/mole deg [3] and that of N_2F_4 was estimated to be 63.5 j/mole deg by assuming a relationship between the heat capacities of N_2F_4 and NF_3 similar to that for N_2H_4 and NH_3 . For this purpose the heat capacity of NF_3 was estimated from vibrational spectra [4] and that of N_2H_4 was obtained from Audrieth and Ogg [5]. The value 135382 j/ohm was found for the energy equivalent of the calorimeter for all experiments.

Table 1

Calibration of Calorimeter				
Run	m_s g	ΔR_c ohms	e j/ohm	E_s j/ohm
1	1.52164	0.296817	-177	135416
2	1.52139	.296938	-177	135348
3	1.51903	.296473	-178	135345
4	1.52020	.296817	-177	135302
5	1.52007	.296724	-178	135331
Mean				135348 $\pm 19^a$
^a Standard deviation of the mean				

2.2 Materials

Six grams of tetrafluorohydrazine were made available for the experiments through the courtesy of W. D. Niederhauser and C. B. Colburn of the Rohm and Haas Company, Redstone Arsenal Research Division. The sample was purified by two bulb to bulb distillations and condensed in a spherical monel bulb suitable for weighing. Although not highly pure the sample was not further purified because of the small amount available. Mass spectrometer analysis² was performed before the experiments started and again at the end of five experiments. The first analysis showed the sample to contain, in mole per cent: N_2O , 1.0; NO_2 , 2.2; CF_4 , 0.12; CO_2 , 0.18; NF_3 , 0.92; SiF_4 , 1.2; N_2F_2 , 0.50; N_2F_4 , 93.88. The second analysis gave the same values with the following exceptions: SiF_4 , 0.80; N_2F_4 , 94.28. On the assumption that SiF_4 was gradually being absorbed by reaction with the vessel walls, the change was considered to be real. The per cent N_2F_4 in the sample was therefore computed for each experiment on the basis of a linear change in the SiF_4 content.

2.3 Experimental heat measurements

In these measurements, procedures were in most respects, the same as in the measurements on the reaction of NF_3 with ammonia, but with a few differences which may be mentioned.

The N_2F_4 was contained in a weighed bulb, and the weight of sample used was determined by weighing before and after loading the bomb. To avoid loss of the gas in the transfer lines after closing the bomb valve the weighing bulb was cooled in liquid nitrogen to condense all N_2F_4 before closing the weighing bulb. This method was found to give a more accurate measurement of the amount of N_2F_4 introduced than previous methods. No attempt was made to measure the amount of ammonia bound in the NH_4F crystals formed as a deposit on the bomb wall.

²Mass spectrometer analyses were performed by S. Schuhmann and S. Bremmer of the Molecular Structure and Properties of Gases Section.

However, an x-ray examination of these crystals³ confirmed that they were NH_4F , and showed no indication of other substances. The limit of sensitivity of the x-ray method is about 2 per cent.

Seven experimental measurements were made of the heat of reaction (1). The data obtained are shown in Table 2. Column (2) shows the mass of sample put into the bomb, and column (3) the number of moles of N_2F_4 (corrected for impurities). Column (4) is the observed mass of product, and column (5), the number of moles of NH_4F corrected for the amount expected from the impurities and divided by 4 to place it on a comparable basis with the N_2F_4 . Columns (6) and (7) are the measured quantities of NH_3 introduced, and recovered, which form the basis of the ammonia corrections. The ammonia decomposed in the course of the reaction is obtained by difference, account being taken of the ammonia required in the formation of the NH_4F . Column (8) is the corrected resistance thermometer change.

3.0 Calculation of Experimental Results

The calculated results of the measurements are shown in Table 3.

ΔE_b is the observed total energy change caused by the bomb reaction. Correction terms applied are: q_1 , the difference $\Delta H - \Delta E$ for the reaction; q_2 , the enthalpy correction to bring the reactants and products to unit fugacity in the ideal gas state; q_3 , a heat capacity correction to convert the reaction heat from 28° to 25°C; q_4 , the energy of the reactions of impurities; and q_5 or q_5' , the energy of decomposition of ammonia. The calculated amount of ammonia decomposed depends upon the amount of the principal reaction, and may be determined either from the mass of sample introduced, leading to correction q_5 , or from the mass of NH_4F observed, leading to correction q_5' . The heat of reaction, $(-\Delta H_{25}^{\circ})$, in joules per mole of reaction (1) is shown in column (9),

³X-ray examinations were carried out by H. E. Swanson of the Constitution and Microstructure Section of the Mineral Products Division.

for which the mass of N_2F_4 introduced is taken as the measure of the amount of reaction. In column (10) is shown $-\Delta H_{25}^{\circ}$ for reaction (1), in which the amount of reaction is determined from the weight of product.

In the calculation of the quantities q_1-q_5 , data for the thermal properties of the several substances involved were selected from the literature as before [1]. For N_2F_4 , the gas imperfections were estimated using the Berthelot equation of state. For this purpose the critical temperature was taken to be 309°K, and the critical pressure, 77 atm, as reported by Colburn [6]. C_p for N_2F_4 was estimated to be 71.9 j/mole deg (see Section 2.1). In calculating the quantity q_3 , the energy contributed by reactions of the impurities, oxides of nitrogen were presumed to form water, and fluorides were presumed to form NH_4F , except for SiF_4 . A separate experiment showed that SiF_4 reacts spontaneously with ammonia when mixed, depositing crystalline $SiF_4(NH_3)_2$, which was identified by its x-ray pattern. SiF_4 is therefore removed from the reaction zone. Further reaction of the product is not considered to be probable in the presence of excess ammonia.

The mean values of $-\Delta H_{25}^{\circ}$ shown at the bottom of Table 3 as calculated on these two bases, differ somewhat, and the measurements based on the mass of crystalline product show much greater variability than those based on the mass of N_2F_4 , as indicated by the standard deviations of the means. The difference, amounting to about one per cent could perhaps be accounted for by loss of NH_4F as dust and by vaporization during the flushing of the bomb prior to weighing, but the larger scatter of the measurements can hardly be accounted for in this way. Because of their greater internal consistency, the results based on mass of N_2F_4 introduced are considered to be more reliable and are used in the subsequent discussion.

Table 2

Experimental Results of Combustion Experiments

(1) Run No.	(2) Mass N_2F_4 g	(3) $n_1 \times 10^3$ moles reaction(1)	(4) Mass NH_4F g	(5) $n_2 \times 10^3$ moles reaction(1)	(6) $n_3 \times 10^3$ moles NH_3 introduced	(7) $n_4 \times 10^3$ moles NH_3 recovered	(8) $\Delta R_c \times 10^5$ ohms
1	0.81844	7.8684	1.1911	7.8631	97.72	17.20	8831.1
2	.71742	6.8972	1.0665	7.0464	98.29	8.41	7976.3
3	.77163	7.4184	1.0856	7.1781	97.09	13.18	8416.2
4	.75225	7.2321	1.0706	7.0842	96.14	12.24	8248.2
5	.78526	7.5494	1.1198	7.4156	93.01	17.16	8483.1
6	.71037	6.8294	1.0360	6.8662	93.76	9.69	7845.9
7	.57125	5.4919	0.8191	5.4333	90.71	2.94	6470.0

Table 3

Calculations of Combustion Experiments

(1) Run	(2) ΔE_b j	(3) q_1 j	(4) q_2 j	(5) q_3 j	(6) q_4 j	(7) q_5 j	(8) q_5' j	(9) $-\Delta H_{25}^\circ$ j/mole N_2F_4	(10) $-\Delta H_{25}^\circ$ j/mole N_2F_4
1	-11955.7	-38.1	-45.5	-1.9	240.6	-794.5	-795.8	1600.7	1602.0
2	-10798.5	-50.0	-39.3	-1.4	210.7	-388.6	-351.9	1604.6	1565.4
3	-11394.0	-43.5	-42.5	-1.4	226.4	-608.8	-668.0	1599.2	1661.0
4	-11166.4	-44.1	-41.4	-1.4	220.0	-565.3	-601.7	1603.8	1642.4
5	-11484.4	-35.4	-41.8	-1.8	230.1	-792.8	-825.8	1606.2	1639.7
6	-10621.9	-46.5	-37.5	-1.4	208.0	-447.4	-438.4	1602.9	1593.0
7	-8759.1	-50.1	-27.9	-0.8	167.1	-135.7	-150.1	1603.5	1623.5
Mean								1603.0	1618.1
Standard Deviation of the Mean								± 0.9	± 12.5



4.0 The Heat of Formation of N_2F_4

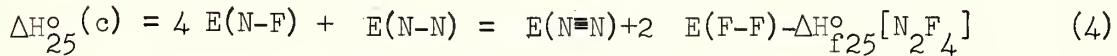
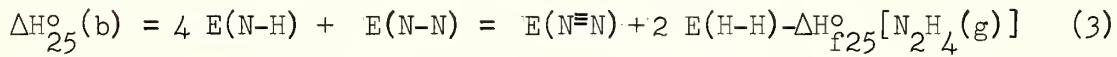
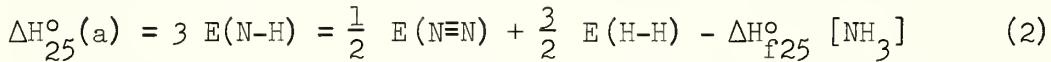
From the heat of reaction (1) it is possible to determine the heat of formation of N_2F_4 . The value -1603.0 ± 0.9 kJ/mole (-383.1 ± 0.2 kcal/mole) combined with $\Delta H_f^{\circ} \text{[NH}_3\text{(g)]} = -11.04 \pm 0.07$ kcal/mole [7], and $\Delta H_f^{\circ} \text{[NH}_4\text{F(c)]} = -111.0 \pm 0.6$ kcal/mole [8], leads to the value

$$\Delta H_f^{\circ} \text{[N}_2\text{F}_4\text{(g)]} = -2.0 \pm 2.5 \text{ kcal/mole.}$$

The principal part of the uncertainty comes from the heat of formation of $NH_4F(c)$. No other values for the heat of formation of N_2F_4 are available for comparison

5.0 Bond Energies in the N_2F_4 Molecule

In the discussion that follows, all values for bond energy, E , are given at 25°C. Using the assumption that $E(N-N)$ is the same in N_2F_4 and N_2H_4 , and that $E(N-H)$ is the same in NH_3 and N_2H_4 , it is possible from the following equations and appropriate auxiliary data to determine the energy of the N-F bond, $E(N-F)$ in N_2F_4 .





By combining relationships (2), (3), and (4) it can be shown that

$$\begin{aligned} E(N-F) = & \frac{1}{6} E(N \equiv N) + \frac{1}{2} E(F-F) - \frac{1}{4} \Delta H_f^{\circ} \text{[N}_2\text{F}_4\text{]} - \frac{1}{3} \Delta H_f^{\circ} \text{[NH}_3\text{]} \\ & + \frac{1}{4} \Delta H_f^{\circ} \text{[N}_2\text{H}_4\text{(g)}] \end{aligned} \quad (4)$$

Substituting the known values: $E(N \equiv N) = 225.92 \pm 0.1$ kcal/mole [9,7], $E(F-F) = 37.7 \pm 1.0$ kcal/mole [10], $\Delta H_f^{\circ} \text{[N}_2\text{H}_4\text{(g)}] = 22.75 \pm 0.13$ kcal/mole [11,12], $\Delta H_f^{\circ} \text{[NH}_3\text{]} = - 11.04 \pm 0.07$ kcal/mole [7], and $\Delta H_f^{\circ} \text{[N}_2\text{F}_4\text{]} = - 2.0 \pm 2.5$ kcal/mole, from the present work, we obtain for the mean N-F bond in N_2F_4 , $E(N-F) = 66.4 \pm 0.8$ kcal/mole. This may be compared with 66.4 ± 0.8 kcal/mole found previously for the mean N-F bond energy in NF_3 . The agreement is undoubtedly partly fortuitous, but lends support to the validity of the assumptions about the constancy of the N-N and N-H bond energies. The heat of formation of $\text{N}_2\text{H}_4\text{(l)}$ was obtained from the experimental determination by Hughes, Corruccini and Gilbert [11] of the heat of formation of liquid hydrazine, 12.050 ± 0.05 kcal/mole, the average of two values determined by different reactions. To obtain the heat of formation in the gas phase, the heat of vaporization $10.70 \pm .075$ kcal/mole determined by Scott, et al, [12] was used. This value was determined with considerably more attention to detail than previously reported values.

In a recent microwave spectroscopic study of N_2F_4 by Lide and Mann [13] the findings were consistent with the assumption that the N-N bond lengths in N_2F_4 and N_2H_4 are the same, and that the N-F bond lengths in N_2F_4 and NF_3 are the same. Thus the above finding about the energy of the N-F bond receives some support from the structure of the molecule.

6.0 References

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