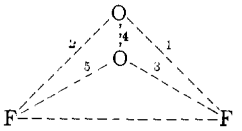
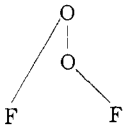
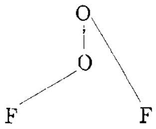
This is contrary to our experimental data. The only way to account for these facts is that there has to be a resonance involving all the bonds of the O_2F_2 structure.

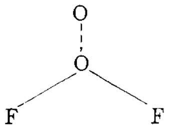
The only possible conclusion is that the structure is not exactly like that of H_2O_2. Using a general tetrahedral structure in which the central O-atom



is above the plane of the paper, three structures are possible, namely


(A)


(B)


(C)

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.

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.

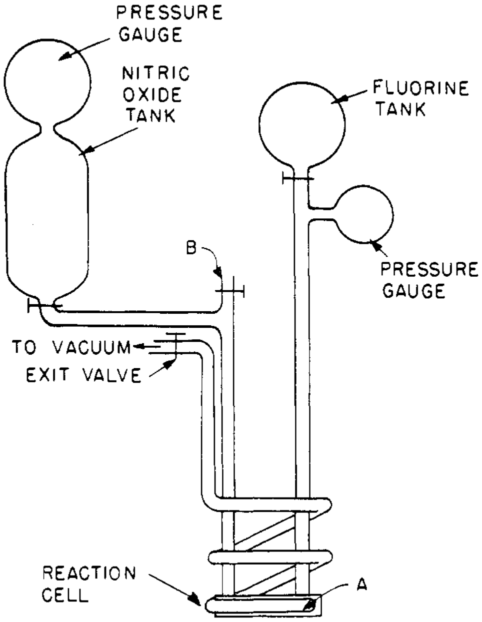

Fig. 1.

The flow system and reaction cell are illustrated by Fig. 1. Fluorine (Penn. Salt Co.) was stored in a 1.582-liter stainless steel tank equipped with a Teflon packed needle valve. Nitric oxide was stored in a 34.4-liter stainless steel tank. Pressure was measured by a 30 cm. diameter gauge (Crosby, Boston) which read 0 to 30 inches of mercury. It was calibrated against a mercury manometer, and it could be read accurately to 0.05 inch (1.3 mm.). The leads to the calorimeter and the heat exchange coil were 6.35 mm. nickel tubing, and the reaction cell was 12 mm. nickel tubing, closed at each end. The tubing and the reaction cell were joined by gold solder. Gases, including diluent nitrogen, were introduced at "B" in Fig. 1. Flow rates were controlled by the exit valve, and the reacted gases were passed through a liquid nitrogen trap. When fluorine alone was pumped out of the system, it was sent through a heated (100°) tube of rock salt, to protect the vacuum pump.

Reactants.—Nitric oxide was prepared by the iodide reduction of nitrite, and it was purified in the usual manner.[8]

In these determinations, fluorine was always the limiting reagent. Its quantity was found by measuring the pressure of a tank of known volume, and molar quantities were obtained by use of the perfect gas equation. It was important to check the mole number obtained this way against a chemical analysis, and at the same time check the purity of the fluorine (stated to be 98% or better by the manufacturers). The tank was filled with fluorine and its pressure read, as in a run, and the contents were slowly drawn through a copper tube filled with rock salt at 100° (and previously saturated with chlorine to prevent loss of fluorine or chlorine to the metal). The fluorine thus freed its equivalent of chlorine which was absorbed in sodium hydroxide solution, reduced to chloride by nitrite, neutralized, cleared of excess nitrous acid by boiling and titrated by the Mohr method for chloride ion.[9]

The purity of fluorine, assuming accuracy of pressure-volume measurements, was found to be 98.9%. In subsequent calculations, the content of the fluorine bulb was regarded as 98.9% fluorine and 1.1% oxygen. Oxygen reacts relatively slowly with nitric oxide and contributes a very small correction factor.

Procedure.—Nitric oxide was stored in its tank at a measured pressure, and the lines were pumped out. Fluorine was placed in its tank, and the lines evacuated. Nitrogen was added to each tank to the same total pressure and sufficient time allowed for complete mixing by diffusion. A weighed quantity of water, about 2 kg., at 24° was added to the calorimeter; room temperature was always between 25 and 27°; and readings of the thermometer were taken every minute for 10 minutes. With the exit valve closed, the valve to the nitric oxide tank was opened, then the valve to the fluorine tank was opened, and the flow was controlled by opening the exit valve. The reactants flowed through the system for about 10 minutes and a desired amount of reaction was attained by controlling the rate of pressure drop. The reactant tanks were sealed off by their valves, and the lines were pumped free of gases. The final pressures of reactants were determined. Temperature readings were made every minute during the reaction and for a 10 minute period following it.

In making calculations, it was assumed that reactants flowed into the calorimeter at room temperature and out of the calorimeter at the calorimeter temperature. A small correction was applied to the difference in heat capacity between reactants and products.

Results

The first determinations of the heat of reaction were made by using equal pressures of fluorine and nitric oxide in 1.6 and 12 liter storage tanks, respectively. This arrangement gave a 5.5-fold dilution factor for the fluorine. The apparent value for the heat of reaction was found to be around 124 kcal./mole, much higher than expected. By increasing the size of the nitric oxide storage tank and diluting the gases with nitrogen, it was possible to determine the apparent heat of reaction as a function of the dilution factor from fivefold to ninety-fold dilution; the dilution factor is defined as the number of moles of nitrogen plus nitric oxide per mole of fluorine before reaction occurred. The apparent value of the heat of reaction is plotted against the dilution factor in Fig. 2. The apparent value of ΔH falls rapidly with increasing dilution at low dilutions, but it is constant between factors of 40 and 90. It is assumed that the steady value at high dilutions is the true heat of reaction; in these terms an explanation for Fig. 2 is readily given. The calculated adiabatic temperature as a function of dilution factor is given in Table I. The exothermic heat of reaction 4 is calculated

$$2ONF + Ni = NiF_2 + 2NO$$

to be 85 kcal./mole. Due to heat conduction the temperature will be lower than the adiabatic value. Nevertheless, it is certain that at low dilutions high temperatures are encountered, and secondary reactions occur. Fluorinated nickel tubing is stable against nitrosyl fluoride even at 200° (and probably somewhat higher). Thus the effect of reaction 4 is negligible at 40-fold and higher dilution.

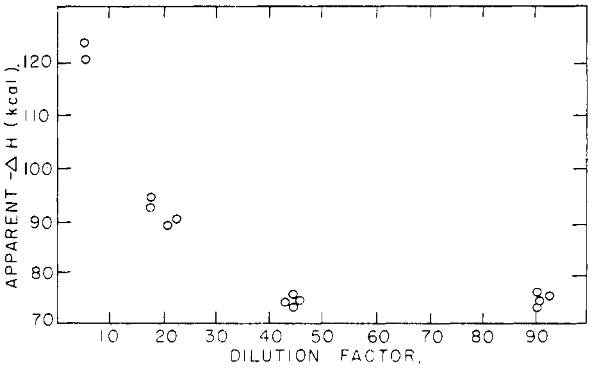

Fig. 2.

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[8] H. L. Johnston and W. F. Giauque, THIS JOURNAL, **51**, 3194 (1929).

[9] E. H. Swift, "Intro. Quant. Analysis," Prentice-Hall, New York, N. Y., 1950.

TABLE I

CALCULATED ADIABATIC TEMPERATURES

Dilution factor[a]	Adiabatic temp., °C.
5.5	1200
18	500
43	250
93	140

[a] Dilution factor DF is defined as number of moles of nitrogen plus nitric oxide per mole of fluorine before reaction occurred.

All determinations of the heat of reaction 1 at dilution factors of 40 or more are listed in Table II, together with pressure measurements, temperature changes in the calorimeter, moles of fluorine, and an estimate of error based on limits of accuracy of pressure and temperature readings. For reaction 1 the value obtained is $-\Delta H^0_{298} = 74.8 \pm 0.8$ kcal./mole.

TABLE II

DATA FOR THE DETERMINATION OF THE HEAT OF REACTION OF $2NO + F_2 = 2ONF$ AT 298°K.

P_{F_2}, mm.	n_{F_2}, moles $\times 10^2$	Dilution factor	Obsd. ΔT	$-\Delta H^0_{298}$	Calcd. % error in ΔH
175.0	1.465	43	0.515	74.5	1.2
123.9	1.037	93	.368	75.1	1.4
176.3	1.479	45	.527	75.5	1.2
126.3	1.059	91	.379	75.7	1.3
280.4	2.345	45	.827	74.7	0.6
276.3	2.316	45	.814	74.4	0.6
154.8	1.296	91	.462	74.7	1.0
151.3	1.268	91	.450	74.4	1.0
			Av.	74.8 ± 0.8	

Discussion

By accepting these values for the standard enthalpy changes at 298°K.

$$NO + {}^1/{}_2F_2 = ONF \qquad \Delta H^0 = -37.4 \text{ kcal., this work}$$

$$^1/_2N_2 + {}^1/_2O_2 = NO \qquad \Delta H^0 = 21.6 \text{ kcal., ref. 7}$$

$$^1/_2F_2 = F \qquad \Delta H^0 = 18 \text{ kcal., ref. 10}$$

one can obtain the standard heat of formation of nitrosyl fluoride

$$^1/_2N_2 + {}^1/_2O_2 + {}^1/_2F_2 = ONF \quad \Delta H^0 = -15.8 \text{ kcal.}$$

and the heat of dissociation of the NF bond

$$ONF = NO + F \quad \Delta H^0 = 55.4 \text{ kcal.}$$

A comparison is made between nitrosyl fluoride and other nitrosyl halides in Table III.

As is well known, the dissociation energy and average bond energy may differ for polyatomic molecules, by virtue of the "reorganization energy" of the residual radical or radicals.[14] The dissociation energy of $NF_3 = NF_2 + F$ is not to be taken as the normal NF single bond energy, because the free NF_2 may be more or less stable than NF_2 in NF_3. For reference purposes the normal single bond energy for NF is one-third the complete dissociation of NF_3 to N and 3F. The dissociation energy of the N–F bond in nitrosyl fluoride is 55.4 kcal., about 9 kcal. less than the single bond in nitrogen trifluoride. The interpretation of this effect is that the NO radical in ONF is about 9 kcal. less stable than it is as a free molecule. The odd electron shared with F becomes an extra half-bond (more or less) in the free nitric oxide molecule, with a gain of about 9 kcal. By extending this value to nitrosyl chloride and nitrosyl bromide, one concludes that the NCl single bond energy is about 47 kcal., and the NBr single bond energy is about 37 kcal.

TABLE III

THERMOCHEMICAL DATA AT 298°K. FOR THE NITROSYL HALIDES AND NITROGEN TRIFLUORIDE

Compound	Heat of formation Δ_fH^0, kcal./mole	Heat of dissociation of N–X, kcal./mole	Ref.
ONF	−15.8	55.4	
ONCl	12.57	38.0	11
ONBr	19.56	28.7	12
NF_3	−27.2	64.6[a]	13

[a] The average bond energy or one-third the dissociation energy of $NF_3 = N + 3F$.

The energies of reactions 2 and 4 can be evaluated

$$NO + F_2 = ONF + F \quad \Delta H^0_{298} = -19.4 \quad (2)$$

$$NO + F = ONF \quad \Delta H^0_{298} = -55.4 \quad (4)$$

Reaction 2 is of special interest in that it is an extremely fast bimolecular step which produces a free atom in an exothermic reaction at room temperature (or Dry Ice temperature for that matter). Reactions of a third molecule with fluorine atoms can be based directly on reaction 2, without need for photo-excitation. Of course, the presence of nitric oxide is inconvenient for many interacting cases.

Acknowledgment.—The financial support of this work provided by the California Research Corporation and the Office of Naval Research is gratefully acknowledged. Reproduction in whole or in part is permttied for any purpose of the United States Government.

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(10) P. W. Gilles and J. L. Margrave, *J. Chem. Phys.*, **21**, 381 (1953).

(11) C. M. Beeson and D. M. Yost, *ibid.*, **7**, 44 (1949).

(12) C. M. Blair, P. D. Brass and D. M. Yost, THIS JOURNAL, **56**, 1916 (1934).

(13) O. Ruff and H. Wallauer, *Z. anorg. Chem.*, **197**, 282 (1931).

(14) M. Szwarc and M. G. Evans, *J. Chem. Phys.*, **18**, 618 (1950).