X-Ray Powder Diffraction.—Powder patterns were made in Philips Electronics 114.7-mm. diameter powder cameras using filtered Cu radiation on a Philips Electronics basic X-ray unit. The samples were in 0.5-mm. soft glass capillaries and lines were measured on an N. P. Nies transparent scale, the intensities estimated visually.

Discussion

Figure 2 shows the typical AsF_6^- ion infrared absorption bands found in $KAsF_6$, $NaAsF_6$, and $AgAsF_6$.[7] The infrared spectrum of the $IO_2F \cdot AsF_5$ product revealed the same characteristic peak centered at 704 cm.$^{-1}$. Our characterization of KIO_2F_2 and $AgIO_2F_2$ demonstrated the distinctive $IO_2F_2^-$ group infrared absorption bands at 855–806 cm.$^{-1}$. The complete absence of the spectrum of $IO_2F_2^-$ ion in the spectrum of our $IO_2F \cdot AsF_5$ product proves that the structure should be represented as $IO_2^+AsF_6^-$.

Evidence for the IO_2^+ iodyl cation was not positively established although it has been postulated in the literature.[1,8–13]

Schmeisser and Brandle[14] found that in hydrogen fluoride iodyl fluoride readily reacted with various compounds which functioned as acids in this system. Iodyl fluoride was therefore thought to dissolve as a base in hydrogen fluoride. Our specific case showed as expected that AsF_5 acts as a stronger acid in the hydrogen fluoride system than IO_2F, for it formed $IO_2^+AsF_6^-$ rather than $AsF_4^+IO_2F_2^-$. However, one may think of iodyl fluoride as being amphoteric, with the nature of the species dependent upon the fluoride ion concentration of the hydrogen fluoride system in which it is dissolved.

$$IO_2F \rightleftharpoons IO_2^+ + F^-$$

$$IO_2F + F^- \rightleftharpoons IO_2F_2^-$$

Our findings were also consistent with this concept for

$$AsF_5 + IO_2F \xrightarrow{HF} AsF_6^- + IO_2^+$$

and

$$Ag^+ + F^- + IO_2F \xrightarrow{HF} AgIO_2F_2$$

Acknowledgment.—The authors wish to thank the Olin Central Analytical Department and specifically Mr. G. P. Tilley for performing the X-ray powder work. We are grateful also to Mr. G. W. Hurt and Mr. J. E. Schingh for the carrying out of the infrared absorption studies.

---

(7) These salts were obtained from Ozark-Mahoning Company of Tulsa, Okla.

(8) K. J. Morgan, *Quart. Rev.* (London), **8**, 123 (1954).

(9) H. A. Lehmann and H. Hesselbarth, *Z. anorg. allgem. Chem.*, **299**, 51 (1959).

(10) J. Arotsky, H. C. Mishra, and M. C. R. Symons, *J. Chem. Soc.*, 2582 (1962).

(11) E. E. Aynsley, R. Nichols, and P. L. Robinson, *ibid.*, 623 (1953).

(12) O. E. Myers and J. W. Kennedy, *J. Am. Chem. Soc.*, **72**, 897 (1950).

(13) F. Aubke and G. H. Cady, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 2K.

(14) M. Schmeisser and K. Brandle, *Advan. Inorg. Chem. Radiochem.*, **5**, 82 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON

Reactions of Fluorine Nitrate

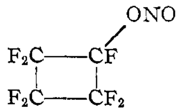
BY BARRY TITTLE AND GEORGE H. CADY

Received September 25, 1964

Since fluorine nitrate, NO_3F, is known to contain an OF group,[1] the substance has now been included among the various compounds under investigation to determine the chemical characteristics of the hypofluorite functional group.[2–6]

In general hypofluorites add across a carbon–carbon double bond in such a way that the F atom of the OF group combines with one carbon atom and the O atom with the other. This appears to be the case for fluorine nitrate. The substance reacts readily with ethylene at room temperature to give a liquid product which almost surely is 1-fluoro-2-nitratoethane, $FCH_2CH_2ONO_2$. A little polymeric material also is formed. The mass spectrum of the liquid product indicates the following species, listed in order of decreasing intensity: HCO^+, (NO^+ and H_2CO^+), NO_2^+, CF^+, CFH_2^+, NO^{2+}, CO^+, CH_2^+, O^+, $CH_2CH_2O^+$, CFH^+, $CFH_2CH_2^+$, F^+. On standing this compound evolves nitrogen dioxide. It can readily be distilled under vacuum. The infrared spectrum of the compound has absorption maxima (μ) at 3.45, w; C–H 6.0, vs; NO_2 asymmetric stretch 7.8, m; symmetric NO_2 stretch 9.2, w; 9.5, w; 9.7, m; 11.15, m; 11.85, ms.

Fluorine nitrate reacts almost quantitatively at room temperature with tetrafluoroethylene to form carbonyl fluoride and CF_3NO_2. It is probable that $C_2F_5ONO_2$ is formed as an intermediate and that this decomposes into COF_2 and CF_3NO_2. Although perfluoroalkyl nitrates have not been prepared, probably because of their rapid decomposition, the cyclic compound



is known. It rearranges even at 20° into $O_2N(CF_2)_3COF$.[7] A similar rearrangement of the hypothetical compound $C_2F_5ONO_2$ would give CF_3NO_2 and COF_2, the observed products of reaction.

Hypofluorites react at about 140° and above with sulfur tetrafluoride as shown in the equation[6]

$$R_fOF + SF_4 \longrightarrow R_fOSF_5$$

$$R_f = CF_3, SF_5, SO_2F$$

When the thermal reaction of fluorine nitrate with sulfur tetrafluoride occurs in a nickel vessel with slowly

---

(1) L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **59**, 13 (1937).

(2) F. B. Dudley, G. H. Cady, and D. F. Eggers, *ibid.*, **78**, 290 (1956).

(3) R. S. Porter and G. H. Cady, *ibid.*, **79**, 5628 (1957).

(4) F. B. Dudley, G. H. Cady, and D. F. Eggers, *ibid.*, **78**, 1553 (1956).

(5) J. Allison and G. H. Cady, *ibid.*, **81**, 1089 (1959).

(6) S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962).

(7) S. Andreades, U. S. Patent 3,040,085; *Chem. Abstr.*, **57**, 16416 (1962). Preprints, 2nd International Symposium on Fluorine Chemistry, American Chemical Society, 1962, p. 106.

rising temperature from 20 to 100° the pressure increases more rapidly above 70° than for an ideal gas. The final pressure after cooling is greater than the initial pressure. At no stage does a pressure drop occur as would be required for the reaction

$$SF_4 + FNO_3 \longrightarrow SF_5ONO_2$$

The products of reaction include SF_6, NO_2F, SOF_2, NO_2, O_2, and SiF_4 but apparently not SF_5ONO_2.

The reaction between sulfur tetrafluoride and fluorine nitrate in a quartz and glass system under irradiation by ultraviolet light gives SF_4O, NO_2, O_2, SO_2F_2, and SiF_4. These probably result from the known decomposition of fluorine nitrate into NO_2F and O_2 followed by reaction of decomposition products with sulfur tetrafluoride. The reaction under ultraviolet light of sulfur tetrafluoride with a mixture of oxygen and nitrogen dioxide to give SF_4O is known[8] and probably accounts for the formation of SF_4O, a product not found in the thermal reaction.

Fluorine nitrate reacts with tetrafluorohydrazine at room temperature to form NF_3, NO_2, NOF, and NO_2F.

Experimental

Fluorine nitrate was prepared by a method similar to that of Skiens and Cady.[9] Adequate precautions were taken against harm by explosions. The addition of fluorine nitrate to a second reactant can initiate an explosive reaction which propagates back through the connecting tubes and causes an explosion in the fluorine nitrate reservoir. This was avoided by expanding the fluorine nitrate into a third, small evacuated chamber and isolating the reservoir. The small quantity of fluorine nitrate was then expanded into the second reactant held in another vessel at lower pressure.

Fluorine nitrate contained in a 1-l. Pyrex glass vessel at a pressure of 12.5 cm. was admitted to a second 1-l. vessel containing tetrafluoroethylene at a pressure of 5 cm. The final pressure was 8.4 cm. If no change in the total number of molecules had occurred, the pressure would have been 8.1 cm. The product was separated by low-temperature fractional codistillation.[10] The more volatile of the two principal fractions had strong infrared absorptions at 775, 965, 1230, and 1910 cm.$^{-1}$ corresponding to carbonyl fluoride.[11] The less volatile principal fraction had strong infrared absorptions at 750, 860, 1150, 1300, and 1620 cm.$^{-1}$ corresponding to CF_3NO_2.[12] Mass spectra of these fractions also corresponded to COF_2 and CF_3NO_2. Small amounts of SiF_4 and NO_2 were also present in the product.

Fluorine nitrate at 22 cm. pressure in a 1-l. Pyrex vessel was admitted to ethylene in a 2-l. vessel at 6 cm. pressure diluted by nitrogen at 4 cm. The pressure after mixing was 14 cm., corresponding to no combination. After 45 min. the pressure was 12 cm. and after 90 min. it was 11 cm. The final pressure was 10 cm., the total reduction being the same as the pressure initially due to NO_3F. The product was removed from the reaction vessel and was separated by bulb to bulb distillation at low pressure.

Fluorine nitrate at 10.2 cm. in a 1-l. vessel was mixed with tetrafluorohydrazine at 7.0 cm. in a 1-l. glass vessel. The final pressure in the 2-l. system was 8.1 cm. The expected pressure assuming no change in number of molecules was 8.6 cm. The products were separated by low-temperature codistillation and identified by infrared spectroscopy to be NF_3, NO_2F, and NOF. A material having the properties of $(NO_2)_2SiF_6$ was also observed. When the reaction of fluorine nitrate with tetrafluorohydrazine occurred in a nickel vessel no nitryl fluorosilicate was found; otherwise the observed products were the same.

Equimolar amounts of SF_4 and fluorine nitrate were introduced into a 5-l. flask to a total pressure of above 5 cm. Irradiation was accomplished by using a mercury vapor lamp. After irradiation for 5 hr. the products were removed, separated by low-temperature codistillation, and identified by infrared spectroscopy.

Equimolar amounts of fluorine nitrate and sulfur tetrafluoride were introduced into a 1.4-l. nickel reactor to a total pressure of 12.5 cm. This mixture was heated to 98° over a period of 2 hr. with pressure readings taken by means of a Booth Cromer pressure transmitter every 5 min. After cooling to room temperature the products were separated by low-temperature codistillation and the fractions identified by infrared spectroscopy. Oxygen was identified by its volatility at low temperature and its density.

Acknowledgment.—The work was performed in part under contract with the Office of Naval Research.

---

[8] W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3838 (1960).

[9] W. E. Skiens and G. H. Cady, *ibid.*, **80**, 5640 (1958).

[10] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

[11] J. Overend and J. C. Evans, *Trans. Faraday Soc.*, **55**, 1817 (1959).

[12] J. Mason and J. Dunderdale, *J. Chem. Soc.*, 759 (1956).

CONTRIBUTION NO. 1601 FROM THE INSTITUTE FOR ATOMIC
RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

The Scandium Trichloride–Scandium System and the Question of the Existence of Solid, Lower Chlorides of Scandium[1]

BY JOHN D. CORBETT AND BOB N. RAMSEY

Received September 28, 1964

The $ScCl_3$–Sc system might be expected to show a substantial amount of reduction of the molten trichloride by metal and even the formation of a reduced, solid phase. The reasons for this are (1) the expectation that, as in other transition metal groups, the stability of the M^{2+} ion $ns^2np^6nd^1$ should increase from La^{2+} to Sc^{2+}, the former being a reasonable interpretation[2] of the solution of up to 9 mole % La in liquid $LaCl_3$,[3] and (2) the prediction from Born–Haber cycle calculations[4] that $ScCl_2$ should be on the borderline of stability. To this point, Polyachenok and Novikov[5] have recently reported thermal analysis data for the $ScCl_3$–Sc system that were interpreted as indicating the formation of the solid phases $ScCl_2$ and $2ScCl_3 \cdot ScCl_2$ ($ScCl_{2.67}$). However, their results are in almost complete disagreement with those reported here, which deny the existence of any lower chloride.

Experimental

Materials.—Scandium metal that was used for reduction of $ScCl_3$ had been vacuum-distilled in tantalum and contained, in p.p.m., O, 750–950; H, 10; Fe, 100; Si, 30; Ca, <25; Ta, 1300; Y, 100; Er, <100; Tm, Yb, Lu, <50 as impurities. The $ScCl_3$ was prepared as before[6] except that commercial HCl

---

[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *Discussions Faraday Soc.*, **32**, 188 (1961).

[3] F. J. Keneshea and D. Cubicciotti, *J. Chem. Eng. Data*, **6**, 507 (1961).

[4] M. Barber, J. W. Linnett, and N. H. Taylor, *J. Chem. Soc.*, 3323 (1961).

[5] O. G. Polyachenok and G. I. Novikov, *Zh. Neorgan. Khim.*, **8**, 2819 (1963); USAEC Translation IS-2.

[6] L. F. Druding and J. D. Corbett, *J. Am. Chem. Soc.*, **83**, 2462 (1961).