obtained in addition to $FSO_2ON(SO_2)F_2$. Since no reaction was observed between $N_2(SO_2F)_4$ and $S_2O_6F_2$ under the same conditions, $N_2(SO_2F)_4$ cannot be an intermediate in the formation of $FSO_2ON(SO_2F)_2$ and probably represents a simple coupling reaction of the R· radicals in the above scheme.

The reaction of covalent fluorosulfate derivatives with fluoride ion has been shown to follow the generalized equation[1,14,15]

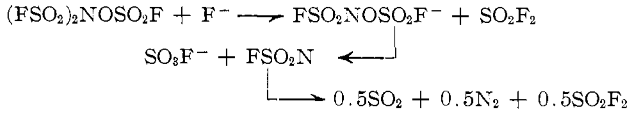
$$ROSO_2F + F^- \longrightarrow RO^- + SO_2F_2$$

The fate of the new anion (RO^-) was found to be dependent on its nature. This reaction was extended to the fluorosulfate derivatives prepared in this study. Both peroxyfluorosulfates, CF_3OOSO_2F and SF_5OOSO_2F, underwent reaction with fluoride ion at ambient temperature in a similar manner

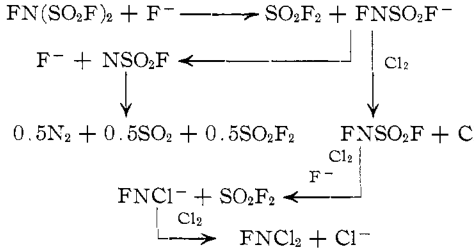
$$ROOSO_2F + F^- \longrightarrow RO^- + 0.5O_2 + SO_2F_2 \quad (R = CF_3 \text{ or } SF_5)$$

Evidence for the nature of the anion formed in this reaction was obtained by fluorination of the residue after the volatiles produced in the reaction had been removed. High yields of either SF_5OF or CF_3OF were produced. It is not known whether the peroxy anion ROO^- is an important species in the reaction scheme. However, when the reaction of CF_3OOSO_2F and KF was carried out in the presence of excess CF_3OF, moderate yields of the trioxide, CF_3OOOCF_3,[8,9] were isolated. This may indicate the existence of CF_3OO^- anions in the system although conclusive evidence is lacking. No reaction was observed when SF_5OOSO_2F and CF_3OF were allowed to interact in the presence of an alkali metal fluoride. Only the decomposition of SF_5OOSO_2F occurred under these experimental conditions as discussed above.

The reaction of $FSO_2ON(SO_2F)_2$ with NaF was also investigated. In this case there are two types of SO_2F groups, and it was of interest to see which type would be the most reactive toward fluoride ion. The reaction was found to follow the scheme (see the Experimental Section)



The reaction of $FN(SO_2F)_2$[16] with the fluoride ion appeared to follow a similar course. Thus, when $FN(SO_2F)_2$ was allowed to contact cesium fluoride in the absence of a solvent, only nitrogen, sulfur dioxide, and sulfuryl fluoride were obtained. When the reaction was carried out in the presence of an equimolar amount of chlorine, a low yield (about 10%) of dichlorofluoramine was produced



Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021-AMC-11536(Z).

[14] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).
[15] M. Lustig and J. K. Ruff, *ibid.*, **3**, 287 (1964).
[16] M. Lustig, *et al.*, *ibid.*, **3**, 1165 (1964).

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The Reaction of Dioxygen Difluoride and Sulfur Dioxide. Transfer of the OOF Group

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Received January 30, 1968

The reaction of dioxygen difluoride with sulfur dioxide produces mainly sulfuryl fluoride and lesser amounts of pyrosulfuryl fluoride and fluorosulfuryl hypofluorite. The mechanism of this reaction was studied using O^{17}-tracer techniques and O^{17} nmr measurements. It was concluded that the sulfuryl fluoride is formed by a simple fluorination reaction. The pyrosulfuryl fluoride is formed *via* an FSO_3· intermediate, which results in scrambling. It was concluded that fluorosulfuryl hypofluorite results *via* an OOF intermediate.

Introduction

The chemistry of dioxygen difluoride (O_2F_2) is quite unique in that O_2F_2 reacts with most substances at temperatures of −160° or below.[1] Even at these low temperatures, a violent reaction or an explosion occurs when O_2F_2 reacts with most organic or inorganic materials containing hydrogen. Many other reactions of O_2F_2 are so violent that cleavage of most bonds occurs and results in simple degradation products.

We found that the reaction of O_2F_2 with sulfur dioxide can be controlled and is particularly useful in

[1] A. G. Streng, *J. Am. Chem. Soc.*, **85**, 1380 (1963).

elucidating the chemistry of O_2F_2. Since the reactions of O_2F_2 are so fast, it is very difficult, if not impossible, to study the mechanisms of reactions by conventional kinetic studies. Therefore, we studied the reaction of O_2F_2 and SO_2 by oxygen-17 tracer techniques.

Results and Discussion

The reaction of O_2F_2 and sulfur dioxide (SO_2) was studied in detail; the results of several reactions are given in Table I. In addition, we attempted to obtain a better understanding of the reaction of O_2F_2 and SO_2 by carrying out individual experiments. Also, the starting materials were appropriately labeled with O^{17} and the positions of O^{17} in the products were determined by O^{17} nmr techniques. Each product is discussed separately.

TABLE I

REACTIONS OF O_2F_2 WITH SO_2

	Temp, °C		
	−160	−160	−183
	Solvent		
	None	None	CF_3Cl
	mmol		
O_2F_2 charged	15.5	20.0	18
SO_2 charged	15.6	10.2	15.4
Products			
O_2	12.0	18.0	14.3
F_2	1.9	9.6	0.1
F_2SO_2	10.3	7.2	12.2
FSO_2OSO_2F	2.7	1.1	1.8
FSO_2OOF	1.5	0.7	0.8
FSO_2OF	Trace	Trace	Trace

Sulfuryl Fluoride.—From these experiments we concluded that the main reaction can be represented as shown in eq 1, although it may not be as simple as

$$SO_2 + O_2F_2 \longrightarrow F_2SO_2 + O_2 \qquad (1)$$

shown. This reaction is comparable to the reaction of fluorine with SO_2 reported by Dudley, Cady, and Eggers,[2] in which F_2SO_2 was also the main product and pentafluorosulfur hypofluorite (SF_5OF) was formed as a minor product. The main difference, however, is that the experiment reported by Dudley, *et al.*, was carried out at 200°, whereas our work was carried out at −160° or lower.

If reaction 1 is a simple fluorination, no oxygen should transfer from O_2F_2 to F_2SO_2. This hypothesis was proven by carrying out the reactions 2 and 3 with O^{17}-labeled compounds.

$$SO^{17}_2 + O_2F_2 \longrightarrow F_2SO^{17}_2 + O_2 \qquad (2)$$

$$SO_2 + O^{17}_2F_2 \longrightarrow F_2SO_2 + O^{17}_2 \qquad (3)$$

The O^{17} nmr spectrum (Figure 1) of the $F_2SO^{17}_2$ from reaction 2 consisted of a triplet line due to $S{=}O^{17}$. The triplet results because of coupling of O^{17} with the two fluorine atoms. The position of the chemical shift of this triplet (−148 ppm) is important because it helps define the region expected for the $S{=}O^{17}$ line in similar compounds.

The O_2 formed in reaction 2 did not contain O^{17}, and the F_2SO_2 formed in reaction 3 did not contain O^{17}. Since scrambling was not observed, we concluded that F_2SO_2 is formed by a simple fluorination reaction.

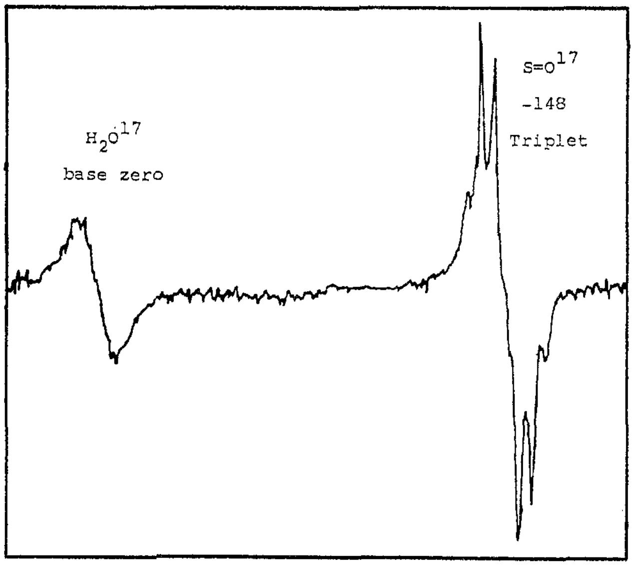

Figure 1.—O^{17} nmr spectrum of F_2SO_2 prepared from the reaction of SO^{17}_2 with O_2F_2.

Fluorosulfuryl Hypofluorite.—A more interesting product of the reaction of O_2F_2 with SO_2 is fluorosulfuryl hypofluorite (FSO_2OOF). (This compound has previously been called peroxysulfuryl difluoride. A referee pointed out that fluorosulfuryl hypofluorite is more suitable.) Later, we will show that FSO_2OOF is formed *via* an OOF intermediate; that is, the OOF group is transferred intact from the O_2F_2 to the FSO_2OOF.

Both the OOF[3–6] and the OF[7–9] radicals have been reported, and the work done to date shows that the OOF radical is more stable. In general, it can be said that O_2F_2 is a source of the OOF radical, whereas the OF radical results from the irradiation of OF_2. It has been shown[9,10] that the photolytic reaction of sulfur trioxide (SO_3) and OF_2 proceeds *via* OF radicals

$$F_2O \xrightarrow{h\nu} F\cdot + OF\cdot \qquad (4)$$

$$SO_3 \xrightarrow{F\cdot} FSO_3\cdot \xrightarrow{OF\cdot} FSO_2OOF \qquad (5)$$

However, no reaction chemistry of O_2F_2 reported to date has been explained in terms of the OOF radical.

The reactions shown in eq 6–8 were carried out, the FSO_2OOF fraction was separated, and its O^{17} nmr spectra were analyzed.

$$O^{17}_2F_2 + SO^{17}_2 \longrightarrow FSO^{17}_2O^{17}O^{17}F + \ldots \qquad (6)$$

$$O^{17}_2F_2 + SO_2 \longrightarrow FSO_2O^{17}O^{17}F + \ldots \qquad (7)$$

$$O_2F_2 + SO^{17}_2 \longrightarrow FSO^{17}_2OOF + \ldots \qquad (8)$$

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

[3] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **44**, 434 (1966).

[4] A. Arkell, *J. Am. Chem. Soc.*, **87**, 4057 (1965).

[5] R. D. Sprately, J. J. Turner, and G. C. Pimentel, *J. Chem. Phys.*, **44**, 2063 (1966).

[6] P. H. Kassai and A. D. Kirshenbaum, *J. Am. Chem. Soc.*, **87**, 3069 (1965).

[7] A. Arkell, R. R. Reinhardt, and L. P. Larson, *ibid.*, **87**, 1016 (1965).

[8] F. Neumayr and N. Vanderkooi, Jr., *Inorg. Chem.*, **4**, 1234 (1965).

[9] R. Gatti, E. H. Starrico, J. E. Sicre, and H. J. Schumacher, *Z. Physik. Chem.* (Frankfurt), **36**, 211 (1963).

[10] I. J. Solomon, A. J. Kacmarek, and J. Raney, *J. Phys. Chem.*, in press.

TABLE II

O^{17} NMR DATA FOR FSO_2OOF SAMPLES

Sample	Chemical shift, ppm, relative to H_2O^{17}		
	$S=O^{17}$	$S—O^{17}$	$O^{17}—F$
$O^{17}{}_2F_2 + SO^{17}{}_2$	−152 (Doublet, $J \sim 31$ cps)	−365	−669 (Doublet, $J > 430$ cps)
$O^{17}{}_2F_2 + SO_2$		−365	−669 (Doublet, $J > 430$ cps)
$O_2F_2 + SO^{17}{}_2$	−152 (Doublet, $J \sim 31$ cps)		

First, FSO_2OOF with a random distribution of O^{17} was prepared (reaction 6), and the O^{17} nmr spectrum (Table II) was found to contain three lines due to the three different oxygen atoms in the molecule. The line at −152 ppm is in the region expected[11] for S=O and it is a doublet, as expected, due to the O^{17}–F^{19} spin–spin coupling. The line at −669 ppm is assigned to the O^{17}–F oxygen atom; it is also a doublet, as expected, since the oxygen is directly attached to a fluorine atom. The singlet at −365 ppm is attributed to the oxygen in the S—O^{17} position.

If the FSO_2OOF results *via* an OOF transfer, the FSO_2OOF prepared according to eq 7 should contain two O^{17} lines—the $FSO_2O^{17}OF$ line and the $FSO_2OO^{17}F$ line—and, as shown in Table II, this was the case. The alternative spectrum (Table II) is expected for the FSO_2OOF prepared according to reaction 8. This spectrum should contain the $FSO^{17}{}_2OOF$ line only, and it does. Therefore we concluded that O_2F_2 reacts with SO_2 to form FSO_2OOF *via* an OOF intermediate.

Disulfuryl Fluoride.—As stated earlier, FSO_2OSO_2F is also a product of the reaction of O_2F_2 with SO_2. To identify the O^{17} lines in the spectrum of this compound, FSO_2OSO_2F containing a random distribution of O^{17} was prepared as in

$$SO^{17}{}_2 + O^{17}{}_2F_2 \longrightarrow FSO^{17}{}_2O^{17}SO^{17}{}_2F + \ldots \qquad (9)$$

The tracer experiments shown in reactions 10 and 11 were also carried out.

$$SO_2 + O^{17}{}_2F_2 \longrightarrow FSO^{17}{}_2O^{17}SO^{17}{}_2O^{17}F + \ldots \qquad (10)$$

$$SO^{17}{}_2 + O_2F_2 \longrightarrow FSO^{17}{}_2O^{17}SO^{17}{}_2F + \ldots \qquad (11)$$

For FSO_2OSO_2F containing a random distribution of O^{17}, the O^{17} nmr spectrum, as expected, contains two lines, −167 and −238 ppm (Figure 2). The two S=O^{17} bonds for this compound are equivalent. The chemical shift for these O^{17} atoms should appear in the S=O^{17} region, and the line should be a triplet due to O^{17}—F^{19} coupling. This was verified by experiment and the line at −167 ppm was assigned to the O^{17} atoms in the S=O^{17} positions. The other line, at −238 ppm, is due to the oxygen atom in the S—O^{17}—S position.

The O^{17} nmr spectra of the FSO_2OSO_2F obtained in the tracer reactions shown in eq 10 and 11 were the same as that shown in Figure 2. Thus it can be stated that scrambling occurs in these reactions. Actually, this result might be expected, since FSO_2OSO_2F probably results *via* an $FSO_3\cdot$ intermediate. If this intermediate contained O^{17} in a preferred position, it would scramble in the manner

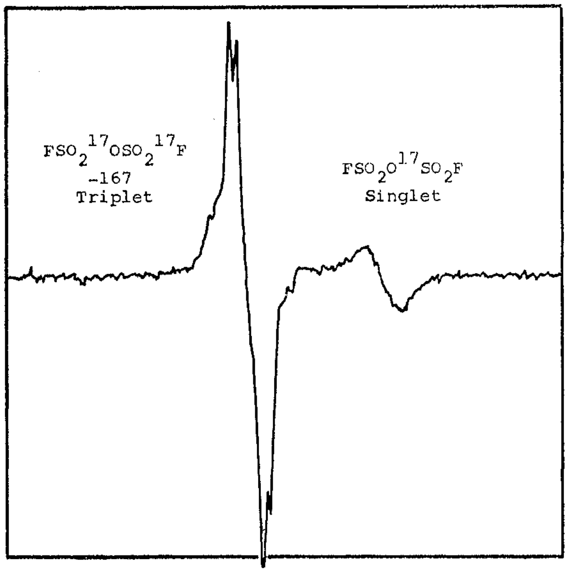
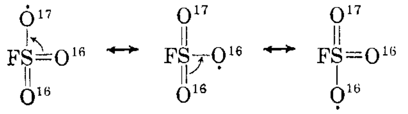


Figure 2.—O^{17} nmr spectrum of $FSO^{17}{}_2O^{17}SO^{17}{}_2F$ prepared from the reaction of $SO^{17}{}_2$ with $O^{17}{}_2F_2$.

 (12)

Conclusion

The reaction of O_2F_2 with SO_2 at −160° or lower produces mainly F_2SO_2, lesser amounts of $F_2S_2O_5$ and FSO_2OOF, and a trace of FSO_2OF. The reaction is difficult to control and the heat of reaction causes some decomposition of O_2F_2 (which probably results in F and OOF). It is deduced that the F_2SO_2 is formed from a simple fluorination reaction.

It is concluded that the FSO_2OOF found in the reaction of O_2F_2 and SO_2 is formed *via* an OOF intermediate. The first step is probably the formation of FSO_2, which adds OOF, but the present data cannot be used to predict the actual mechanism, other than stating that it does involve an OOF intermediate.

In determining the structure of O_2F_2 by microwave spectroscopy, Jackson[12] found that the O–O distance (1.217 ± 0.003 Å) is particularly short and that the O–F distance (1.575 ± 0.003 Å) is particularly long. Thus, the weakest bond in O_2F_2 is the O–F bond. As pointed out earlier,[3-6] the OOF radical has been shown to exist at low temperature. Also, since FSO_2OF is not

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[11] H. A. Christ, P. Diehl, H. R. Schneider, and H. Dahn, *Helv. Chim. Acta*, **44**, 865 (1961).

[12] R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

formed in substantial amounts in the reaction of O_2F_2 with SO_2, the OF radical is probably not an intermediate in the reactions of O_2F_2. The conclusion that the OF radical is not an intermediate in the chemistry of O_2F_2 is substantiated by the fact that OF_2 is not formed in the decomposition of O_2F_2.

Experimental Section

System for Handling O^{17}.—Since the enriched oxygen is very expensive, a method was needed for quantitatively transferring the gas in the vacuum system. Since oxygen exhibits a vapor pressure of approximately 158 mm at $-196°$, it cannot be fully condensed at this temperature. The pressure can be lowered in two ways: either the temperature can be lowered, or the oxygen can be absorbed on a substrate. At liquid helium temperature, the vapor pressure of oxygen is negligible; however, the use of liquid helium is inconvenient and time consuming. The pressure of the absorbed oxygen on Type 13X Linde Molecular Sieves at $-196°$ was found to be less than 0.01 mm when the weight ratio of molecular sieves was 10:1 or greater.

Mass spectral analysis of the oxygen before and after condensation showed that there was no exchange of the enriched oxygen with the oxygen in the molecular sieves.

It was found that the enriched oxygen as obtained from the supplier contained about 3 mol % hydrogen, which would create a serious problem if it were not removed. A convenient method for removing the hydrogen was to condense the bulk sample of gas at 196° in a molecular sieve trap and pump out the hydrogen.

Preparation of O_2F_2.—O_2F_2 was prepared by using the method previously reported.[1] The O_2F_2 enriched in O^{17} was made by using 10% enriched oxygen (YEDA Research and Development Co. Ltd.) in place of ordinary oxygen.

Preparation of Labeled Sulfur Dioxide.—Enriched SO_2 was prepared by allowing sulfur to react with 10% enriched oxygen at 300°.

Reaction of O_2F_2 and SO_2.—After the O_2F_2 was prepared, it was allowed to drain to the bottom of the reactor. A measured amount of SO_2 was distilled into the reactor while the O_2F_2 was maintained at liquid nitrogen temperature. The liquid nitrogen dewar was slowly lowered, allowing the SO_2 to melt and make contact with the O_2F_2. If a solvent was used, it was also distilled into the reactor and used to wash down the reactants. The reactor was then maintained at the desired reaction temperature until the red color of the O_2F_2 disappeared.

Product Analysis.—The reactor was kept at $-196°$ (all of the products except O_2 and F_2 are nonvolatile at this temperature). The O_2 and F_2 formed were allowed to pass through a sodium chloride trap maintained at 200° (the F_2 is converted to Cl_2), through a liquid nitrogen trap to condense the Cl_2 formed, and into a molecular sieve trap maintained at $-196°$ in order to recover the oxygen. The chlorine and oxygen were measured by pressure determination in a calibrated volume.

The remaining products were then separated by trap-to-trap distillation or the Cady[13] codistillation method. The FSO_2OSO_2F, FSO_2OOF, and SO_2F_2 were recovered at -95, -126, and $-160°$, respectively. Both infrared and nmr analyses were used to characterize the products, but F^{19} nmr analysis was the best method, since the chemical shifts for all compounds in question had previously been reported.[14]

Nmr Spectra.—The O^{17} nmr spectra were obtained at 8.13 Mc with the conventional Varian DP-60 equipped with a low-temperature, wide-line dewar coil. The cooling system was altered slightly to obtain better temperature control and to allow rapid insertion of the sample. Gaseous nitrogen that had been previously cooled by passage through a copper coil immersed in liquid nitrogen was used for cooling. The temperature was controlled to within ±1° by varying the flow of nitrogen.

The spectra of F_2SO_2, FSO_2OOF, and FSO_2OSO_2F were obtained at -100, -10, and 25°, respectively. The O^{17} chemical shifts are given with respect to H_2O^{17}. Since it was not possible to use an internal standard for the calculation of chemical shifts, the magnetic field was calibrated before and after each experiment. In the case of high resolution, intensity ratios were computed by integration of signal areas. The F^{19} spectra were observed at 56.4 Mc.

Acknowledgment.—Technical direction was provided by the Director of Engineering Sciences, SREP, Air Force Office of Scientific Research, Contract No. AF44620-68-C-0039.

(13) G. H. Cady and D. P. Siegworth, *Anal. Chem.*, **31**, 618 (1959).

(14) G. Franz and F. Neumayr, *Inorg. Chem.*, **3**, 921 (1964).

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Explosion Temperatures of Lead Azide Crystals in Molten Salt Environments

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Received December 8, 1967

Lead azide crystals which usually explode at temperatures below 320° have minimum explosion temperatures of 500° when dropped into molten alkali halides and 620° when dropped into molten alkali nitrates. Calculations indicate that the high explosion temperatures observed in molten salts may be due to the greatly improved conditions for heat transfer to the surroundings. In alkali nitrate melts lead oxide is formed instead of catalytically acting lead metal which may be the cause for the further increased explosion temperature.

Introduction

The isothermal decomposition of lead azide, $PbN_6 \rightarrow Pb + 3N_2$, is a slow process at temperatures as high as 280°.[2] Nevertheless, raising the temperature of the apparatus only 20–40° is sufficient to cause explosions. This happens because the decomposition rate attains a critical value beyond which no equilibrium between the rate of heat production and rate of heat loss is possible. Self-heating results which leads to explosion.

In experiments not previously reported by this investigator, the temperature increase due to self-heating was

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[1] Energy Conversion Research Division, U. S. Army Mobility Equipment Research and Development Center, Fort Belvoir, Va. 22060.

[2] (a) D. A. Young, *J. Chem. Soc.*, 3141 (1964); (b) W. E. Garner and A. S. Gomm, *ibid.*, 2123 (1931).