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Preparation of Nitrosyl Tetrafluorochlorate¹

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A new compound, nitrosyl tetrafluorochlorate, NOClF₄, has been prepared from nitrosyl fluoride, ONF, and chlorine trifluoride at temperatures below 0°. The material is a white, crystalline solid and a powerful oxidizing agent, igniting on contact or reacting explosively with a variety of organic materials. Dissociation pressure measurements give for the enthalpy of formation of NOClF₄ a value of ΔH_f° (298°K.) = -68.6 kcal./mole. Reaction between ONF and bromine pentafluoride at 0° may have produced nitrosyl hexafluorobromate, NOBrF₆. Attempts to prepare nitryl tetrafluorochlorate, NO₂ClF₄, and nitryl hexafluorobromate, NO₂BrF₆, by reaction of nitryl fluoride, O₂NF, with ClF₃ or BrF₅, respectively, were unsuccessful.

Introduction

Studies on the interaction of nitrosyl and nitryl fluorides with halogen fluorides have led to the preparation of several new and novel powerful fluorinating agents. Woolf² in 1950 postulated the existence of nitrosyl tetrafluorobromate, NOBrF₄, resulting from the reaction between bromine trifluoride and nitrosyl fluoride. Chrétien and Bouy³ later prepared the material by reaction of ONF and BrF₃, or by the interaction of NO and BrF₃ at 20°. Nitrosyl tetrafluorobromate is a white solid (*d* 2.85 g./cm.³) which reacts violently with cold water and forms nitrosyl hexafluorosilicate, (NO)₂SiF₆, when treated with silicon tetrafluoride.



Woolf and Emeléus,⁴ as well as Aynsley, Hetherington, and Robinson,⁵ observed that when nitryl fluoride, O₂NF, was passed into bromine trifluoride, the BrF₃ became yellow and quite viscous. Although the above investigators were unable to recover a solid product from the BrF₃ solution, it was believed that nitryl tetrafluorobromate, NO₂BrF₄, had been formed, the yellow color being due to the presence of the nitryl (NO₂⁺) ion. Aynsley, *et al.*, did succeed, however, in synthesizing and isolating nitryl hexafluoroiodate, NO₂IF₆. To date, no other nitrosyl or nitryl derivative of the halogen fluorides has been reported in the literature.

Bases of the type MClF₄ and MBrF₆, where M may be cesium, rubidium, or potassium, have been prepared. The tetrafluorohalates CsClF₄, RbClF₄, and KClF₄ have been prepared both through direct reaction of elementary fluorine with the corresponding alkali metal halides⁶⁻¹⁰ and as the result of solvolysis reactions in chlorine trifluoride.¹¹ Evidence for the existence of the hexafluorobromate ion, BrF₆⁻, has been presented by Muetterties¹² in the apparent synthesis of CsBrF₆ from CsF and BrF₃. In addition to Cs-

BrF₆, the bases RbBrF₆ and KBrF₆ have been prepared by Whitney, *et al.*,¹¹ *via* solvolysis reactions of the corresponding alkali metal fluoride in bromine pentafluoride.¹³

In this paper are reported the synthesis and isolation of a new nitrosyl polyhalide, nitrosyl tetrafluorochlorate, NOClF₄, formed *via* the solvolysis reaction of ONF in chlorine trifluoride. Some thermodynamic data for the compound are also given.

Experimental

Materials.—Chlorine trifluoride and nitric oxide, both of reported 99% purity, were obtained from the Matheson Co. Purification of ClF₃ to remove traces of HF was accomplished by allowing the material to distil under vacuum through a bed of NaF pellets maintained at 100° in a Monel pipe which was heated by means of a Fisher combustion tube furnace. The ClF₃ was then fractionated under vacuum to remove traces of F₂, Cl₂, and ClF. Fractionation was accomplished by a series of trap-to-trap distillations at -78° followed by collection of the ClF₃ in a trap at 0°.

Elemental F₂, obtained from Pennsalt Chemicals Corp., was passed through NaF pellets at 100° prior to use.

Nitrosyl fluoride was prepared after the method of Brauer.¹⁴ Elemental F₂, at a rate of 31 ml./min., and NO, at a rate of 65 ml./min., were passed into one end of a 1-in. diameter Monel tube. Slight external heating of the metal tube was required to initiate the reaction, after which the formation of ONF was self-sustaining and proceeded smoothly. The nitrosyl fluoride was collected in nickel traps maintained at -120° by means of melting ethyl bromide baths. Over a period of 5 hr., 31.6 g. (0.645 mole) of ONF was obtained corresponding to an 80% yield based upon F₂ consumed. Comparison of the infrared spectrum of this material with the spectrum of ONF as given by Woltz, *et al.*,¹⁵ indicated that the product was reasonably pure, containing only small amounts of NO₂ and O₂NF. Total impurities were estimated to be approximately 2 mole %.

Nitryl fluoride, O₂NF, was conveniently prepared by the method of Aynsley, *et al.*⁵ A stream of F₂ at approximately 4 g./hr. diluted with N₂ (1:1 by volume) was passed over 50 g. of dry reagent grade NaNO₂ in a Pyrex tube at room temperature. As a precautionary measure the tube containing the sodium nitrite was flamed out immediately before use. Good yields of O₂NF were obtained at low F₂ flow rates. If the flow of fluorine gas was excessive a yellow flame appeared over the bed of NaNO₂ and considerable attack on the Pyrex tube occurred. The gaseous product, consisting of nitryl fluoride contaminated with nitrogen dioxide and excess fluorine, was passed through nickel traps cooled to -119° by means of melting ethyl bromide to collect O₂NF and NO₂. Unreacted F₂ passed through the cold traps to the vent. The product was separated from NO₂ by fractionation under vacuum through several traps maintained at -23° by melting CCl₄ baths. The nitryl fluoride was stored at Dry Ice temperature in nickel bombs fitted with Monel needle valves for

(1) This work was supported by the Advanced Research Projects Agency and monitored by the Bureau of Naval Weapons, Department of the Navy, Contract NOrd-18210.

(2) A. A. Woolf, *J. Chem. Soc.*, 1053 (1950).

(3) A. Chrétien and P. Bouy, *Compt. rend.*, **246**, 2493 (1958).

(4) A. A. Woolf and H. J. Emeléus, *J. Chem. Soc.*, 1050 (1950).

(5) E. E. Aynsley, G. I. Hetherington, and P. L. Robinson, *ibid.*, 1119 (1954).

(6) H. Bode, *Naturwiss.*, **37**, 477 (1950).

(7) H. Bode and E. Klesper, *Z. anorg. allgem. Chem.*, **267**, 97 (1951).

(8) H. Bode and E. Klesper, *ibid.*, **313**, 161 (1961).

(9) L. B. Asprey, J. L. Margrave, and M. E. Silverthorn, *J. Am. Chem. Soc.*, **83**, 2955 (1961).

(10) D. H. Kelly, B. Post, and R. W. Mason, *ibid.*, **85**, 307 (1963).

(11) E. D. Whitney, R. O. MacLaren, C. E. Fogle, and T. J. Hurley, *ibid.*, **86**, 2583 (1964).

(12) E. L. Muetterties, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 514.

(13) For the record, the reported preparation of CsBrF₆ by Muetterties in 1961 should be noted. This work supersedes the reported synthesis of the bases MBrF₆ described in ref. 11.

(14) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," F. Enke, Stuttgart, 1954.

(15) P. J. H. Woltz, E. A. Jones, and A. H. Nielsen, *J. Chem. Phys.*, **20**, 378 (1952).

use in the exploratory synthesis experiments discussed at the conclusion of this paper.

Apparatus.—Due to the reactive nature of the compounds handled in this work, experiments were conducted in a general purpose vacuum system in order to exclude air and moisture. The system consisted of both Pyrex and metal sections, the sections being joined by means of a copper to Pyrex No. 774 (Housekeeper) seal. The glass portion of the apparatus consisted of a nitrogen gas drying column, a mercury manometer, a three-way stopcock which was used for either opening the system to the vacuum pump or introducing nitrogen into the apparatus, and a liquid nitrogen cooled trap. The trap served to protect the mercury manometer and Duo-Seal pump from accidental attack by halogen fluoride vapors. The metal portion of the equipment was constructed of 0.25-in. o.d. copper tubing, Hoke miniature forged Monel needle valves equipped with Teflon packing, and Monel traps. Silver-soldered connections were used on the traps and reactors, and flared connections in the rest of the apparatus. Steel cylinders containing ClF_3 were attached to the system through the HF absorber. A thin layer of Teflon "T-Film" thread compound¹⁶ was used on all threaded connections. Pressures were measured on Helicoid gauges equipped with stainless steel Bourdon tubes operating in the range 30 in. to 30 p.s.i. pressure. Each part of the apparatus was rigorously cleaned and carefully dried before assembly.

In the production of ONF, F_2 and NO gas flows were measured with calibrated Fisher-Porter precision bore Flowrators with stainless steel floats. Polyethylene tubing was used for all metal to glass connections. ONF was stored in Hoke Type 304 stainless steel cylinders equipped with Monel needle valves.

Synthesis of NOClF_4 was conducted in 500-ml. polyethylene reactors fitted with threaded caps, Monel needle valves, and flared connections. Thermal decomposition studies were performed in nickel tubes, 22-mm. diameter, 150 mm. long, threaded at the top, and connected through Hoke Monel needle valves to the general purpose metal vacuum line. Dissociation pressures were measured with the Helicoid gauges described above.

A special infrared cell was constructed for this work. The cell body was machined from nickel bar stock. The cell windows were calcium fluoride disks obtained from the Perkin-Elmer Corp. The windows were sealed to the cell body by means of carefully machined Teflon "O" rings and a paste prepared from "T-Film," Teflon thread compound, and Kel-F grease. Hoke Monel needle valves and Imperial brass flared fittings were used in filling and evacuating the cell. Infrared data were obtained on a Perkin-Elmer double beam Model 21 infrared spectrophotometer equipped with sodium chloride optics.

Procedure.—Nitrosyl tetrafluorochlorate was very conveniently prepared by condensing ClF_3 and ONF directly into the 500-ml. polyethylene reactor at -78° . The amount of ClF_3 and ONF employed in the synthesis reaction was determined from the measured volume and known density of the reactants. Nitrosyl fluoride was always employed in a slight molar excess. Allowing the reactor and its contents to reach -25° under vacuum was found sufficient to remove unreacted ONF. Material remaining in the reactor at -25° was a white crystalline solid, stable only at low temperatures (see Table I).

TABLE I
DISSOCIATION VAPOR PRESSURES FOR NOClF_4

Temp., °K.	Pressure, atm.	
	Increasing temp.	Decreasing temp.
213	0.020	
223	0.044	
233	0.088	0.092
243	0.173	0.177
253	0.340	0.347
263	0.701	
273	1.37	
283	3.10	

In spite of the relative instability of this material, it could be analyzed by quickly transferring a portion of the solid to a small polyethylene container, then into a Parr bomb for sodium peroxide fusion, followed by standard analytical techniques. The above operations were performed in a drybox under a N_2 atmosphere with the NOClF_4 , polyethylene containers, and miscellaneous handling equipment cooled to -78 by means of Dry Ice.

(16) Eco Engineering Co., Newark, N. J.

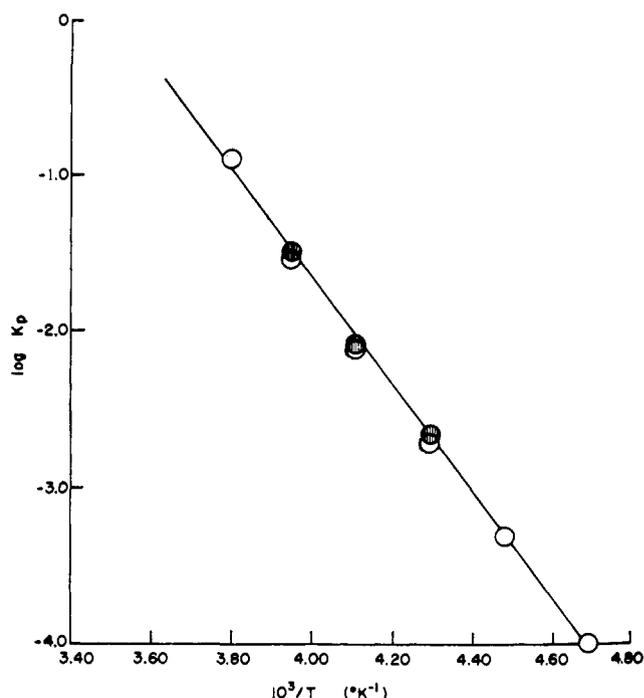
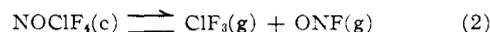


Fig. 1.—Equilibrium dissociation pressures for NOClF_4 vs. reciprocal temperature: open circles, increasing temperature measurements; closed circles, decreasing temperature measurements.

Results and Discussion

The reaction between ONF and ClF_3 at low temperatures led to the formation of a white solid product. *Anal.* Calcd. for NOClF_4 : N, 9.90; Cl, 25.1; F, 53.7. Found: N, 9.44 ± 0.24 ; Cl, 21.5 ± 0.1 ; F, 54.2 ± 0.1 . The white solid was found to be a powerful oxidizing agent, reacting violently with water and explosively with organic solvents such as ether and ethanol. The material ignited paper on contact.

In Table I are given some equilibrium dissociation pressures for NOClF_4 . In Fig. 1, equilibrium dissociation pressures for NOClF_4 are plotted vs. reciprocal temperature. From the slope of this curve, a heat of reaction of $\Delta H = 15.8$ kcal./mole was determined for the reaction



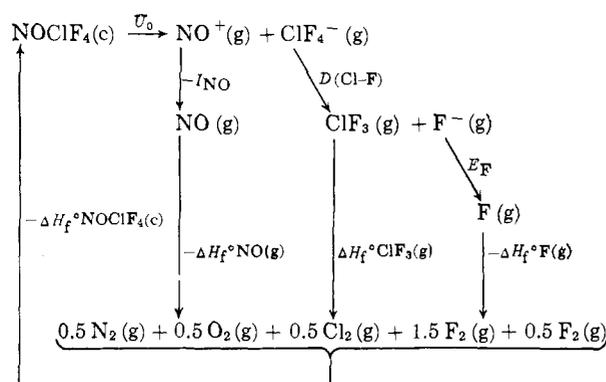
At the conclusion of a typical decomposition study, the decomposition products were again cooled to -78° and the resulting solid analyzed. Found: N, 9.03 ± 0.23 ; Cl, 20.7 ± 0.1 ; F, 54.7 ± 0.2 . This is considered a good demonstration of the reversibility of reaction 2.

The heat of formation of $\text{ClF}_3(\text{g})$ is $\Delta H_f^\circ_{298} = -37.0$ kcal./mole.¹⁷ The standard enthalpy of formation of ONF has been given by Johnston and Bertin¹⁸ as $\Delta H_f^\circ_{298} = -15.8$ kcal./mole. Accepting the above figures the following standard enthalpy of formation of nitrosyl tetrafluorochlorate was obtained: $\Delta H_f^\circ_{298} = -68.6$ kcal./mole or -485 cal./g.

The following Born-Haber cycle was used to determine the lattice energy of nitrosyl tetrafluorochlorate.

(17) National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., Feb. 1, 1952.

(18) H. S. Johnston and H. J. Bertin, Jr., *J. Am. Chem. Soc.*, **81**, 6402 (1959).

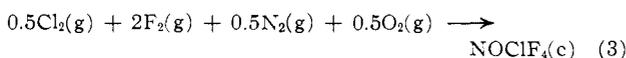


The lattice energy of NOClF_4 is therefore given by the relation

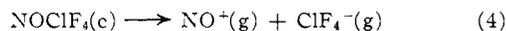
$$U_0 = I_{\text{NO}} + \Delta H_{f\text{NO}(\text{g})} - D_{(\text{Cl}-\text{F})} - \Delta H_{f\text{ClF}_3(\text{g})} - E_{\text{F}} + \Delta H_{f\text{F}(\text{g})} + \Delta H_{f\text{NOClF}_4(\text{c})}$$

and found to be 148 kcal./mole, a value in the range of that expected for solid, univalent alkali metal halides.^{19,20}

One may obtain an estimate of the entropy change in the formation of NOClF_4 from the elements

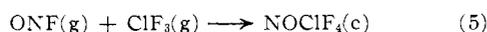


from an estimation of the lattice entropy of NOClF_4 , defined by the hypothetical reaction



and the entropies of the elements.²¹ Altshuller²² has calculated the entropy of the NO^+ gaseous ion to be 46.1 cal./deg./mole. Assuming $\text{NO}^+(\text{g})$ to have the same ΔS of vaporization as $\text{NH}_4^+(\text{g})$ ²³ gives for the entropy contribution of the NO^+ ion in a solid compound (NOClF_4) a value of 16.1 cal./deg./mole. Latimer²⁴ gives for the entropy contribution of the ClO_4^- ion in solid compounds a value of 26.0 cal./deg./mole, and from tables given in ref. 24 the entropy contribution of the ClF_4^- ion in $\text{NOClF}_4(\text{c})$ was estimated to be 32.0 cal./deg./mole. The lattice entropy of NOClF_4 is therefore taken to be 48.1 cal./deg./mole.

The entropy change in the formation of NOClF_4 as given by eq. 3 is, therefore, $\Delta S_{298} = -123$ cal./deg./mole. From the above calculated value of the lattice entropy of $\text{NOClF}_4(\text{c})$, and the entropies of $\text{ClF}_3(\text{g})$ and $\text{ONF}(\text{g})$ as given by Kelley and King,²¹ the entropy change associated with the equation



is found to be $\Delta S_{298} = -78.8$ cal./deg./mole. The Gibbs free energy change for the reaction is expressed as $\Delta F = -15,800 + 78.8T$ cal./mole.

(19) V. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience Publishers, Inc., New York, N. Y., 1950.

(20) T. C. Waddington in "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, H. J. Emeléus and A. G. Sharpe, Ed., Academic Press, Inc., New York, N. Y., 1959, pp. 157-221.

(21) K. K. Kelley and E. G. King, "Entropies of the Elements and Inorganic Compounds," U. S. Bureau of Mines Bulletin 592, U. S. Government Printing Office, Washington, D. C., 1961.

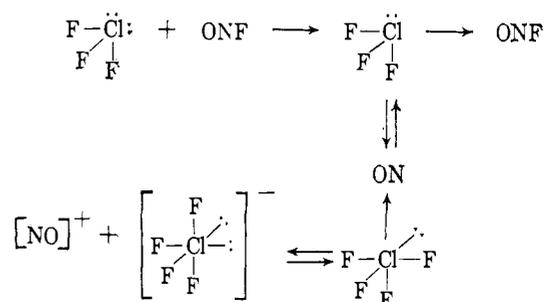
(22) A. P. Altshuller, *J. Chem. Phys.*, **28**, 1254 (1958).

(23) A. P. Altshuller, *ibid.*, **26**, 404 (1957).

(24) W. M. Latimer, "Oxidation Potentials," 2d Ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, Appendix III.

From the above, $\Delta F = 0$ at 200°K. Considering the several assumptions made in the above calculations, the thermodynamically predicted spontaneity of the reaction at temperatures below -73° is in good agreement with the equilibrium dissociation vapor pressure of NOClF_4 shown in Table I.

It is, of course, possible that nitrosyl tetrafluorochlorate may be a molecular complex, $\text{F}_3\text{Cl}\cdot\text{ONF}$, a covalent compound, or (we presume) an ionic nitrosyl salt of the hypothetical acid, HClF_4 , *i.e.*, $\text{NO}^+\text{ClF}_4^-$. The following proposed scheme for the reaction between ONF and ClF_3 is similar to the mechanism proposed by Rogers and Katz²⁵ for the exchange of fluorine between ClF_3 and HF , *i.e.*



The proposed intermediate molecular complex (I) in the formation of NOClF_4 is consistent with the



hypothesis put forward by Rogers and Katz that the exchange of fluorine atoms between ClF_3 and HF proceeds through formation of intermediate complexes of type II.

Attempted Preparation of Nitrosyl Hexafluorobromate (NOBrF_6), Nitryl Tetrafluorochlorate (NO_2ClF_4), and Nitryl Hexafluorobromate (NO_2BrF_6).—Following the experimental procedure outlined above for the formation of nitrosyl tetrafluorochlorate, attempts were made to form NOBrF_6 from ONF and BrF_5 , and NO_2ClF_4 and NO_2BrF_6 from O_2NF and ClF_3 or BrF_5 , respectively. When pure ONF and BrF_5 were mixed at -25° , no reaction was observed. Interestingly enough, however, when the experiment was repeated in the presence of a small amount of NOClF_4 , a white solid product was formed. The material was found to be very stable, however, and chemical analyses and dissociation pressure measurements did not yield reproducible results.

Attempts to cause nitryl fluoride to react with either bromine pentafluoride or chlorine trifluoride at low temperatures were unsuccessful. Indeed, it was observed that the combined vapor pressures of the systems $\text{O}_2\text{NF} + \text{ClF}_3$ and $\text{O}_2\text{NF} + \text{BrF}_5$ always exhibited positive deviations from Raoult's law.

(25) M. T. Rogers and J. J. Katz, *J. Am. Chem. Soc.*, **74**, 1375 (1952).