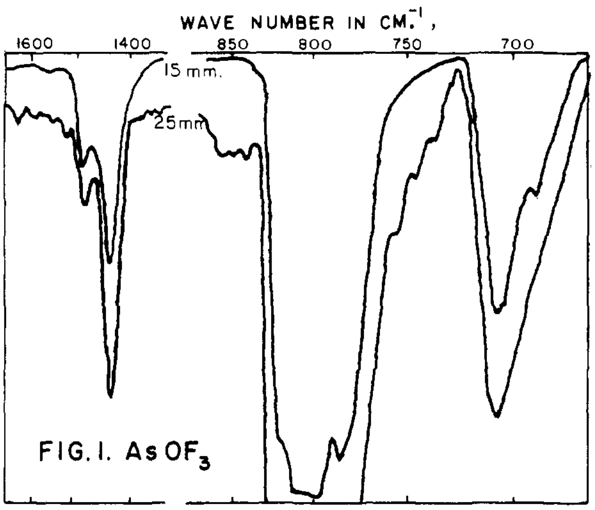

FIG. 1. $AsOF_3$

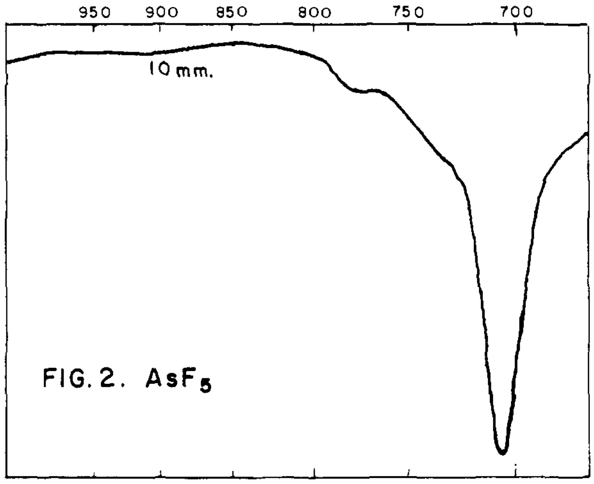

FIG. 2. AsF_5

Infrared Spectrum.—The infrared spectrum of the arsenyl fluoride using a 10 cm. long Pyrex glass cell, with sodium chloride windows was taken over the pressure range 2–15 mm. by means of a double beam Perkin-Elmer spectrometer, Model 21. The infrared absorption frequencies for As–F and As–O have not yet been reported. The absorption spectra of $AsOF_3$ and AsF_5 are given in Figs. 1 and 2. The following inferences were drawn.

Table I

Vapor Pressure of Arsenyl Fluoride

Temp., °K.	Pressure, mm.	Temp., °K.	Pressure, mm.
210.7	105.5	223.6	228.3
215.3	150.3	226.6	270.2
218.0	168.3	228.1	275.3

(1) AsF_5 at a pressure of 10 mm. gives a peak at 705 cm.$^{-1}$. The Raman spectrum of AsF_3 has been studied,[7] and As–F stretch has been observed in 707 cm.$^{-1}$. A peak has appeared at 703 cm.$^{-1}$ for $AsOF_3$. This is attributed to As–F stretching frequency.

(2) Two other peaks appeared for $AsOF_3$, one at 784 cm.$^{-1}$ and the other at 811 cm.$^{-1}$. These peaks are absent in AsF_5 spectra. Hence they are attributed to As–O link. Raman spectra of various arsenates have been studied.[8,9] Peaks in this region have been reported, *e.g.*, 810 cm.$^{-1}$ for Na_3AsO_4; 815 and 867 cm.$^{-1}$ for H_3AsO_4; 833 and 870 cm.$^{-1}$ for NaH_2AsO_4 and 836 cm.$^{-1}$ for $NaHAsO_4$.

(3) Two other peaks appeared for $AsOF_3$ in the small wave length region, one at 1425 cm.$^{-1}$ and the other at 1480 cm.$^{-1}$. These peaks may have been due to overtones. Further study however is required to confirm the actual nature of these peaks.

Mass Spectrum.—Mass spectrum analysis was made in a Consolidated Engr. Co. Type 21-103 spectrometer. Peaks for mass numbers 148 ($AsOF_3^+$), 129 ($AsOF_2^+$), 110 ($AsOF^+$), 91 (AsO^+), 156 (AsF_4^+), 132 (AsF_3^+), 113 (AsF_2^+) and 94 (AsF^+) were found. No peak for mass number 167 ($AsOF_4^+$) was obtained. The AsF_4^+ peak may have come out of the reaction of the fluoride ion and $AsOF_3$.

It is a pleasant duty of the author to acknowledge indebtedness to Professor G. H. Cady of the University of Washington for his help during the progress of the work. This research was supported in part by the Office of Naval Research.

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[7] D. M. Yost and J. E. Sherborne, *J. Chem. Phys.*, **2**, 125 (1934).

[8] Ghose and Das, *J. Phys. Chem.*, **36**, 586 (1932).

[9] Feher and Morgenstern, *Naturwissenschaften*, **25**, 618 (1937).

Seattle 5, Washington

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Thermal Decomposition of Fluorine Nitrate

By William Eugene Skiens and George H. Cady

Received June 6, 1958

Fluorine nitrate decomposes explosively into NOF and O_2. The slow thermal decomposition at about 100° is represented by the equation $NO_3F \rightarrow NO_2F + {}^1/_2O_2$. This is a first-order reaction, involving a Lindemann-Hinshelwood mechanism, and the rate is described by the equation $K_\infty = 5.80 \times 10^{13} \exp(29700/RT)$ sec.$^{-1}$. Although the experiments do not clearly indicate any one mechanism, it may be that the rate controlling step is $NO_3F \rightarrow NO_3 + F$, and that this is followed by $NO_3 + NO_3 \rightarrow 2NO_2 + O_2$ and $NO_2 + F \rightarrow NO_2F$.

Fluorine nitrate has been known from the time of its discovery[1] to be unstable and explosive. The present investigation has shown that the rate of thermal decomposition may be followed easily in the vicinity of 100° and at fairly low pressures. The reaction has been studied under various conditions of temperature and pressure and in the presence of added foreign gases.

Experimental

Materials.—Potassium nitrate of "reagent grade" which contained less than 0.001% potassium nitrite was used. It was powdered, dried at 130-150°, and then stored in a vacuum desiccator. Fluorine in cylinders was obtained from the Pennsylvania Salt Manufacturing Company and was used without treatment except to pass the gas through a Monel Metal trap cooled with Dry Ice. Water-pumped nitrogen was passed through silica gel, Anhydrone (magnesium perchlorate) and a trap cooled with Dry Ice. Other

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[1] G. H. Cady, This Journal, **56**, 2635 (1934).

gases were commerical products of high quality and were used without treatment unless specifically mentioned.

Fluorine nitrate was prepared by a method similar to that described by Yost and Beerbower.[2] Fluorine (flow rate, 1/2 to 1 liter/hour) was diluted with about 20 times its volume of nitrogen and the mixture was then passed into a Teflon tube (3/4 in. i.d.) loosely packed with powdered potassium nitrate. The reaction to produce fluorine nitrate and potassium fluoride liberated enough heat to make the Teflon tube become warm. When trials were made with a considerably lower ratio of nitrogen to fluorine, the temperature of the solid reactant rose, causing the fluorine nitrate to decompose. A test sample of the product was collected in a U-tube at −183° for 20 to 30 seconds. This sample was then allowed to warm for two minutes. A copper wire was then inserted into the U tube. A spark from a Tesla coil was allowed to jump to the wire. This caused a sharp explosion when fluorine nitrate was being produced at a satisfactory rate. After this test revealed a good yield of product, the stream of gas was passed through a trap at −183° for a collection period of 0.5 to 2 hr. The excess fluorine and nitrogen were later pumped away from the condensed fluorine nitrate and the product was then stored at −183° in an evacuated trap. This trap and the adjoing stopcock were enclosed in a wooden shield to decrease the damage when an explosion occurred.

The purity of the product was checked by gas density determinations, infrared spectrograms and mass spectrograms. The iodine released from a cold potassium iodide solution by a weighed sample of the gas was titrated with sodium thiosulfate as another check on the purity. These determinations indicated that the purity of the fluorine nitrate was better than 99% and probably was at least 99.5%. No decomposition of the product (stored at −183°) was noted for periods up to two weeks.

The compound, as previously reported, was found to be extremely explosive in both the gaseous and solid states. Explosions often occurred in the condensed material with no apparent cause. These explosions were violent and they sometimes scattered particles of unexploded material which burst into flame upon hitting the floor. These particles acted as an incendiary agent.

Procedure.—A few preliminary runs made in a Pyrex bulb at about 100° indicated that a reaction was occurring with glass. Subsequent decomposition studies were carried out in reactors made from aluminum of the highest purity commercially obtainable. They were cylindrical vessels of 7.5 cm. diameter and 20.3 cm. length and were connected by aluminum tubing to the glass vacuum line. The two reactors were of the same dimensions and construction except that one was packed with aluminum turnings to increase the inner surface area by a factor of 7.3 and the surface-to-volume ratio by a factor of 12. The reactors were treated before use by filling them with fluorine at about 1 atmosphere pressure and allowing the fluorine to remain for a week at 150°. They were also repeatedly filled with fluorine nitrate at about 200 mm. pressure and allowed to stand at 110–115°. After this type of "seasoning" the rates of decomposition of fluorine nitrate in the two reactors became essentially equal as well as reproducible.

Since no induction period was observed in the decomposition and 5 to 10 minutes were required to evaporate a sample of reactant for a run, a large bulb was used to contain the sample of the reactant immediately before use. This large expansion bulb had two "cold fingers" attached to it, and samples of fluorine nitrate and other gases could be condensed and allowed to evaporate and mix slowly at low pressures before being placed in the reactors. Allowing the reactant to stand in the Pyrex bulb at room temperature for periods up to 25 minutes had no effect on the rate of decomposition. After the desired pressure was obtained in the expansion bulb, the stopcocks to the reactors were opened and the gas was allowed to expand rapidly into the aluminum reactors. The stopcocks above the manometers were closed and the decomposition was followed manometrically.

The reactors were immersed in an oil-bath in which the temperature was controlled to ±0.1°. The small manometers (3 mm., i.d.) were connected to the reactors by 1 mm. capillary tubing to reduce the volume outside the thermostat. These manometers were removable and were filled either with Kel-F fluorocarbon polymer oil No. 3 or with mercury covered by about 2 cm. of this oil. The oil retarded the reaction of fluorine nitrate with the mercury surface. The choice of liquid for the manometers depended upon the pressure range of the run.

To determine the maximum pressure at which fluorine nitrate could be handled safely, samples at increasingly higher pressure were put in a bulb containing a sealed-in tungsten wire. The bulb was grounded. When a spark was caused to jump from the wire in the bulb to the ground, the sample of fluorine nitrate exploded. It was found that at pressures above 350–400 mm. of mercury the explosion became quite violent. Pressures above this were not used in the study.

Results

Spark induced explosive decompositions in the aluminum reactors resulted in a pressure rise to twice the initial reactant pressure. The products in this case, as determined by gas density determinations, infrared spectrograms and other analytical techniques, were oxygen and nitrosyl fluoride. This decomposition occurred according to the equation

$$NO_3F \longrightarrow NOF + O_2 \qquad (1)$$

The runs involving the slow thermal decomposition were carried out in pairs using the packed and unpacked aluminum reactors simultaneously. The decomposition was studied over the range 80.0 to 106.8°. At 80.0° the reaction was quite slow, the half-life being about 7 hr., while at 106.8° the reaction was 50% complete in approximately 0.5 hr. The final pressure, as determined from 20 runs which were allowed to go to completion in both the packed and unpacked reactors, was 1.5 times that of the initial reactant pressure. The reactant pressure, as determined from this final-to-initial pressure ratio, was found to follow a first-order rate law very well through at least 50–70% completion. Some deviation of the rate was noted in the region beyond about two-thirds completion of the reaction.

Gas density determinations, infrared spectrograms and mass spectrograms all indicated the decomposition to result in only two products, oxygen and nitryl fluoride. To verify the identity of the latter, a large sample of fluorine nitrate was decomposed. After removing the oxygen, the melting point of the remaining material was found to be −163.8 ± 0.5° and the boiling point was −71.8 ± 0.5°. These values agreed well with recent data in the literature on the m.p. (−166 ± 0.5°) and b.p. (−72.4 ± 0.2°) of nitryl fluoride.[3] The stoichiometry of the decomposition corresponded to the equation

$$NO_3F \longrightarrow NO_2F + {}^1/_2O_2 \qquad (2)$$

The first-order rate constant was found to decrease with decreasing initial reactant pressure, showing a "fall-off" region of the type characteristic of a unimolecular or quasi-unimolecular reaction having a Lindemann–Hinshelwood mechanism. A number of runs were performed at 106.8°, in which the initial pressure of the reactant was varied from less than 2 mm. to more than 200 mm. of mercury. Figure 1 shows a plot of the rate constant k against initial pressure P_i. A very definite "fall-off" region is noted below 50 mm.

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[2] D. M. Yost and A. Beerbower, THIS JOURNAL, 57, 782 (1935).

[3] J. H. Simons, "Fluorine Chemistry," Ed. by J. H. Simons, Vol. I, Academic Press Inc., New York, N. Y., 1950, p. 89.

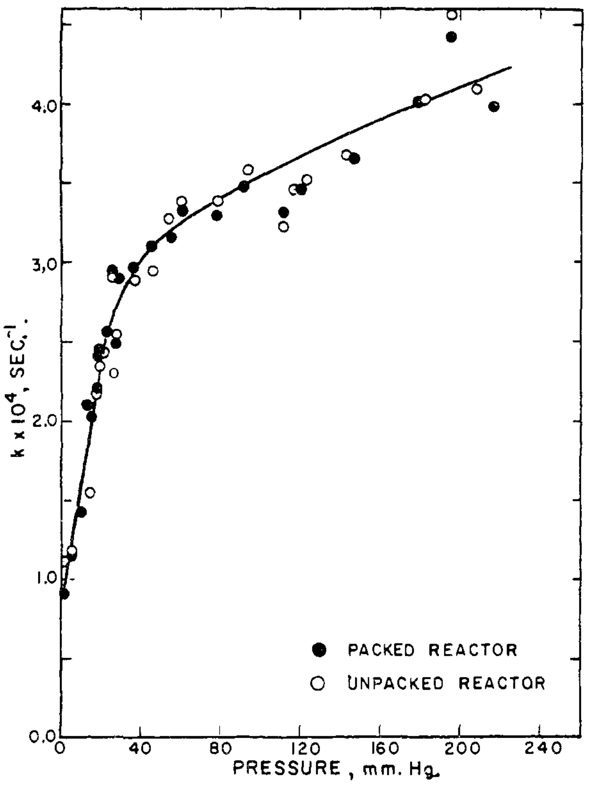

Fig. 1.—Change of rate constant with initial pressure at 106.8°.

pressure. The reaction would be expected to become second order with respect to pressure at pressure considerably less than 1 mm. The data, even at 2 mm., followed a first-order rate law about as well as the runs at much higher pressures, although the rate constant was considerably smaller at this low pressure than at 200 mm. At 106.8° the rate constant was observed to change by a factor of about four over a pressure change of slightly more than 100-fold. Interest was centered largely in the pressure region above the extreme fall-off of the rate, but the explosive characteristics of fluorine nitrate prevented study in the region above 240 mm. The results of runs at four temperatures are shown in Table I.

Either argon or oxygen, when added to the reactant, increased the rate of decomposition in the fall-off region as expected of an inert gas. Both gases were about 50% as efficient as the reactant itself in activating or transferring energy to the reactant molecule.

Other foreign gases were added with the hope that they might give information about the mechanism of decomposition of fluorine nitrate. The effect of nitrogen dioxide was to increase the rate of reaction markedly, although fluorine nitrate did not react noticeably with nitrogen dioxide at room temperature in the mixing bulb. The rate constants were 10 to 50 times those obtained for fluorine nitrate alone, under similar conditions of temperature and pressure. The rates in the two reactors did not agree as well in these runs as in the runs with reactant alone. When the ratio of nitrogen dioxide to fluorine nitrate was greater than 1, the rates in the packed reactor were 1.3 to 1.8 times those in the unpacked. The rate did not appear to be a first-order function of the nitrogen dioxide pressure, and the effect of temperature was less than when fluorine nitrate alone was used. Table II summarizes the runs in which nitrogen dioxide was present.

TABLE I

THERMAL DECOMPOSITION OF NO_3F FIRST-ORDER RATE CONSTANTS

Initial pressure NO_3F (mm.)	$k(\times 10^4$, sec.$^{-1})$ Unpacked reactor	$k(\times 10^4$, sec.$^{-1})$ Packed reactor	Initial pressure NO_3F (mm.)	$k(\times 10^4$, sec.$^{-1})$ Unpacked reactor	$k(\times 10^4$, sec.$^{-1})$ Packed reactor
106.8°			99.5°		
1.9	1.11	0.92	10.9	1.03	1.07
6.0	1.15	1.13	23.0	1.25	1.26
10.0	1.43	1.43	45.2	1.48	1.48
12.9	2.08	2.10	68.2	1.74	1.71
15.0	1.54	2.03	130.5	1.91	2.02
18.2	2.17	2.21	187.5	2.07	2.11
19.6	2.60	2.70	239.5	1.98	2.08
19.7	2.35	2.42		$k (\times) 10^5$, sec.$^{-1}$	
19.7	2.35	2.46		90.8°	
21.4	2.44	2.47	8.2	3.52	3.50
22.6	3.04	2.62	22.0	5.19	4.86
25.2	2.92	2.96	35.9	6.20	6.15
28.2	2.56	2.90	51.8	6.40	6.45
36.1	2.93	2.98	59.8	8.09	8.10
45.5	2.95	3.11	68.8	7.12	7.08
53.7	3.28	3.16	87.8	7.46	7.46
60.0	3.39	3.34	117.9	7.05	6.91
77.1	3.39	3.30	146.1	7.81	7.42
91.5	3.64	3.48	158.8	7.51	7.59
110.6	3.23	3.32	197.4	9.13	9.25
117.5	3.46	3.46	206.9	8.16	8.19
122.2	3.52	3.52		80.0°	
143.7	3.71	3.69	59.5	1.74	2.00
180.0	4.05	4.03	105.2	1.64	1.59
194.0	4.59	4.45	106.7	1.96	1.96
211.4	4.10	3.99	124.5	1.74	1.82
			173.7	2.22	2.28
			237.3	2.10	2.10

TABLE II

RATE OF DECOMPOSITION OF NO_3F IN PRESENCE OF NO_2

t, °C.	Initial pressure NO_3F (mm.)	Pressure NO_2 (mm.)	$k(\times 10^3$, sec.$^{-1})$ Unpacked reactor	$k(\times 10^3$, sec.$^{-1})$ Packed reactor
106.8	20.6	11.4	1.25	1.91
106.8	21.3	21.1	2.10	2.86
106.8	6.7	30.4	2.34	3.81
106.8	14.7	33.8	2.49	4.01
90.8	22.8	23.8	1.03	1.90
90.8	52.4	51.2	1.30	2.05
90.8	50.5	25.2	1.03	1.17
90.8	50.5	5.2	0.39	0.42
80.0	108.2	103.8	1.35	1.74

Fluorine nitrate exploded upon contact with nitric oxide even at low pressures and room temperature.

Fluorine was found to accelerate the slow decomposition but to a smaller extent than nitrogen dioxide. Analysis showed the fluorine concentration at the end of such a run to be the same as it was initially. The increase in the rate constant was 3 to 3.5 times that of reactant alone at 90.8°,

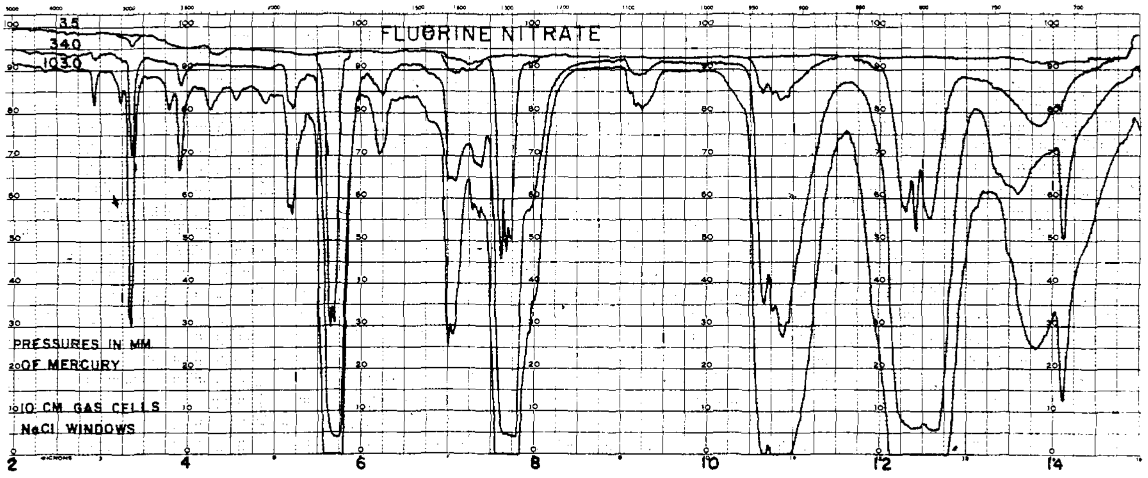

Fig. 2.—Infrared spectrum of fluorine nitrate.

while the rate constant with a similar amount of added nitrogen dioxide was more than 20 times that for fluorine nitrate alone. A decrease in the pressure of fluorine by as much as 20-fold resulted in little change in the rate constant, as shown in Table III.

TABLE III

RATE OF DECOMPOSITION IN PRESENCE OF F_2

t, °C.	Initial pressure NO_3F (mm.)	Pressure F_2 (mm.)	$k(\times 10^4$, sec.$^{-1})$ Unpacked reactor	Packed reactor
106.8	21.0	22.0	3.54	4.79
106.8	15.8	31.8	3.88	5.18
90.8	51.3	147.1	2.51	2.46
90.8	102.1	103.3	2.52	2.60
90.8	102.3	36.3	2.38	2.42
90.8	104.0	12.1	2.17	2.20

Nitryl fluoride, one of the products of the decomposition, was added. It appeared to react more rapidly with glass than fluorine nitrate, and it was difficult to mix the two gases in the mixing bulb without obtaining nitrogen dioxide, which accelerated the decomposition. Thus, considerable care was taken to eliminate nitrogen dioxide. The effect of nitryl fluoride seemed to be only that of an inert gas. A mixture of nitryl fluoride and oxygen, obtained by decomposing fluorine nitrate, also behaved as an inert gas.

Chlorine and bromine were used as additives since they had acted as inhibitors in the thermal decomposition of trifluoroacetyl hypofluorite.[4] Each of these substances had only the effect of an inert gas and the decomposition products were only oxygen and nitryl fluoride.

Hydrogen, added to the reactant, increased the rate of decomposition, although not as greatly as did nitrogen dioxide. The rate did not follow a first-order law but appeared to increase as the reaction progressed. Infrared spectrograms showed that the products contained large amounts of nitrogen dioxide and silicon tetrafluoride. Hydrogen fluoride also was observed. The silicon tetrafluoride probably was formed by the reaction of hydrogen fluoride with glass of the infrared cell and the vacuum line when the products were removed from the aluminum reactors.

Rate constants for the decomposition of fluorine nitrate in the presence of equal pressures of methane indicated that the effect of methane also was only that of an inert gas. The increase in pressure was 50% of the initial pressure of fluorine nitrate. Infrared spectrograms showed no detectable products resulting from a reaction with methane.

Carbon monoxide did not appear to affect the rate of decomposition of fluorine nitrate greatly, when the rate was calculated from the initial reactant pressure. The final pressure was not 1.5 times the initial reactant pressure, however, and relatively large amounts of carbon dioxide were observed in the infrared spectrum.

The infrared spectrum of fluorine nitrate is shown in Fig. 2. The spectrum was obtained with a Perkin-Elmer Model 21 Spectrometer and the cell for the gas was 10 cm. long. It had windows of sodium chloride.

Discussion

The kinetic studies showed the thermal decomposition to be first order. The effect of initial reactant pressure on the rate constant was observed over a 100-fold pressure change at 106.8°. The rate constant changed by a factor of about 4 over this pressure range. This behavior might be expected if the rate-determining step were unimolecular and if it followed a Lindemann–Hinshelwood type mechanism. An inert gas, argon, increased the rate in the extreme fall-off region as might be expected for a unimolecular reaction.

Effect of Packing the Reactor.—The unpacked reactor had an area/volume ratio of 0.56 cm.$^{-1}$, while the area/volume ratio of the packed reactor was about 12 times this. In a total of 50 simultaneous runs in these two reactors, the average percentage difference between the rate constants in the two reactions was less than 1%. Under the conditions of this study there was no significant effect of surface upon the rate. The reaction appeared to be homogeneous.

Effect of Added Gases.—Nitrogen dioxide increased the rate of decomposition markedly and

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(4) R. D. Stewart and G. H. Cady, THIS JOURNAL, **77**, 6110 (1955).

the effect of temperature on the rate constant was considerably less than with the reactant alone. This indicates a lower value for the activation energy for the reaction with added nitrogen dioxide. At these temperatures nitrogen dioxide is known to react very rapidly with nitrogen trioxide or fluorine. Possibly nitrogen dioxide reacts directly with fluorine nitrate. A reaction of the following nature may occur

$$NO_3F + NO_2 \longrightarrow NO_2F + NO_3 \qquad (3)$$

Subsequent steps entailing the decomposition of nitrogen trioxide to form nitrogen dioxide are possible by a mechanism similar to that proposed for nitrogen pentoxide.

$$NO_3 + NO_2 \longrightarrow NO_2 + NO + O_2 \qquad (4)$$

$$NO_3 + NO \longrightarrow 2NO_2 \qquad (5)$$

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (6)$$

Nothing is known concerning the activation energy for step 3, but Ogg estimates a value of about 5 kcal. for (4).[5] The activation energy for (5) is approximately zero and that for (6) is zero or negative.[6] Steps 4, 5 and 6 are all relatively fast and of low activation energy, and (3), if it occurs, may be the slowest step.

Added fluorine also increased the rate constant, to a lesser extent than nitrogen dioxide. If the thermal decomposition were to proceed by a mechanism involving the reactions 3, 4, 5 and 6, fluorine might be expected to act as an inhibitor, since it reacts very rapidly with nitrogen dioxide at this temperature.[7]

The fluorine should remove any nitrogen dioxide as nitryl fluoride and inhibit a chain reaction involving nitrogen dioxide. No inhibition was noted and this was an indication that the decomposition did not occur *via* a nitrogen dioxide chain. The effect of fluorine may have been due to a direct attack by fluorine on the reactant molecule.

Although added hydrogen eventually increased the rate of reaction, the initial 4% of the reaction occurred at the normal first order rate for fluorine nitrate diluted by an inert gas. The rate did not continue to obey a first-order law but appeared to be of an order less than one. Large amounts of nitrogen dioxide were found in the products after completion of the run, and the increasing rate may have been due to an increasing concentration of nitrogen dioxide. The products, which included silicon tetrafluoride and hydrogen fluoride, indicated a reaction of hydrogen with the fluorine nitrate or an intermediate species. Hydrogen is reported not to react with nitryl fluoride below 200–300°.[8] Since the initial rate was about that expected of fluorine nitrate, it is probable that hydrogen fluoride was produced by reaction of an intermediate (*i.e.*, fluorine atoms) with hydrogen as shown in equations 7 and 8.

$$NO_3F \longrightarrow NO_3 + F \qquad (7)$$

$$F + H_2 \longrightarrow HF + H \qquad (8)$$

The decomposition of nitrogen trioxide to nitrogen dioxide would produce the observed increased rate as time passed.

The decomposition of fluorine nitrate in the presence of carbon monoxide produced about equal quantities of carbon dioxide and oxygen. This suggested that about $^1/_3$ of the oxygen normally formed by the decomposition had reacted with carbon monoxide. No carbonyl fluoride was found in the products. The presence of carbon dioxide may be explained on the basis of work by Brown and Crist on the reaction of carbon monoxide with nitric oxide and oxygen.[9] These authors found that the reaction of nitrogen dioxide with carbon monoxide to produce carbon dioxide was negligible below 150° but that a mixture of carbon monoxide, oxygen and nitric oxide reacted with the formation of carbon dioxide at 25°. The formation of carbon dioxide was postulated to occur through the formation and reaction of nitrogen trioxide.

$$2NO + O_2 \longrightarrow 2NO_3 \qquad (9)$$

$$NO_3 + CO \longrightarrow NO_2 + CO_2 \qquad (10)$$

The production of carbon dioxide from carbon monoxide and fluorine nitrate may very well have resulted from the reaction of the carbon monoxide with nitrogen trioxide obtained by the decomposition of fluorine nitrate.

Activation Energy.—The runs at the higher pressures shown in Fig. 1 are definitely beyond the region of rapid change of rate with initial pressure. Values for the rate constant at infinite pressure, k_∞, were obtained by plotting the reciprocal of the rate constant k *versus* the reciprocal of the initial pressure P_i, and extrapolating the curve to infinite pressure. The values for k_∞ at the temperatures of the study are given in Table IV.

TABLE IV

RATE CONSTANTS AT INFINITE PRESSURE

Temp., °K.	k, sec.$^{-1}$	Temp., °K.	k, sec.$^{-1}$
353.2	2.46×10^{-5}	372.7	2.21×10^{-4}
364.0	8.38×10^{-5}	380.0	4.85×10^{-4}

With these values for k_∞, a plot of their temperature dependence was made to determine the activation energy. When log k_∞ was plotted *versus* $1/T$, the experimental points lay on a straight line yielding an activation energy of 29.7 kcal. The expression for the rate constant was

$$k_\infty = 5.80 \times 10^{13} \exp(-29{,}700/RT) \text{ sec.}^{-1}$$

The frequency factor was about that expected for a "normal" first-order unimolecular reaction. The activation energy was somewhat higher than the 25 kcal. found by Stewart and Cady[4] for the inhibited decomposition of trifluoroacetyl hypofluorite. It was lower than the 40.6 ± 3 reported for oxygen difluoride.[10]

Mechanism.—The stoichiometry of the decomposition corresponds to equation 2. To obtain nitryl fluoride and oxygen as products, it is necessary that the oxygen–fluorine bond be severed and a nitrogen fluorine bond formed. A nitrogen–oxygen bond must also be broken to result in the

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[5] R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 338 (1947).

[6] M. Bodenstein and Lindner, *Z. physik. Chem.*, **100**, 68 (1922).

[7] R. L. Perrine and H. S. Johnston, *J. Chem. Phys.*, **21**, 2202 (1953).

[8] E. E. Aynsley, G. Hetherington and P. I. Robinson, *J. Chem. Soc.*, 1119 (1954).

[9] F. B. Brown and R. H. Crist, *J. Chem. Phys.*, **9**, 840 (1941).

[10] W. Koblitz and H. J. Schumacher, *Z. physik. Chem.*, **25B**, 283 (1934).

oxygen observed. The reaction is first order and homogeneous and may contain a unimolecular step, although the reaction probably is not a simple unimolecular reaction. The unimolecular step may be the slow and rate-determining step, however. The subsequent steps may be more complex. The oxidation of carbon monoxide to carbon dioxide strongly suggests the presence of nitrogen trioxide as one of the intermediate species. The appearance of hydrogen fluoride in the products of the reaction in the presence of hydrogen suggests fluorine atoms as another intermediate. In view of these and other results previously mentioned, this decomposition mechanism is proposed.

$$NO_3F \longrightarrow NO_3 + F \qquad (7)$$

$$NO_3 + NO_3 \longrightarrow 2NO_2 + O_2 \qquad (11)$$

$$NO_2 + F + M \longrightarrow NO_2F + M \qquad (12)$$

Equation 7 is assumed to be the slow and rate-determining step. Since carbon monoxide reacts only to a very slight extent ($\sim$3%) even in comparatively high concentration of atomic oxygen to produce carbon dioxide, the formation of carbon dioxide when fluorine nitrate decomposes in the presence of carbon monoxide cannot be explained as due to atomic oxygen.[11] The steps 11 and 12 are more obscure, since the decomposition of nitrogen trioxide or the reaction of fluorine atoms can occur in a number of ways. Step 11, or the decomposition of nitrogen trioxide, could occur partially by reactions such as those in equations 4 and 5, if nitrogen dioxide were present. In every case, however, the reactions with the exception of (7) are relatively fast and of low activation energy. Reaction 11 probably has the highest activation energy of these fast reactions and it is estimated at only about 8 kcal.[12] Equation 12 is described by Perrine and Johnston as the fast step in the mechanism for the reaction of nitrogen dioxide with fluorine.[7] Nitryl fluoride also may be formed by steps such as (13) and (14) at these low concentrations of chlorine and nitrogen dioxide.

$$F + F + M \longrightarrow F_2 + M \qquad (13)$$

$$NO_2 + F_2 \longrightarrow NO_2F + F \qquad (14)$$

The latter reaction is relatively fast and of low activation energy (10.5 kcal.).

Assuming the proposed mechanism, the value of 29.7 kcal. obtained for the activation energy may be attributed to the strength of the oxygen–fluorine bond in fluorine nitrate.

Although a chain mechanism with nitrogen trioxide or nitrogen dioxide as the chain carrier might be anticipated, the lack of inhibition of the decomposition by any of the added gases indicates that such a chain did not exist.

A mechanism involving the rearrangement of the fluorine nitrate molecule with the fluorine atom attaching itself to the nitrogen with the expulsion of an oxygen atom was rejected. It did not account for the products observed in the presence of hydrogen or carbon monoxide. A change in electron multiplicity also would have been necessary and this would have occurred only with very low probability.

There is also the possibility that the rate-controlling step is

$$NO_3F \longrightarrow NO_2 + OF \qquad (15)$$

rather than reaction 7 and that (15) may be followed by fast reactions such as

$$OF \longrightarrow O + F \qquad (16)$$

$$NO_2 + F \longrightarrow NO_2F \qquad (17)$$

$$M + O + O \longrightarrow O_2 + M \qquad (18)$$

Support for this mechanism is furnished by the pyrolysis of methyl nitrate[13] and ethyl nitrate[14] with activation energies of 39.5 and 39.9 kcal., respectively. For each compound, the rate determining step is considered to be

$$RONO_2 \longrightarrow RO + NO_2 \qquad (19)$$

and the activation energy to be the $-O-NO_2$ bond energy. This mechanism does not explain the oxidation of added carbon monoxide to carbon dioxide unless one assumes the oxidizing agent to be OF.

The authors favor the mechanism represented by equations 7, 11 and 12, but they are not convinced that it is correct.

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