samples were sealed in capillary tubes for n.m.r. examination. Samples of the *cis* isomer react slowly (completely in two weeks) with the glass with formation of silicon tetrafluoride and nitrous oxide. Samples of the *trans* isomer were essentially unchanged after a month in a sealed glass tube.

It also has been observed that mercury reacts much more rapidly with *cis*-N_2F_2 than it does with the *trans* isomer.

When heated, the *trans* isomer is converted into the *cis* isomer. In glass vessels the isomerization is accompanied by the formation of silicon tetrafluoride and nitrous oxide.

trans-N_2F_2 was found to isomerize in a heated copper tube with little or no side reaction. The isomerization occurred above 225° and as the temperature was increased the rate of the process increased, as expected. Above 300° decomposition to fluorine and nitrogen was extensive. Recoveries of N_2F_2 range from essentially quantitative at the low temperatures to about 60% at 300°. The *cis* isomer predominated at these temperatures.

To establish the existence of an equilibrium mixture of the isomers, mixtures of various compositions were passed through the copper tube at 285° with these results

	Initial % *trans* N_2F_2	Final % *trans* N_2F_2
Run I	90.5	13.3
Run II	59.4	12.7
Run III	2.0	13.7

These data obviously represent an equilibrium between the two isomers. An approximate value for the heat of isomerization is 27.5 ± 5.0 kcal./mole. The activation energy for this isomerization apparently is fairly high since only a small amount (1–2%) of isomerization takes place at room temperature during two weeks time.

An extremely interesting reaction of N_2F_2 is its catalytic effect on polymerization of various monomers. It has been observed that a pressure of 300 mm. of N_2F_2 over these monomers led to their polymerization in twelve hours or less at room temperature: methyl methacrylate, styrene and cyclopentadiene. Difluorodiazine also catalyzed the polymerization of tetrafluoroethylene at 125°. At temperatures in the neighborhood of 140° polymeric substances were formed in the presence of N_2F_2 with ethylene and propylene. These polymers are not, however, polyethylene and polypropylene since they contained fluorine.

Difluorodiazine was first reported by Haller[8] as arising from the thermal decomposition of fluorine azide. Bauer[5] reported that electron diffraction of this difluorodiazine indicated a mixture of *cis* and *trans* isomers.

Caution should be used in working with difluorodiazine in the presence of organic material and it never should be condensed into or onto organic material, as the danger of explosion is great. Mercury manometers should be protected with Kel-F[9] oils and hydrocarbon and silicon stopcock greases should be avoided in favor of Kel-F[9] stopcock grease.

(8) J. F. Haller, Ph.D. Thesis, Cornell University, 1942.

(9) Trade mark of Minnesota Mining and Manufacturing Co., Minneapolis, Minnesota.

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Heat of Formation of O_2F_2 and O_3F_2[1,2]

BY A. D. KIRSHENBAUM, A. V. GROSSE AND J. G. ASTON[3]

RECEIVED JUNE 4, 1959

A method has been developed for determining heats of formation of substances that decompose spontaneously below 0°. The heats of decomposition of liquid O_2F_2 and liquid O_3F_2 into gaseous oxygen and fluorine have been determined directly at temperatures of 190 and 121°K., respectively, by this method. From these values the heats of formation of the gaseous compounds at 298°K. have been calculated along with the relevant bond energies. A comparison of these bond energies with values in other compounds indicates considerable resonance stabilization. The heats of formation, $\Delta H_{298°K.}$ for O_2F_2 and O_3F_2 are $+4.73 \pm 0.30$ and $+6.24 \pm 0.75$ kcal./mole, respectively. The $\Delta H_{121°K.}$ of the reaction $O_3F_2(l) \rightarrow O_2F_2(l) + {}^1/_2O_2(g) = -1.91 \pm 0.15$ kcal./mole.

O_2F_2 has been known for some time[4] but proof of the existence of O_3F_2, its preparation and chemical and physical properties have only recently been reported.[5] O_2F_2 and O_3F_2 are stable below 195 and 120°K., respectively. At higher temperatures, however, O_2F_2 decomposes into $O_2 + F_2$ while O_3F_2 decomposes stepwise as

$$\begin{array}{l} O_3F_2 \longrightarrow O_2F_2 + {}^1/_2O_2 \\ \underline{O_2F_2 \longrightarrow O_2 + F_2} \\ O_3F_2 \longrightarrow 1{}^1/_2O_2 + F_2 \end{array}$$

This paper presents values of the heat of formation of O_2F_2 and O_3F_2 obtained by direct measurement of the heat of decomposition of the compounds into the elements.

Choice of Method.—In these studies it has been possible to use apparatus of an almost conventional sort by merely adapting the room temperature submarine calorimeter[6–8] for operation at rela-

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(1) Presented before the Physical Chemical Division at the Boston ACS Meeting, April 7, 1959.

(2) This work was financed by the Army Ballistic Missile Agency, Redstone Arsenal, Huntsville, Alabama.

(3) Dept. of Chemistry, The Pennsylvania State University, Consultant to the Research Institute.

(4) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **211**, 204 (1933).

(5) A. D. Kirshenbaum and A. V. Grosse, THIS JOURNAL, **81**, 1277 (1959).

(6) W. F. Giauque and R. C. Archibald, *ibid.*, **59**, 561 (1937) (see Fig. 4 of their paper).

(7) J. G. Aston and C. W. Ziemer, *ibid.*, **68**, 1405 (1946).

(8) F. T. Gucker, Jr., F. D. Ayres and T. R. Rubin, *ibid.*, **58**, 2118 (1936).

tively low temperatures (120 to 230°K.). The operation of a calorimeter of the conventional design requires a calorimetric fluid of low melting point and for this purpose dichlorodifluoromethane, CCl_2F_2 (Freon-12), was found to be ideal.

The procedure in these studies was to measure the heat content $\int C_p dT$ of the empty system from a temperature at which the compound was stable to one where the compound decomposed rapidly. A similar determination with a sample of the compound placed in the bomb portion of the calorimeter then was made. The difference between the two values, after suitable corrections and calculations, gave a direct value at either the initial or final temperature.

In this method it is necessary to have a bath surrounding the apparatus at approximately the mean temperature of the calorimeter. A Dry Ice–trichloroethylene bath (195°K.) was used for this purpose.

Preliminary results indicated values of 5 ± 2 kcal./mole and 10 ± 5 kcal./mole for $\Delta H_{298°K}$ for O_2F_2 and O_3F_2, respectively, and it seemed desirable to obtain values good to better than ±0.5 kcal./mole. It was impossible to keep the value of $\int C_p dT$ for the calorimeter below 4 kcal. and not practical to use over 0.08 mole of sample. Thus, the contribution of 500 cal. from the heat of decomposition to the total value of the energy added is 1%. However, using this type of apparatus, ΔH is determined for the two processes

$$O_2F_2(l) \longrightarrow O_2(g) + F_2(g) \text{ at } 190°K.$$

and

$$O_3F_2(l) \longrightarrow O_2F_2(l) + {}^1/_2O_2(g) \text{ at } 121°K.$$

To calculate values of ΔH at 298.16°K. for the processes

$$O_2F_2(g) \longrightarrow O_2(g) + F_2(g)$$

and

$$O_3F_2(g) \longrightarrow 1{}^1/_2O_2(g) + F_2(g)$$

requires a knowledge of the heat of vaporization of O_2F_2 and O_3F_2 and the heat capacity of O_2F_2. At present the heats of vaporization can only be estimated from Trouton's rule. The error introduced by this process is itself close to 500 cal.

If properly interpreted spectra were available for O_2F_2 and O_3F_2, gaseous heat capacities could be calculated to a far greater accuracy than needed. However, such data are not available and therefore a guided guess of the average heat capacities over the appropriate temperature range had to be made. In view of the possible errors introduced in the heats of vaporization, the error introduced by such a guess is not significant.

Since it is desirable to have these as the only sizable uncertainties, a higher accuracy than 1% in the measured values is necessary. It was decided to attempt to keep the experimental uncertainties to better than 0.2%. This accuracy was obtained as demonstrated by the determination of the enthalpy difference of carbon tetrachloride between 120 and 230°K., which includes the heat of transition. When the heats of vaporization and the other auxiliary data are better known, the experimental data presented in this paper should make it possible to obtain a value good to 0.2 kcal.

Method and Apparatus.—The calorimeter, as shown in Fig. 1, consisted of a copper bomb (A) which served as the reaction vessel (4 cm. in diameter and 16.5 cm. long) surrounded by Freon 12(dichlorodifluoromethane, m.p. 116°K., b.p. 243°K.) in a silvered dewar with an unsilvered strip for observation (5 cm. i.d. and 53 cm. deep) (B). The dewar, in turn, was surrounded by a Dry Ice–trichloroethylene bath (195°K.) in an insulated Plexiglas container (C). The copper bomb was connected through supports (E) to a rod (D) which passed through a stuffing box (F) which was part of the cover (G). The cover was bolted to a flanged rim of copper (H) which was cemented on to the top of the dewar (B). Through vertical motion of the rod, the bomb served as the calorimeter stirrer.

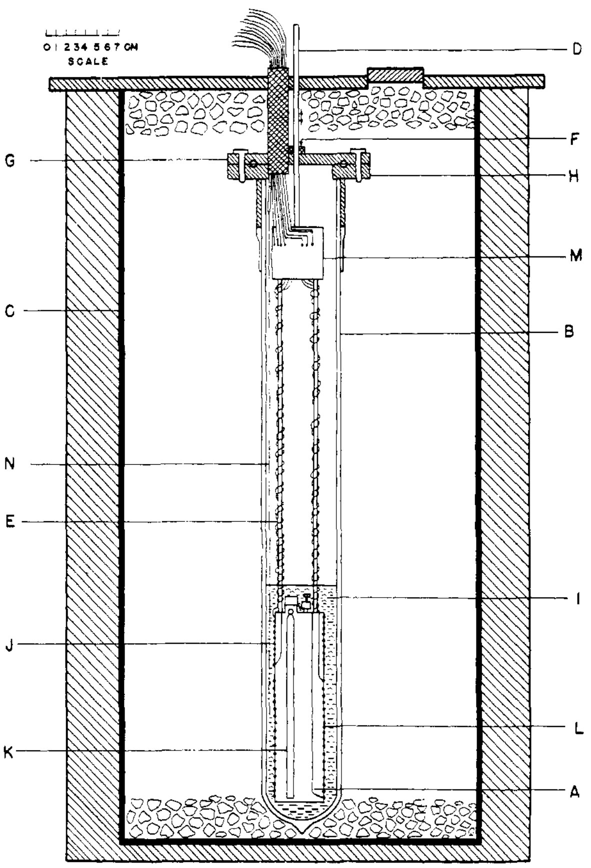

Fig. 1.—Calorimeter: A, copper bomb; B, dewar with unsilvered strip; C, insulated Plexiglas container, Dry Ice–trichloroethylene bath; D, stainless steel rod; E, bomb supports; F, stuffing box; G, cover of calorimeter; H, flanged rim; I, Freon 12; J, constantan heater; K, platinum sample tube; L, copper resistance thermometer; M, Bakelite block; N, copper–constantan thermocouple.

A fine cross was etched on the unsilvered part of the dewar which, along with a cathetometer having a precision of 0.1 mm., was used to read the level of the Freon 12(I), thus determining the amount of Freon in the calorimeter.

The heater (J) (25 ohms of No. 30 B. & S. constantan wire) was cemented on the upper third of the bomb (A) with potential leads taken out according to the compensating system. These leads were wrapped around the supports (E). The lower two-thirds of the reaction vessel was wrapped with a copper resistance thermometer (L) of No. 36 B. & S. copper wire with current and potential leads taken out at the reaction vessel. All leads terminate at terminals in a Bakelite block (M) just below the top of the calorimeter. These terminals are connected to the measuring apparatus by heavier wires. A standard copper–constantan thermocouple (N) was used to calibrate the copper resistance thermometer in place.

The copper–constantan thermocouple was read on a 100,000 microvolt range Leeds and Northrup White single potentiometer with a Leeds and Northrup Type R galvanometer (C.D.R.X., 50 ohms). The assembly was capable of measuring to 0.5 microvolt. The resistance thermometer was connected in series with a 10 ohm N.B.S. type standard resistor. A thermometer current of 1.7 milliamp. was used and the potential drop across the thermometer and the 10 ohm standard resistor was measured by means of the White single potentiometer. By use of a voltage divider and a 0.1 ohm Reichanstalt type standard resistor, the heater potential and current could be measured directly on the same White potentiometer.

Heat Leak Correction.—An exaggerated graph of the variation of the calorimeter temperature with time through a heating period is shown in Fig. 2. Curve "a" is the actual heating curve. Initially, when making the heat leak correction the difference in temperature between that indicated by curve "a" and the bath was multiplied by the Newton's Law Constant. This value together with a constant term which included the heat of stirring gave the heat leak per minute. This value was then integrated over the heating period.

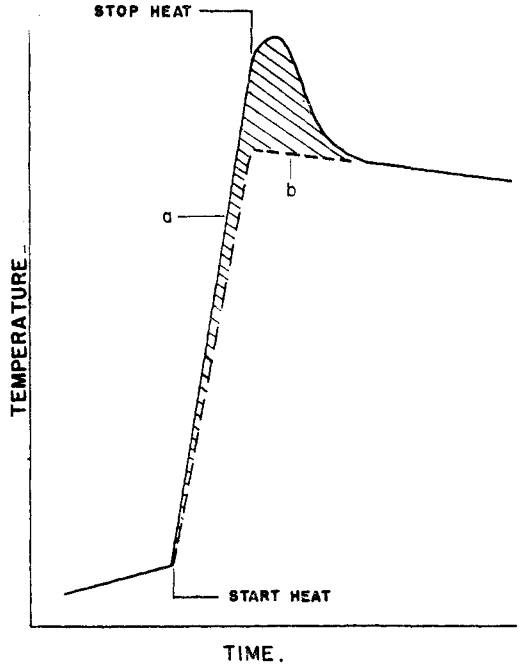

Fig. 2.—Heating period curve of calorimeter.

After several runs it was found that in the run with the empty calorimeter, the difference in the correction produced by using curve "b" in place of curve "a" was the same as in the corresponding run (*i.e.*, over the same temperature range) with the full calorimeter within experimental error. It was thus possible to make correction on the basis of the hypothetical curve "b" without any appreciable error. Since this method of correction involved much less labor, it was followed in later work.

Calibration of Calorimeter.—The heat capacity of the calorimeter was determined over the temperature range of 120 to 230°K. with a precision of better than 0.2%. For the empty calorimeter, the difference in enthalpy was 5,988.7 ± 7.5 cal. between the temperatures 121.00 and 186.00°K, and 4,145.5 ± 7.8 cal. between 190.00 and 230.00°K.

A check on the accuracy of the method was made by determining the heat content of two samples of CCl_4, one from 123.321 to 218.340°K. and the other from 124.060 to 237.263°K. including its heat of transition at 225.35°K. The experimental values found were 487 and 4,449 cal. for 0.232 and 1.194 moles, respectively. The values deduced from the accurate data of Hicks, *et al.*,[9] were 488.3 and 4,434.9 cal. for the above samples. This demonstrates an accuracy of better than 0.2% of the total heat input for the filled calorimeter which were 9,447.7 and 17,946.3 cal., respectively.

Handling of the Oxygen Fluorides.—The O_3F_2 and O_2F_2 had to be kept in a dry atmosphere since moisture would react with them to yield HF and correspondingly high values for the heat of formation. The O_3F_2 and the O_2F_2 were kept, respectively, below 90 and 116°K., to avoid thermal decomposition. They were transferred and weighed under similar conditions.

Results and Calculations

A. O_2F_2.—From the values shown in Table I, $\Delta E_{(1)}$ for the dissociation of one mole was found to be −1,120 ± 100 cal./mole for the reaction

$$O_2F_2(l) \longrightarrow O_2(g) + F_2(g) \text{ at } 190°\text{K.} \qquad (1)$$

Since O_2F_2 has a boiling point of 216.2°K., from Trouton's rule[10]

$$\Delta H_{\text{vap}} \simeq 216.2°\text{K.} \times 21.2 \text{ cal./°K.} = 4583 \pm 100 \text{ cal.}$$
$$\Delta E_{\text{vap}} = 4583 - RT\,(T = 190°\text{K.})$$
$$= 4205 \pm 100 \text{ cal./mole}$$

For the reaction

$$O_2F_2(g) \longrightarrow O_2(g) + F_2(g) \text{ at } 190°\text{K.} \qquad (2)$$
$$\Delta E_{(2)} = \Delta E_{(l)} + \Delta E_{(\text{vap.})} = -5324 \pm 200 \text{ cal./mole}$$

Taking the mean C_v for both O_2 and F_2 as 5 cal./mole°K., and assuming a mean C_v of 10.0 ± 1 cal./mole°K. for O_2F_2 which was estimated from a guess at the vibrational assignment, then

$$\Delta C_v = 5 + 5 - 10.0 = 0$$

At 298°K., the heat of reaction is

$$\Delta E_{298°\text{K.}} = \Delta E_{(2)} + \Delta C_v\,(298 - 190°\text{K.}) \qquad (3)$$
$$= -5324 \pm 300 \text{ cal./mole}$$
$$\Delta H_{298°\text{K.}} = \Delta E_{298°\text{K.}} + \Delta nRT \qquad (4)$$
$$= -4728 \pm 300 \text{ cal./mole}$$

since $\Delta n = 1$. Therefore, for the heat of formation from the elements

$$F_2(g) + O_2(g) \longrightarrow O_2F_2(g) \text{ at } 298°\text{K.}$$

the sign of ΔH is reversed and $\Delta H_{298°\text{K.}}$ becomes 4.73 ± 0.30 kcal./mole.

B. O_3F_2.—Ozone fluoride decomposes stepwise to its elements

$$O_3F_2 \longrightarrow O_2F_2 + {}^1/_2O_2 \qquad (5)$$
$$O_2F_2 \longrightarrow O_2 + F_2 \qquad (6)$$
$$O_3F_2 \longrightarrow 1{}^1/_2O_2 + F_2 \qquad (7)$$

The heat of formation of O_3F_2 was determined by measuring the heat evolved in reaction 5 and com-

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(9) J. F. G. Hicks, J. G. Hooley and C. C. Stephenson, THIS JOURNAL, **66**, 1065 (1944).

(10) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **217**, 85 (1934)

TABLE I

ΔE for $O_2F_2(l) \rightarrow O_2(g) + F_2(g)$ at 190°K.

Run no.	1	2	3	4	5	6
Wt. of O_2F_2, g.	5.468	3.968	5.923	4.246	5.082	3.537
Moles O_2F_2	0.07811	0.05669	0.08462	0.06066	0.07260	0.05053
Heat input, empty calorimeter, cal.	4145.5 ± 8	4145.5	4145.5	4145.5	4145.5	4145.5
Heat input, filled, cal.	4057.5 ± 8	4083.0	4050.1	4079.2	4064.4	4087.5
Empty-filled, cal./sample	88.0	62.5	95.4	66.3	81.1	58.0
$\Delta E_{(1)}$, cal./mole	1130 ± 100	1100	1130	1090	1120	1150

TABLE II

ΔE for $O_3F_2(l) \rightarrow O_2F_2(l) + {}^1/_2O_2(g)$ at 121°K.

Run no.	1	2	3	4
Moles O_3F_2	0.05060	0.05066	0.04678	0.05053
Heat input, empty calorimeter, cal.	5988.7 ± 7	5988.7	5988.7	5988.7
Heat input, full calorimeter, cal.	5885.4 ± 7	5881.2	5896.0	5886.9
Empty-full, cal./sample	103.3	107.5	92.7	101.8
$\Delta E_{(8)}$, cal./mole	2040 ± 150	2120	1980	2010

bining it with the values found in the previous section for reaction 6. From the values shown in Table II, $\Delta E_{(8)}$ for the reaction

$$O_3F_2(l) \text{ at } 121°\text{K.} \longrightarrow O_2F_2(l) + {}^1/_2O_2(g) \text{ at } 121°\text{K.} \quad (8)$$

was calculated to be −2040 ± 150 cal./mole.

To obtain the heat of the reaction

$$O_2F_2(l) \longrightarrow O_2(g) + F_2(g) \text{ at } 121°\text{K.} \quad (9)$$

from the value of 190°K., the specific heat of the liquid O_2F_2 was required as well as the values for gaseous O_2 and F_2. Using the same apparatus, the average specific heat of the liquid O_2F_2 was determined for three samples of O_2F_2 over the temperature range of 121 to 186°K. and was found to be −24.5 ± 0.7 cal./mole°K.

Using the average C_v for both O_2 and F_2 as 5 cal./mole°K., that for $O_2F_2(l)$ as 24.5 ± 0.7 cal./mole°K., and $\Delta E_{(1)}$ equal to −1,120 ± 100 cal./mole for the reaction

$$O_2F_2(l) \longrightarrow O_2(g) + F_2(g) \text{ at } 190°\text{K.}$$

$$\Delta E_{(9)} \text{ at } 121°\text{K.} = \Delta E_{(1)} - \Delta C_v\,(190 - 121°\text{K.}) = -120 \text{ cal./mole}$$

For complete decomposition of O_3F_2 to the elements at 121°K.

$$O_3F_2(l) \longrightarrow 1^1/_2O_2(g) + F_2(g) \text{ at } 121°\text{K.} \quad (10)$$

$$\Delta E_{(10)} = \Delta E_{(8)} + \Delta E_{(9)} = -2160 \pm 250 \text{ cal./mole}$$

If O_3F_2 did not decompose its boiling point would be approximately that of O_2F_2. Using Trouton's rule

$$\Delta E_{(\text{vap})}\ O_3F_2 = -4341 \pm 200 \text{ cal./mole at } 121°\text{K.}$$

Therefore, for the reaction

$$O_3F_2(g) \longrightarrow 1^1/_2O_2(g) + F_2(g) \text{ at } 121°\text{K.} \quad (11)$$

$$\Delta E_{(11)} = \Delta E_{(10)} + \Delta E_{\text{vap.}} = -6500 \pm 450 \text{ cal./mole}$$

Taking the mean C_v for $O_2(g)$ and $F_2(g)$ as 5.0 cal./mole°K. and assuming a C_v of 16.0 ± 1.5 cal./mole°K. for $O_3F_2(g)$, then for the above reaction at 298°K.

$$\Delta E_{298°\text{K}} = \Delta E_{11} + \Delta C_v\,(298 - 121°\text{K.}) = -7130 \pm 750 \text{ cal./mole}$$

$$\Delta H_{298°\text{K}} = \Delta E_{298°\text{K.}} + \Delta nRT \text{ where } \Delta n = 1^1/_2 = -6240 \pm 750 \text{ cal./mole}$$

Therefore, for the heat of formation

$$F_2(g) + 1^1/_2O_2(g) \longrightarrow O_3F_2(g) \text{ at } 298°\text{K.}$$

the sign is reversed and

$$\Delta H \text{ at } 298°\text{K. becomes } 6.24 \pm 0.75 \text{ kcal./mole}$$

Discussion

Using the value found for the heat of formation of O_2F_2 (4.73 kcal./mole) and taking the heats of dissociation of O_2 into 2O and F_2 into 2F as 118.4[11] and 37.8[12] kcal./mole, respectively, the heat of dissociation of O_2F_2 into atoms of O + F was calculated to be 151.5 kcal./mole.

In order to dissociate O_2F_2 into atoms, two O–F and one O–O bond have to be split. Evans, Munson and Wagman[12] reported the best value for the heat of formation of OF_2 as −7.6 ± 2 kcal./mole. Using this value, the heat of atomization of OF_2 becomes 89.4 kcal./mole. Assuming that the energy to split an O–F bond equals one-half of the energy needed to split OF_2 into O + 2F, the energy to split the O–O bond in F–O–O–F is calculated to be 62.1 kcal.

It was shown experimentally that the heat of decomposition of the reaction

$$O_3F_2(l) \longrightarrow O_2F_2(l) + {}^1/_2O_2(g) \text{ at } 121°\text{K. or } \Delta H_{121°\text{K.}} = -1.91 \pm 0.15 \text{ kcal./mole}$$

This required the splitting of two O–O bonds, and then the formation of a new O–O bond and the elimination of one O-atom. Using the above ΔH value coupled with $^1/_2$ the heat of dissociation of O_2 (59.2 kcal.), the energy to split an O–O bond in O_3F_2 = 61.1 kcal. This is ~ 12 kcal. higher than the value for H_2O_2 (48–50 kcal.).[13,14] Infrared data have been obtained by Dr. Harmon Brown[15] and showed that O_2F_2 has an H_2O_2 type structure. The calculated force constants, however, indicated that the O–O bond was weaker than in H_2O_2. For ready reference Dr. Brown's data on O_2F_2 and data on H_2O_2 are given in Table III.

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(11) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, N.B.S., Circ. 500, p. 8, 1952.

(12) W. H. Evans, T. R. Munson and D. D. Wagman, *J. Research Natl. Bur. Standards*, **55**, 147 (1955).

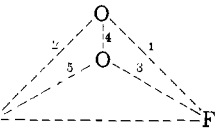
(13) P. A. Giguère, *J. Chem. Phys.*, **30**, 322 (1959).

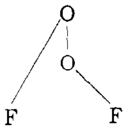
(14) L. P. Lindeman and J. C. Guffy, *ibid.*, **30**, 322 (1959).

(15) Infrared absorption spectra was determined at the authors' request by Dr. Harmon Brown of the National Bureau of Standards and will be published by him shortly.

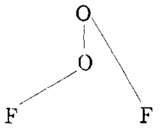
This is contrary to our experimental data. The only way to account for these facts is that there has to be a resonance involving all the bonds of the O_2F_2 structure.

The only possible conclusion is that the structure is not exactly like that of H_2O_2. Using a general tetrahedral structure in which the central O-atom is above the plane of the paper, three structures are possible, namely where the bonds 2, 3 and 4 in (A), 1, 4 and 5 in (B) and 3 and 5 in (C) are the usual covalent bonds; while bond 4 in (C) is a coördinate covalent link. Structures (A) and (B) are slightly distorted H_2O_2 structures and, if they exist, would decompose into F_2 and O_2. Structure (C) (if it exists) would also decompose into O_2 and F_2 just as COI_2 decomposes into CO and I_2. If the structure is a resonance hybrid of (A), (B) and (C), the observed decomposition into O_2 and F_2, the lower heat of formation value and the infrared data would be explained. This also would explain the lowering of O–O force constant.

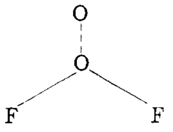




(A)



(B)



(C)

TABLE III

COMPARISON OF O_2F_2 AND H_2O_2

	Force constants in millidynes/Å. K_{FO}	K_{OO}	K_{HO}
O_2F_2	5.2	2.9	..
H_2O_2	..	3.6	6.5

It is premature to write the structure for O_3F_2; however, its structure would involve resonances of the type just outlined. With this type of structure, the apparently surprising stability of this compound would seem reasonable.

Acknowledgment.—The authors wish to thank Dr. Harmon Brown of National Bureau of Standards for determining the infrared spectra for O_2F_2.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AND STANFORD UNIVERSITY]

Heat of Formation of Nitrosyl Fluoride[1]

BY HAROLD S. JOHNSTON AND HENRY J. BERTIN, JR.

RECEIVED JUNE 1, 1959

The reaction between nitric oxide and fluorine, $2NO + F_2 = 2ONF$, is very fast, complete and quantitative. The heat of the reaction was determined ($-\Delta H^0_{298} = 74.8$ kcal./mole) by mixing the diluted gaseous reactants in a calorimeter under conditions of steady flow. From this value and other thermodynamic quantities from the literature, the standard enthalpy of formation of nitrosyl fluoride is -15.8 kcal. and the dissociation energy for the reaction $ONF = NO + F$ is 55.4 kcal. The "reorganization energy" for the NO radical in going from nitrosyl fluoride to the free molecule nitric oxide is about 9 kcal.

Ruff, Menzel and Newman[2] and Faloon and Kenna[3] have found that nitric oxide and fluorine react rapidly to produce nitrosyl fluoride. In dry systems with fluorinated nickel surfaces the reaction is quantitative and complete as written

$$2NO + F_2 = 2ONF \qquad (1)$$

In the presence of moisture, glass, copper oxide, etc., nitrogen dioxide and nitryl fluoride may be formed as side products. In an effort to measure the rate of reaction of nitric oxide and fluorine in a flow system with fast mixing, it was found that the reaction was much faster than such a system could handle and that it was chemiluminescent.[4] The very high rate and luminosity suggested a rate study by Polanyi's method of the diffusion flame,[5] and such a study is now in progress. The mechanism which seems probable for this situation is

$$NO + F_2 = ONF + F \qquad (2)$$

$$NO + F \rightleftarrows ONF^* \longrightarrow ONF + h\nu \qquad (3)$$

$$NO + F + M \longrightarrow ONF + M \qquad (4)$$

In order to get some insight into the meaning of the observed cold flame, into the magnitude of heat release and into the possible endothermic nature of reaction 2, a study was made of the absorption spectrum of nitrosyl fluoride, the flame spectrum from this reaction and the heat of reaction of nitric oxide and fluorine. This article describes the determination of the heat of reaction between nitric oxide and fluorine.

Experimental

Apparatus.—The apparatus consisted of a vacuum jacketed calorimeter, a system for storing and measuring the pressure of the reactants and a vacuum system for pumping the gases through a reaction cell and heat exchange coil immersed in the calorimeter. The calorimeter was a one gallon dewar flask, loaded with two kilograms of water and equipped with a stirrer and insulation on top. Temperature measurements were made with a Beckmann thermometer, calibrated between 21.5 and 26.5°. The effective heat capacity of the calorimeter was determined from the heat of solution of potassium chloride.[6,7]

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[1] Submitted to the committee on graduate study of Stanford University in partial fulfillment of the requirements for the Ph.D. degree by Henry J. Bertin, Jr., 1957.

[2] O. Ruff, W. Menzel and W. Newman, *Z. anorg. Chem.*, **208**, 293 (1932).

[3] A. V. Faloon and W. B. Kenna, THIS JOURNAL, **73**, 2937 (1951).

[4] H. S. Johnston and D. R. Herschbach, Nat. Meeting of A.C.S., New York, 1954.

[5] M. Polanyi, "Atomic Reactions," Williams and Norgate, London, 1932.

[6] W. P. White, "The Modern Calorimeter," Chemical Catalog Co., New York, N. Y., 1928.

[7] Rossini, Wagman, Evans, Levine and Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular 500 of N.B.S., U. S. Govt. Printing Office, Washington, D. C., 1952.