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Some Reactions of Pentafluorosulfur Hypofluorite and Trifluoromethyl Hypofluorite[1]

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The reaction of pentafluorosulfur hypofluorite with sulfur dioxide in the liquid phase gives SF_5OSO_2F. Pentafluorosulfur hypofluorite reacts with sulfur tetrafluoride to give SF_5OSF_5, SF_5OOSF_5, and $SF_5OSF_4OSF_5$, while a similar reaction in the presence of oxygen gives $SF_5OSF_4OOSF_5$ and $SF_5OSF_4OOSF_4OSF_5$ as additional products. These new peroxides react with benzene to give $C_6H_5OSF_4OSF_5$. The reaction of trifluoromethyl hypofluorite with sulfur tetrafluoride gives CF_3OSF_5 as the only product. Trifluoromethyl hypofluorite, sulfur tetrafluoride, and oxygen react to give $CF_3OSF_4OSF_5$, $CF_3OSF_4OOSF_5$, and a compound believed to be $CF_3OSF_4OOSF_4OCF_3$. A reaction scheme which accounts for these products is proposed.

Van Meter and Cady[2] studied the reactions of trifluoromethyl hypofluorite with sulfur dioxide. The new esters CF_3OSO_2F, $CF_3OSO_2OCF_3$, $CF_3OSO_2OSO_2F$, and $CF_3OSO_2OSO_2OCF_3$ were obtained from a mixture of products.

The reactions of pentafluorosulfur hypofluorite with both sulfur dioxide and sulfur tetrafluoride and of trifluoromethyl hypofluorite with sulfur tetrafluoride have now been investigated. The reactions were carried out in the liquid phase at temperatures from 0 to 90° in autoclaves which would withstand corrosion by these very reactive materials. This is in contrast to the conditions used by Van Meter and Cady,[2] who studied their reaction in the gas phase at 170–185°.

The effect of added oxygen on the reactions with sulfur tetrafluoride has also been studied.

Reaction between Pentafluorosulfur Hypofluorite and Sulfur Dioxide.—Pentafluorosulfur hypofluorite reacts with sulfur dioxide to give sulfur hexafluoride, sulfuryl fluoride, sulfur trioxide, and pentafluorosulfur fluorosulfate, SF_5OSO_2F.

The sulfur hexafluoride corresponds to the carbon tetrafluoride produced in the reaction between trifluoromethyl hypofluorite and sulfur dioxide.[2] The compounds SF_5OSO_2F and CF_3OSO_2F form a similar pair. The production of sulfur trioxide and the absence of longer chain compounds in the present work are points of difference between the two reactions.

Since this work was completed pentafluorosulfur fluorosulfate has also been prepared by the photochemical reaction of sulfur dioxide with SF_5Cl, $SF_5{\cdot}SF_5$, or SF_5OOSF_5.[3] It has also been shown to be present in the higher boiling fraction which results from the fluorination of sulfur in the presence of oxygen.[4]

Reactions of Pentafluorosulfur Hypofluorite with Sulfur Tetrafluoride.—A wider range of products was obtained from the reaction of pentafluorosulfur hypofluorite with sulfur tetrafluoride than from the corresponding reaction with sulfur dioxide. The products were SF_5OSF_5, SF_5OOSF_5, and $SF_5OSF_4OSF_5$. The gas-phase reaction[5] at 140° gave similar products except that no $SF_5OSF_4OSF_5$ was formed.

A reliable elementary analysis of $SF_5OSF_4OSF_5$ could not be obtained and so the identity of the compound was established by a quantitative pyrolysis at 200°. The results of the pyrolysis showed that the reaction occurring was

$$2SF_5OSF_4OSF_5 \longrightarrow 3SF_6 + SO_2F_2 + 2SOF_4$$

One of the products of the reaction of pentafluorosulfur hypofluorite with sulfur tetrafluoride is $S_2F_{10}O_2$. This suggested that a similar reaction in the presence of oxygen might give $S_2F_{10}O_2$ as a major product and so provide a convenient method of preparation for this peroxide. Consequently, the reaction between pentafluorosulfur hypofluorite, sulfur tetrafluoride, and oxygen was studied over the temperature range 0–90°.

All the products previously made by the reaction in the absence of oxygen were obtained and, in addition, two new peroxides, $SF_5OSF_4OOSF_5$ and $SF_5OSF_4OOSF_4OSF_5$. The variation in the quantities of liquid products with final reaction temperature is shown in Fig. 1. It is seen that the proportion of $SF_5OSF_4OOSF_4OSF_5$ in the product decreases with increasing temperature while that of SF_5OOSF_5 increases. The proportion of $SF_5OSF_4OOSF_5$ increases sharply from 0 to 20° to but thereafter slowly declines. These results may be attributed to decreasing stability of the compounds with increasing chain length. The decomposition which occurs at the higher temperature follows the reaction scheme

$$\begin{tikzcd} SF_5OSF_4OOSF_4OSF_5 \arrow[r] & SF_5OSF_4OOSF_5 + SOF_4 \arrow[d] \\ & SF_5OOSF_5 + SOF_4 \end{tikzcd}$$

A study of the pyrolysis of $SF_5OSF_4OOSF_4OSF_5$ confirmed that such decomposition did occur and also helped to establish the identity of this peroxide.

The reaction of the peroxides with benzene was used to provide further evidence of their structure. It has

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[1] Paper presented to "Second International Symposium on Fluorine Chemistry," Estes Park, Colorado, July 17–20, 1962.

[2] W. P. Van Meter and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 6006 (1960).

[3] H. J. Emeléus and K. J. Packer, *J. Chem. Soc.*, 771 (1962).

[4] B. Cohen and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 754 (1962).

[5] S. M. Williamson and G. H. Cady, *ibid.*, **1**, 673 (1962).

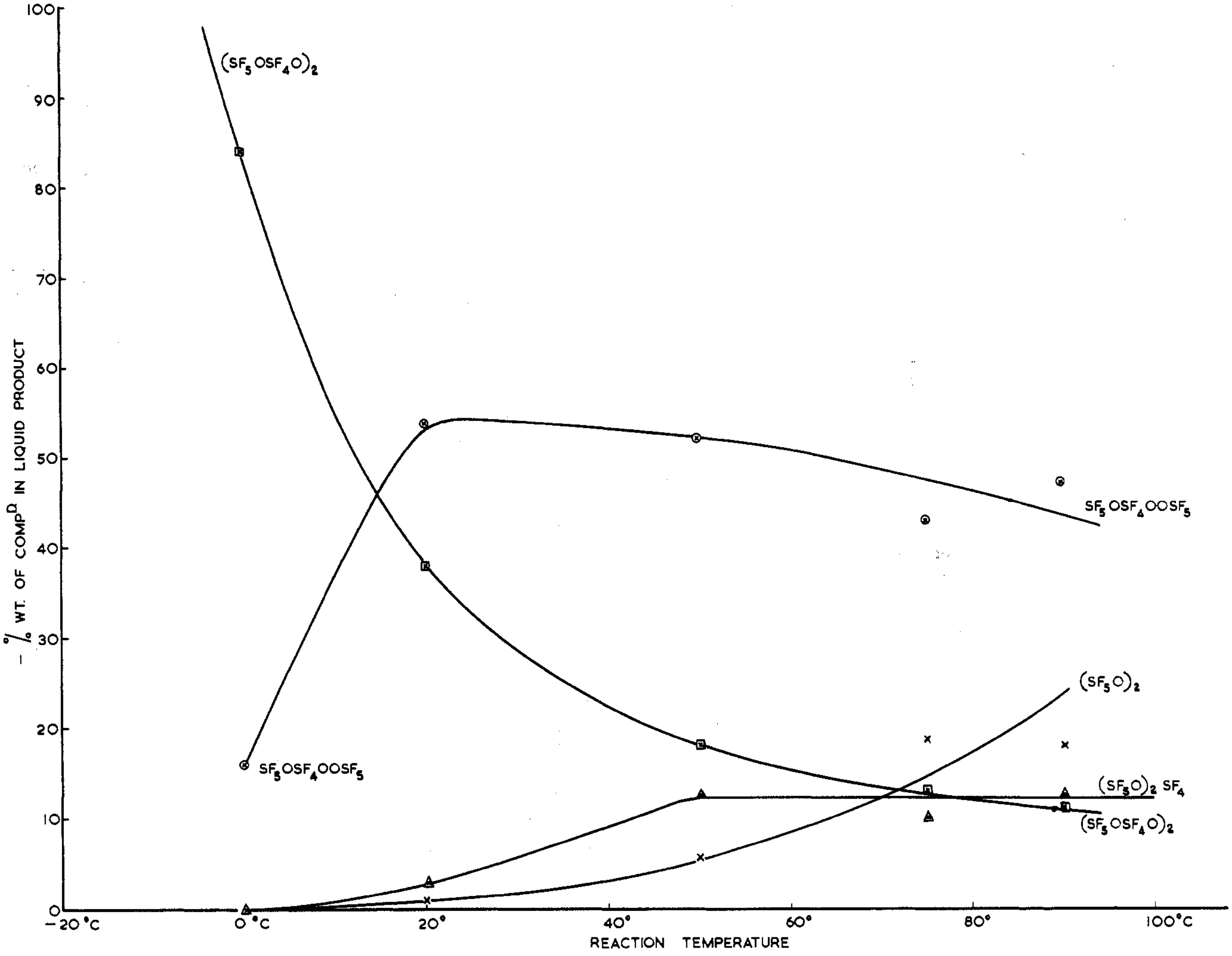

Fig. 1.—Variation of reaction products with temperature.

been shown[6] that SF_5OOSF_5 reacts with benzene at 150° to give $C_6H_5OSF_5$. The compound $SF_5OSF_4OOSF_5$ reacts with benzene at 75° to give mainly $C_6H_5OSF_5$ but a little $C_6H_5OSF_4OSF_5$ is also obtained. Under similar conditions $SF_5OSF_4OOSF_4OSF_5$ gives approximately equal quantities of $C_6H_5OSF_5$ and $C_6H_5OSF_4OSF_5$. This indicates, though it does not rigidly prove, that the highest boiling peroxide has the symmetrical structure given above rather than the structure $SF_5OSF_4OSF_4OOSF_5$.

Reaction of Trifluoromethyl Hypofluorite with Sulfur Tetrafluoride.—Trifluoromethyl hypofluorite reacts with sulfur tetrafluoride to give CF_3OSF_5 as the only product.

$$CF_3OF + SF_4 \longrightarrow CF_3OSF_5$$

The reaction in the presence of oxygen was studied only briefly but it appears to be basically similar to the corresponding reaction of pentafluorosulfur hypofluorite.

The new compounds $CF_3OSF_4OSF_5$ and $CF_3OSF_4OOSF_5$ were positively identified and a third compound, probably $CF_3OSF_4OOSF_4OCF_3$, was also produced. It is possible that the third compound is $CF_3OSF_4OSF_4OCF_3$, but the accuracy of elementary analysis for compounds of this type is such that no certain distinction can be made. The peroxide formulation is preferred by analogy with the corresponding compound $SF_5OSF_4OOSF_4OSF_5$ formed in the reaction between pentafluorosulfur hypofluorite, sulfur tetrafluoride, and oxygen.

Chemical Properties of Compounds Containing the $SF_5O\cdot$ Groups.—All the compounds containing the $SF_5O\cdot$ group react with sodium iodide in acetone to liberate iodine. The reaction is more vigorous the higher the molecular weight, and for a given oxide–peroxide pair, $SF_5OSF_4OSF_5$ and $SF_5OSF_4OOSF_5$, for example, the peroxides are very much more reactive. This behavior is in marked contrast to that of SF_6 and SF_5CF_2X, which give no reaction with sodium iodide, but similar to that of $SF_5{\cdot}SF_5$ and SF_5Cl. The tendency of the $SF_5\cdot$ group to act as an oxidizing agent is thus dependent on the group to which it is attached.

The compound SF_5OSF_5 has been shown to be extremely toxic to rats. It is the least reactive of all the compounds described in this work and so it must be assumed that all these materials are toxic. The compounds all have a sharp odor but it is likely that this is detectable only at a concentration well above that which

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[6] J. R. Case, R. H. Price, N. H. Ray, H. L. Roberts, and J. Wright, *J. Chem. Soc.*, 2107 (1962).

could be tolerated for long periods. Extreme caution should be exercised in handling these compounds.

Experimental

Trifluoromethyl hypofluorite,[7] pentafluorosulfur hypofluorite,[8] and sulfur tetrafluoride[9] were prepared by known methods. Sulfur dioxide was purchased from British Drug Houses Ltd. and used as received.

Reactions were carried out in a "Hastelloy C" autoclave of 125 cc. capacity which was fitted with an electromagnetically-operating reciprocating stirrer. The autoclave had a maximum safe-working pressure of 3000 atm. A bursting disk (usually set at 500 atm.) was fitted close to the head of the vessel. The autoclave was heated by a copper-block electric furnace and the temperatures measured were the temperatures of the outer wall of the vessel adjacent to the furnace. A cooling bath was used for reactions below room temperature and the temperatures recorded are those of the bath.

The autoclave was charged with reagents by first evacuating it, cooling with liquid air, and distilling in the required amount of reagent from a weighed cylinder. When it was desired to add oxygen to the reagents, this was done by adding it first at a pressure of 80 atm. to an intermediate vessel of 80 cc. capacity, from which it was added to the autoclave cooled in liquid air.

After a reaction the autoclave was cooled to room temperature and any gas pressure remaining was released through a system of traps cooled in liquid air. The autoclave was dismantled in a fume chamber. The liquid products were decanted and subsequently handled by conventional techniques.

Gas chromatographic analyses were carried out using columns packed with "Chromosorb" on which dinonyl phthalate or silicone grease had been deposited. The columns were maintained at a suitable temperature.

Reaction of Pentafluorosulfur Hypofluorite with Sulfur Dioxide.—Pentafluorosulfur hypofluorite (36 g.) and sulfur dioxide (30 g.) were heated at 50° for 10 hr. The gaseous products (46 g.) were shown by infrared spectroscopy and gas chromatographic analysis to contain sulfur hexafluoride and sulfuryl fluoride as major components. The liquid product fumed in air and contained sulfur trioxide. This was removed by refluxing with water. The remaining liquid (10 g.) formed a heavy lower layer and after drying was shown by gas chromatograhic analysis to contain only one compound. This was identified as pentafluorosulfur fluorosulfate, b.p. 38°. *Anal.* Calcd. for $F_6O_3S_2$: F, 50.5; S, 28.3; mol. wt., 226. Found: F, 50.6; S, 28.6; mol. wt., 223. The principal bands of the infrared spectrum are at 1492 (s), 1253 (s), 946 (vs), 886 (s), 829 (triplet) (s), 572 (doublet) (s) cm.$^{-1}$.

Reaction of Pentafluorosulfur Hypofluorite with Sulfur Tetrafluoride. (a) In the Absence of Oxygen.—Pentafluorosulfur hypofluorite (53 g.) and sulfur tetrafluoride (40 g.) were heated to 75° for 12 hr. The gaseous products (48.6 g.) were analyzed by gas chromatography and shown to contain sulfur hexafluoride (13.5 g.), sulfur tetrafluoride (21 g.), and thionyl tetrafluoride (13.9 g.). The liquid product was distilled and gave three fractions: (i) b.p. 31° (14.7 g.), (ii) b.p. 49° (12.2 g.), and (iii) b.p. 92° (13.9 g.).

Fraction (i) was identified by its infrared spectrum[10] as bis-(pentafluorosulfur) oxide.

Fraction (ii) was similarly identified as bis-(pentafluorosulfur) peroxide.[11]

Fraction (iii) was $SF_5OSF_4OSF_5$; $d_t = 2.1478 - 0.00289t$; $\log P = 7.659 - 1747/t$, from which $\Delta H_{\text{vap}} = 7.993$ cal. mole^{-1}. *Anal.* Calcd. for $F_{14}O_2S_3$: F, 67.5; S, 24.4; mol. wt., 394. Found: F, 68.5; S, 26.7; mol. wt., 388. The infrared spectrum had principal bands at 968 (vs), 953 (vs), 938 (s), 851(s), 806 (s), 785 (s), 535 (s) cm.$^{-1}$.

(b) In the Presence of Oxygen.—Pentafluorosulfur hypofluorite (33.5 g.) and sulfur tetrafluoride (72 g.) were distilled into the 125-cc. autoclave and oxygen (9 g.) was added as described above. The vessel was heated to 75° for 12 hr. The gaseous products (44 g.) were shown to be sulfur hexafluoride (3.3 g.), sulfur tetrafluoride (26.3 g.), and thionyl tetrafluoride (14.1 g.). The liquid product was distilled and gave five fractions. Fraction (i), b.p. 31° (6.6 g.), was SF_5OSF_5. Fraction (ii), b.p. 49° (8.8 g.), was SF_5OOSF_5. Fraction (iii), b.p. 92° (4.4 g.), was $SF_5OSF_4OSF_5$. Fraction (iv), b.p. 99° (19.4 g.), was $SF_5OSF_4OOSF_5$. *Anal.* Calcd. for $F_{14}O_3S_3$: F, 64.9; S, 23.4. Found: F, 62.3; S, 25.0. The infrared spectrum had principal bands at 960 (vs), 945 (vs), 875 (s), 849 (s), 798 (vs), 721 (m), 597 (s), 589 (s), 548 (s) cm.$^{-1}$. Fraction (v), b.p. 59° (20 mm.), was $SF_5OSF_4OOSF_4OSF_5$; $\log P = 8.709 - 2479/t$, which corresponds to a b.p. of 152° at 760 mm.; $\Delta H_{\text{vap}} = 11{,}342$ cal. mole^{-1}. The principal bands of the infrared spectrum were at 959 (vs), 944 (vs), 873 (m), 848 (vs), 820 (w), 803 (vs), 610–594 (doublet) (vs), 550–543 (doublet) (vs) cm.$^{-1}$.

A series of similar experiments at different reaction temperatures was carried out and the results are plotted in Fig. 1. The quantity of SOF_4, which is relatively large, is not shown because it would so distort the scale that the more interesting features would be obscured.

Pyrolysis Experiments.—The compounds $SF_5OSF_4OSF_5$, $SF_5OSF_4OOSF_5$, and $SF_5OSF_4OOSF_4OSF_5$ were pyrolyzed at 300° for 12 hr. in a 55-cc. autoclave. The products were quantitatively analyzed by gas chromatography. It was not possible to distinguish between SOF_4 and SO_2F_2 using this method but the ratio of these two compounds was measured by infrared spectroscopic analysis.

Pyrolysis of 0.0127 mole of $SF_5OSF_4OSF_5$ gave SF_6 (0.0187 mole) and $SO_2F_2 + SOF_4$ (0.0187 mole). The ratio of SO_2F_2:SOF_4 was found to be 1:2. This corresponds to

$$2SF_5OSF_4OSF_5 \longrightarrow 3SF_6 + 2SOF_4 + SO_2F_2$$

Pyrolysis of 0.009 mole of $SF_5OSF_4OOSF_4OSF_5$ gave SOF_4 (0.026 mole) and $S_2F_{10}O_2$ (0.005 mole).

Reaction of $SF_5OSF_4OOSF_4OSF_5$ with Benzene.—$SF_5OSF_4OOSF_4OSF_5$ (6 g.) was refluxed with dry benzene (20 ml.) for 2 hr. The gaseous product (1 g.) was identified as thionyl tetrafluoride. The liquid products were fractionated and after the unreacted benzene had been removed a fraction (3 g.), b.p. 60° (20 mm.), was obtained. This fraction was resolved into two components on a silicone grease gas chromatographic column.

The first fraction was identified as $C_6H_5OSF_5$, the second fraction was identified as $C_6H_5OSF_4OSF_5$. *Anal.* Calcd. for $C_6H_5O_2F_9S_2$: C, 20.95; H, 1.45; S, 18.6; F, 49.7. Found: C, 21.2; H, 1.4; S, 19.3; F, 48.0. The infrared spectrum had principal bands at 1480 (m), 1176 (m), 1152 (m), 912 (vs), 880 (vs), 815 (s), 766 (vs), 708 (m), 692 (s). cm. $^{-1}$

Reactions of $SF_5OSF_4OOSF_5$ with Benzene.—$SF_5OSF_4OOSF_5$ (5 g.) was refluxed with dry benzene (25 ml.) for 12 hr.

After the removal of unreacted benzene the remaining liquid product (2 g.) was identified by gas phase chromatography as mainly $C_6H_5OSF_5$ with a small amount of $C_6H_5OSF_4OSF_5$.

Reaction of Trifluoromethyl Hypofluorite with Sulfur Tetrafluoride. (a) In the Absence of Oxygen.—Trifluoromethyl hypofluorite (15 g.) and sulfur tetrafluoride (50 g.) were heated to 75° for 10 hr. A trace of liquid was produced but the main portion of the product was gaseous. The gas was expanded into an aspirator over first water and then 5 *N* sodium hydroxide. There remained 30 g. of a gas which was distilled on a Podbielniak column to yield a trace of trifluoromethyl hypofluorite, b.p. −46°, and a main fraction, b.p. −10° (27 g.), which was trifluoromethoxysulfur pentafluoride, CF_3OSF_5. *Anal.* Calcd. for CF_8SO: C, 5.7; F, 71.7; S, 15.1; mol. wt., 212. Found: C, 5.6; F, 70.1; S, 15.8; mol. wt., 215. The infrared spectrum had principal bands at 1274 (s), 1243 (s), 1202 (vs), 990 (m),

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(7) K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

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

(9) F. Nyman and H. L. Roberts, *J. Chem. Soc.*, 3180 (1962).

(10) H. L. Roberts, *ibid.*, 2774 (1960).

(11) C. I. Merrill and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 298 (1961).

937 (vs), 857 (triplet) (vs), 704 (triplet) (vs), 704 (triplet) (m), 606 (s) cm.$^{-1}$.

(b) **In the Presence of Oxygen.**—In a set of three reactions trifluoromethyl hypofluorite (75 g.) and sulfur tetrafluoride (113 g.) were heated to 75° in the presence of oxygen. The gaseous products (130 g.) were expanded over 5 *N* sodium hydroxide and much reaction took place. The unhydrolyzed portion was CF_3OSF_5.

The liquid products (56 g.) were refluxed for 1 hr. under 5 *N* potassium hydroxide, washed with water and saturated brine, and dried over magnesium sulfate. Distillation of the liquid yielded no definite fractions and samples ($\sim$1 cc.) of the compounds present were isolated by gas chromatography. They were, in order of elution (known compounds were identified by their retention time and infrared spectrum): Fraction (i), b.p. 49°, was SF_5OOSF_5. Fraction (ii), b.p. 78°, was CF_3OSF_4-OSF_5. *Anal.* Calcd. for $CF_{12}O_2S_2$: C, 3.6; F, 67.8; S, 19.1; mol. wt., 336. Found: C, 3.6; F, 67.4; S, 18.8; mol. wt., 340. The infrared spectrum had principal bands at 1279 (s), 1247 (s), 1191 (vs), 986 (m), 941 (vs), 898 (m), 844 (vs), 741 (w), 719 (w), 614 (w), 594 (w), 571 (w) cm.$^{-1}$. Fraction (iii), b.p. 102°, was $CF_3OSF_4OOSF_4OCF_3$. *Anal.* Calcd. for C_2F_{14}-O_4S_2: C, 5.8; F, 63.7; S, 15.3. Found: C, 6.0; F, 66.8; S, 16.3. The infrared spectrum had principal bands at 1279 (vs), 1244 (vs), 1198 (vs), 1181 (vs), 984 (s), 935 (s), 923 (s), 854 (vs), 846 (vs), 837 (vs) cm.$^{-1}$. Fraction (iv), a trace only, was $SF_5OSF_4OOSF_4OSF_5$. Fraction (v), b.p. 125°, was CF_3-OSF_4OOSF_5. *Anal.* Calcd. for $CF_{12}O_3S_2$: C, 3.4; F, 64.7; S, 18.2; mol. wt., 352. Found: C, 3.4; F, 64.6; S, 18.1; mol. wt., 355. The infrared spectrum had principal bands at 1279 (vs), 1245 (vs), 1190 (vs), 985 (s), 942 (vs), 927 (s), 903 (s), 869 (s), 840 (vs), 797 (vs), 546 (s) cm.$^{-1}$.

A trace of a component of longer retention time was detected but it could not be identified.

Discussion

The reactions of pentafluorosulfur hypofluorite and trifluoromethyl hypofluorite with sulfur dioxide and sulfur tetrafluoride show considerable similarities and it seems likely that they occur by a similar mechanism. This possibility should be treated with some care, however, because the work of Van Meter and Cady[2] on the CF_3OF–SO_2 reaction was carried out in the vapor phase at a relatively high temperature, while the reactions considered in this work were studied in the liquid phase below 100°. The scheme of reactions outlined below is shown to be consistent with the observed products and some attempt is made to correlate the results obtained but it is realized that this is only one of several which could be proposed.

In the proposed mechanism which follows, the hypofluorites are written as RO–F, where R is $CF_3\cdot$ or $SF_5\cdot$.

Initiation

$$RO\text{–}F + SO_2 \longrightarrow RO\cdot + SO_2F\cdot$$
$$RO\text{–}F + SF_4 \longrightarrow RO\cdot + SF_5\cdot$$

This reaction is likely to be exothermic because one O–F bond is lost and one S–F is gained, the latter being the stronger bond.[12] A simple recombination of these two radicals, possibly involving a wall or a third body, accounts for the formation of SF_5OSO_2F, CF_3OSO_2F, SF_5OSF_5, and CF_3OSF_5.

Propagation and Termination

$$SO_2F\cdot + RO\text{–}F \longrightarrow SO_2F_2 + RO\cdot$$
$$SF_5\cdot + RO\text{–}F \longrightarrow SF_6 + RO\cdot$$

This reaction accounts for the formation of SO_2F_2 and SF_6. This is the only significant reaction of $SO_2F\cdot$ and $SF_5\cdot$ in the absence of oxygen, because no products of the type $SF_5\cdot SF_5$ or $SF_5\cdot SF_4\cdot$ are obtained.

$$RO\cdot + SF_4 \longrightarrow ROSF_4\cdot \tag{a}$$
$$RO\cdot + SO_2 \longrightarrow ROSO_2\cdot$$
$$RO\cdot + SF_4 \longrightarrow R\cdot + SF_4O \tag{b}$$
$$RO\cdot + SO_2 \longrightarrow R\cdot + SO_3$$

All these reactions must occur to some extent. Reaction (b) accounts for the presence of SO_3 in reactions of SO_2 and for SF_4O in reactions of SF_4. Reaction (b) is of more importance when R is $SF_5\cdot$ because in this case SO_3 and SOF_4 occur in greater quantity than when R is $CF_3\cdot$. When R is $CF_3\cdot$ the formation of CF_4 follows from the production of $CF_3\cdot$ in reaction (b).

$$CF_3\cdot + CF_3O\cdot F \longrightarrow CF_4 + CF_3O\cdot$$

Reaction (a) gives the radicals $ROSF_4\cdot$ and $ROSO_2\cdot$, which are similar in reactivity to either $SF_5\cdot$ or $FSO_2\cdot$. The reactions

$$ROSO_2\cdot + ROF \longrightarrow ROSO_2F + RO\cdot$$
$$ROSF_4\cdot + ROF \longrightarrow ROSF_5 + RO\cdot$$

account for the products SF_5OSO_2F, CF_3OSO_2F, SF_5OSF_5, and CF_3OSF_5. A radical recombination of the type

$$2RO\cdot \longrightarrow ROOR$$

will explain the formation of SF_5OOSF_5 while reactions

$$ROSO_2\cdot + RO\cdot \longrightarrow ROSO_2OR$$
$$ROSF_4\cdot + RO\cdot \longrightarrow ROSF_4OR$$

will give $CF_3OSO_2OCF_3$, $SF_5OSF_4OSF_5$, and CF_3OSF_4-OSF_5. The absence of any products derived from $SF_5OSO_2\cdot$ in the SF_5OF–SO_2 reaction other than SF_5OSO_2F suggests that this radical has only a short lifetime.

In the presence of oxygen, a reaction following the initial reaction

$$SF_5OF + SF_4 \longrightarrow SF_5\cdot + SF_5O\cdot$$

is likely to be

$$SF_5\cdot + O_2 \longrightarrow SF_5OO\cdot$$

which is known to be a probable reaction in the photochemical oxidation of SF_5Cl.[10] The radical CF_3-$OSF_4\cdot$ or $SF_5OSF_4\cdot$ would be expected to pick up oxygen in a similar manner. The reactions

$$SF_5\cdot + ROSF_4OO\cdot \longrightarrow ROSF_4OOSF_5$$
$$ROSF_4\cdot + ROSF_4OO\cdot \longrightarrow ROSF_4OOSF_4OR$$

now at once account for the formation of SF_5OSF_4-$OOSF_5$, $CF_3OSF_4OOSF_5$, $SF_5OSF_4OOSF_4OSF_5$, and $CF_3OSF_4OOSF_4OCF_3$. It is for this reason that the structure $CF_3OSF_4OOSF_4OCF_3$ is preferred to CF_3-$OSF_4OSF_4OCF_3$ in the assignment of structures to the products of the CF_3OF–SF_4–O_2 reaction, although this is clearly not a rigorous proof.

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(12) T. L. Cottrell, "Strength of Chemical Bonds," Butterworths, London, 1954, pp. 280 and 282.