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"Reactions of Pentafluorosulfur Hypofluorite with Cl_2, Br_2, I_2, NO, NO_2 and PF_3"

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REACTIONS OF PENTAFLUOROSULFUR HYPOFLUORITE (SF_5OF) WITH Cl_2, Br_2, I_2, NO, NO_2 and PF_3.

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Some of the known reactions of pentafluorosulfur hypofluorite (SF_5OF) give products containing one or more SF_5O groups in the molecule. For example, SF_5OF adds to ethylene to give $F_5SOCH_2CH_2F$,[1] to COF_2 to give F_5SOOCF_3,[2] to SO_3 to give F_5SOOSO_2F[2] or to SOF_4 to give F_5SOOSF_5.[3] The reaction with N_2F_4 gives F_5SONF_2 and NF_3.[4] The reaction of CO with SF_5OF,[1] however, gives COF_2 and SOF_4 as products. In the present work, several new reactions of SF_5OF have been investigated, in which SOF_4 is produced.

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1. S. M. Williamson and G. H. Cady, Inorg. Chem., 1, 673 (1962).
2. (a) C. I. Merrill, Thesis: "Synthesis, Physical Properties and Reactions of Some Pentafluorosulfur Compounds", University of Washington, 1962. (b) C. I. Merrill and G. H. Cady, J. Am. Chem. Soc., 85, 909 (1963).
3. C. I. Merrill and G. H. Cady, J. Am. Chem. Soc., 83, 298 (1961).
4. J. K. Ruff, Inorg. Chem. 4, 1788 (1965).

The defluorination of SF_5OF to SOF_4 is a more general type of reaction than previously has been realized. Each of the substances, Br_2, I_2, NO, NO_2 and PF_5 reacted at room temperature or below to give SOF_4. Chlorine was not found to react even at 130°. At 160° the substances SF_6 and SOF_4 were found as products, but these may have resulted from pyrolysis of SF_5OF[1] rather than its reaction with Cl_2.

In the reactions of pentafluorosulphur hypofluorite with Br_2, I_2 and NO_2, the reaction products were examined when the reaction was only partially complete. In each case, a mixture of SOF_4 and SF_5OF, but no other S - F compounds was found. In the reactions with the halogens, when only the more volatile part of the reaction mixture was examined at this stage, the number of moles of the SOF_4/SF_5OF mixture was about the same as that of the SF_5OF taken. Thus, only a very small quantity of new OSF_5 compounds could have been present in the partly reacted mixture. It is concluded that if such compounds are intermediates in these reactions, they are unstable under the reaction conditions employed.

The supposition that SF_5O - M compounds may be unstable intermediates in these reactions is supported by the finding that the reactions studied produced SOF_4 rather than $SF_5O\ OSF_5$. The apparent instability of the OSF_5 group may be contrasted with the comparative stability of the OSO_2F group, of which many new compounds have recently been made.

EXPERIMENTAL

Materials - Pentafluorosulphur hypofluorite was made by the reaction of fluorine with thionyl fluoride in the presence of excess cesium fluoride.[5] The reaction bomb was placed in an explosion shield and held at 75° for about eight hours to ensure complete reaction. Other gaseous reagents, except nitrogen dioxide, were commercial samples purified by vacuum fractionation. Nitrogen dioxide was made by oxidation of a measured quantity of purified nitric oxide, with excess dry oxygen. Bromine was dried over P_2O_5 before vacuum fractionation, and iodine (Baker Analysed Reagent) was dried by pumping on it at -23° for 20 minutes.

Procedure - Except for nitrogen dioxide (see above), the reagents were measured out by pressure in a calibrated volume of a conventional Pyrex vacuum system, and condensed into the reaction vessel. In the reactions of SF_5OF with the halogens and with the oxides of nitrogen, the reaction vessel was a 30 ml. prefluorinated stainless steel bomb, fitted with a brass and stainless steel needle valve. In the reaction with phosphorus trifluoride, a 500 ml. Pyrex flask, fitted with a glass and Teflon grease-free valve,[6] was employed. Products were separated by vacuum

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[5] J. K. Ruff and M. Lustig, Inorg. Chem., 3, 1422 (1964).

[6] Fischer and Porter "Lab Crest" 4 mm. Quick Opening In Line Valve, Cat. No. 795-120-0004.

fractionation or fractional codistillation[7] and identified by their infrared spectra and vapor densities. In the cases of SF_5OF and SOF_4 the characteristic infrared absorptions used in identification were those at 935, 888, 614 and 585 cm^{-1} for SF_5OF, and those at 1383, 928, 821, 637 and 567 cm^{-1} for SOF_4.[8] Substances which attacked glass, such as the halogen fluorides and the nitrogen oxyfluorides, were handled in an all-metal transfer manifold, and their infrared spectra were examined in a nickel cell fitted with silver chloride windows.

Reaction of pentafluorosulfur hypofluorite with (a) bromine - Br_2 (0.1652 g, 1.034 mmole) and SF_5OF (3.06 mmole) did not appear to react at 0° in 2 1/2 hours. After 2 hours at room temperature, a mixture (3.19 mmole) containing a little bromine was pumped from the reaction vessel at -82°. The infrared spectrum of this material was due only to SF_5OF and SOF_4. The mixture was recombined, and after 44 hours at room temperature the material transferable in vacuum at -82° (3.29 mmole) had the infrared spectrum of pure SOF_4, and was slightly colored with bromine. The material involatile at -82° was pale yellow in color, and in contact with Pyrex glass, Br_2 and SiF_4 were rapidly generated. While this product almost certainly was BrF_3, the infrared spectrum of BrF_3

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

[8] F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., J. Am. Chem. Soc., 78, 1553 (1956).

could not be detected, even when the glass-free manifold was used. Since SiF_4 was observed in this case, the BrF_3 must have reacted with a silicon-containing material in the grease[9] used to lubricate some metal-metal joints.

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9. Kel-F #90 Grease, supplied by the 3M Company.

(b) With iodine - I_2 (0.2685 g, 1.06 mmole) and SF_5OF (5.66 mmole) reacted partially in 2 hours at room temperature, and a mixture (5.44 mmole: M = 136) of SF_5OF and SOF_4 was separated. The recombined mixture was left for a further 18 hours at room temperature, when the material which could be transferred in vacuum at -82° was SOF_4 (5.33 mmole) with M = 125.7. (Calculated for SOF_4: M = 124.0. The material involatile at -82° (0.4684 g.) showed the infrared spectrum of IF_5,[10] and attacked glass to yield SiF_4 and a white solid.

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10. R. C. Lord, M. A. Lynch, Jr., W. C. Schumb and E. J. Slowinski, Jr., J. Am. Chem. Soc., 72, 522 (1950).

(c) With nitric oxide - SF_5OF (1.00 mmole) when mixed with 2.01 mmole of NO reacted completely in 23 hours at room temperature. (In a preliminary small-scale experiment, it was established that reaction of SF_5OF was complete in 30 minutes at room temperature.) The infrared spectrum of the product indicated NO, NO_2 and SOF_4. No other S - F compounds were detected, nor was NOF.[11]

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11. P. J. Woltz, E. A. Jones and A. H. Nielson, J. Chem. Phys. 20, 378 (1952).

SOF_4 was not completely isolated from the mixture. The fraction passing a trap at -112° (1.32 mmole; M = 107.9) was chiefly SOF_4, and an infrared spectrum of this mixture, measured in a 10 cm. cell at ca. 200 mm. pressure, showed unidentified absorptions at about 1800 cm^{-1}, but no absorptions other than for SOF_4 in the S - F stretching region. It is highly probable that NOF was initially formed, but subsequently destroyed by reaction with the apparatus.

(d) With nitrogen dioxide - NO_2 (2.04 mmole) and SF_5OF (1.00 mmole) reacted partially in 4 hours at room temperature. There was then 2.47 mmole of product, whose infrared spectrum indicated NO_2, SF_5OF, SOF_4 and NO_2F.[12] The recombined mixture was left for a further 20 hours at room temperature. The products were then SOF_4 and NO_2F. The latter slowly attacked glass, to yield NO_2 and SiF_4. SOF_4 (1.0 mmole; M = 129.5) slightly contaminated with SF_5OF, was separated.

(e) With phosphorus trifluoride - PF_3 (1.02 mmole) and SF_5OF (1.04 mmole) reacted with a bright, slightly bluish flash about 2 minutes after the reaction flask had been removed from a liquid oxygen cooling bath. The mixture was left at room temperature for 45 minutes. There was then 2.02 mmole of product, whose infrared spectrum indicated SOF_4 and PF_5.[13] Codistillation of the mixture

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12. R. E. Dodd, J. A. Rolfe and L. A. Woodward, Trans. Farad. Soc. 52, 145 (1956).

13. J. P. Pemsler and W. G. Planet, Jr., J. Chem. Phys., 24, 920 (1956).

yielded SOF_4 (0.951 mmole; M = 123), while the PF_5 reacted with the apparatus to yield some POF_3.

<u>(f) With chlorine</u> - Cl_2 (1.01 mmole) and SF_5OF (3.06 mmole) did not react appreciably in various periods of heating, up to 15 hours at 100°. After 90 hours at 130°, the mixture (4.04 mmole) had an infrared spectrum which indicated the presence of some SOF_4, but a great deal of SF_5OF remained. The mixture was finally heated for 6 1/2 days at 160°. Volatile products were then pumped from the reaction bomb at -112°. These (3.97 mmole; M = 120.2) had the color of chlorine and gave the infrared spectrum of SOF_4 and SF_6. The chlorine was determined by Volhard's method after alkaline hydrolysis of the mixture. 10 ml. of 3% H_2O_2 solution was added to each 10 ml. aliquot of hydrolysis mixture to reduce hypochlorite to chloride. The chloride found represented 1.860 mg. atom Cl. The bomb, containing the material retained at -112°, weighed 0.0490 g. more than it had weighed empty, before the experiment, and it lost only 0.0115 g. on pumping at room temperature

[illegible]

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13. ABSTRACT

Pentafluorosulfur hypofluorite (SF_5OF) ~~is~~ reduced to thionyl tetrafluoride (SOF_4) at room temperature or below by Br_2, I_2, NO, NO_2, or PF_3. Chlorine does not react with SF_5OF at temperatures up to 130°C.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Pentafluorosulfur hypofluorite						
Chlorine						
Bromine						
Iodine						
Nitric oxide						
Nitrogen dioxide						
Phosphorus trifluoride						