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The Reaction of Dioxygen Difluoride with Sulfur Oxides and with Sulfur Oxyfluorides

IRVINE J. SOLOMON, ANDREW J. KACMAREK, and JACK M. McDONOUGH
IIT Research Institute, Technology Center, Chicago, Ill. 60616

Dioxygen difluoride (O_2F_2) is considerably less stable than previously reported. The reaction of O_2F_2 with SO_2 at −160° C. produced mainly F_2SO_2 and lesser amounts of FSO_2OOF and FSO_2OSO_2F. The FSO_2OSO_2F was accounted for by several routes. The F_2SO_2 did not react further with O_2F_2. The reaction of O_2F_2 with the SO_3 produced equimolar amounts of FSO_2OF and $F_2S_2O_6$, which was resistant to further attack of O_2F_2. In contrast to previous attempts to produce SOF compounds by allowing H_2SO_4 to react with fluorinating agents, small amounts of FSO_2OF were formed when O_2F_2 and H_2SO_4 were allowed to react. H_2SO_5 was more reactive toward O_2F_2 than H_2SO_4. The reaction of O_2F_2 and F_2SO produced F_4SO, which did not react further with O_2F_2.

THE CHEMISTRY of dioxygen difluoride (O_2F_2) is unusual since it reacts with most substances at temperatures of −160° C. or below (*12*). Even at these low temperatures, a violent reaction or an explosion occurs when O_2F_2 reacts with any organic material and most inorganic materials containing hydrogen. Many other reactions of O_2F_2 are so violent that simple degradation products result. The reactions of O_2F_2 with various sulfur oxides and with sulfur oxyfluorides can be controlled, and products are formed at −100° C. or lower. Temperatures of 200° to 300° C. are necessary for the formation of these products by conventional fluorination reactions.

RESULTS

Stability of O_2F_2. It was necessary to understand the decomposition of O_2F_2 before studying its chemistry so that decomposition would not be confused with actual reaction. The completeness of a reaction was usually assessed by the disappearance of the red color of the O_2F_2.

O_2F_2 decomposes to oxygen and fluorine, and from all indications to date, it probably decomposes via fluorine atoms. Since fluorine atoms react with most or all of the materials studied, O_2F_2 can act merely as a source of fluorine atoms—i.e., as a simple fluorinating agent. But if the actual chemistry of O_2F_2 is to be determined, the reaction conditions must be those under which O_2F_2 is stable. It is difficult to achieve this ideal situation, since heat released during the reaction serves to decompose the unaltered O_2F_2. However, some success was achieved.

Frisch and Schumacher (*5, 6*) have reported that liquid O_2F_2 decomposes at the rate of 4.3% per day at −78° C. and that its half-life at −50° C. is 220 minutes. The authors found, however, that O_2F_2 is considerably less stable than previously reported and observed a 4% per day decomposition at −160° C. This decomposition was calculated from the average quantities of oxygen and fluorine formed during a 1-day period. Data were not taken over an extended period of time because we did not intend to study the kinetics of decompositions of O_2F_2. Since most of the reactions of O_2F_2 are complete in a matter of seconds or minutes, it was thought that if the reactions were carried out at −160° C. or lower, very little decomposition of O_2F_2 would occur.

Reaction of O_2F_2 with SO_2. The reaction of O_2F_2 with sulfur dioxide (SO_2) at −160° C. was previously studied in detail (*11*). The main reaction is that shown in Equation 1, and two minor products (pyrosulfuryl fluoride, FSO_2OSO_2F, and peroxysulfuryl difluoride, FSO_2OOF) are formed via an OOF intermediate.

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

The main product of this reaction is the same as that reported for the reaction of fluorine with SO_2 (*3*), however pentafluorosulfur hypofluorite was a minor product in the latter reaction.

In further elucidating the chemistry of the SO_2-O_2F_2 system, we found that F_2SO_2 does not react with O_2F_2; actually a stable solution is formed. Its stability is further demonstrated by the facts that F_2SO_2 is stable in the presence of decomposing O_2F_2 (or F atoms) and is also unaffected by passage through a silver difluoride (AgF_2) catalytic reactor with excess fluorine (*3*).

The presence of $F_2S_2O_5$ as a reaction product of O_2F_2 and SO_2 could have occurred by several routes. Photolytic reactions were used to simulate the free-radical conditions caused by the presence of fluorine atoms, and room-temperature reactions were used to simulate the conditions that the products were exposed to during separation. Although peroxysulfuryl difluoride, FSO_2OOF, is quite stable at room temperature, it decomposes rapidly in the presence of ultraviolet light. Neumayr and Vanderkooi (*7*) found that FSO_2OOF was quite unstable when exposed to ultraviolet light; it decomposed to $F_2S_2O_5$, F_2SO_2, and noncondensible gas. The mole ratio of $F_2S_2O_5$ to F_2SO_2 was approximately 2.

The authors also confirmed the fact that FSO_2OOF is quite unstable when exposed to ultraviolet light; however, a somewhat different product distribution was observed, and the noncondensible gas was oxygen:

$$\underset{10.5\ \text{cc.}}{FSO_2OOF} \xrightarrow[24\ \text{hr.}]{25^\circ\ h\nu} \underset{8.7\ \text{cc.}}{F_2SO_2} + \underset{1.0\ \text{cc.}}{F_2S_2O_5} + \underset{7\ \text{cc.}}{O_2} \tag{2}$$

No reactant was recovered.

We found that $F_2S_2O_5$ is also formed by the reaction of FSO_2OOF with SO_2:

$$\underset{25.5\ \text{cc.}}{FSO_2OOF} + \underset{16.8\ \text{cc.}}{SO_2} \xrightarrow[1\ \text{hr.}]{25^\circ} \underset{18.4\ \text{cc.}}{SO_2F_2} + \underset{5.8\ \text{cc.}}{F_2S_2O_5} + \underset{10.0\ \text{cc.}}{O_2} \tag{3}$$

Roberts (*8*) reported that $F_2S_2O_5$ is also formed by the reaction of FSO_2OF with SO_2 at 195° C. The reaction occurs at room temperature, but it is quite slow:

$$\underset{3.2\ \text{mmoles}}{FSO_2OF} + \underset{3.1\ \text{mmoles}}{SO_2} \xrightarrow[6\ \text{days}]{25^\circ\ \text{C.}} \underset{1.3\ \text{mmoles}}{F_2S_2O_5} \tag{4}$$

A total of 1.6 mmoles of FSO_2OF and 1.2 mmoles of SO_2 was recovered. Small amounts of ($F_2S_3O_8$) and higher polymers were also detected in the products of Equations 2, 3, and 4.

Thus $F_2S_2O_5$ can be produced in various ways, but it is difficult to predict exactly how it is formed in the reaction of SO_2 with O_2F_2. However, because of its ease of formation, it probably occurs via all the above routes.

Reaction of O_2F_2 with SO_3. The reaction of SO_3 and O_2F_2 is very vigorous, and explosions occur if the reaction is carried out in the absence of a solvent. The results of the reaction of O_2F_2 and SO_3 in two solvents are given in Table I. In each case, SO_3 was fluorinated to give nearly equimolar amounts of FSO_2OF and $F_2S_2O_6$. Essentially all of the oxygen and half of the fluorine from the original O_2F_2 was released in the form of oxygen and fluorine. Large amounts of polymer containing fluorine, sulfur, and oxygen were also formed.

Thus, the reaction of SO_3 with O_2F_2 is similar to the catalytic fluorination of SO_3 (*2*) in which $F_2S_2O_6$ is favored when the reaction is carried out below 170° C., and FSO_2OF is favored above 170° C. Apparently, $F_2S_2O_6$ is fluorinated only at higher temperatures; this fact was further demonstrated in the following experiment.

Table I. Reactions of SO_3 with O_2F_2

Reaction Conditions	Results, Solvent F_2SO_2	Results, Solvent $C_2F_4Cl_2$
Temperature, ° C.	−80	−80
Time, hr.	56	56
SO_3 used, mmoles	11	52
O_2F_2 used, mmoles	17	52
Results, mmoles		
F_2 released	1.5	23.0
O_2 released	13.0	48.7
$F_2S_2O_6$ formed	2.6	5.5
FSO_2OF formed	2.8	5.6

Reaction of O_2F_2 with $F_2S_2O_6$. To define further the chemistry of O_2F_2, the reaction of $F_2S_2O_6$ with O_2F_2 was studied:

$$\underset{22\ \text{mmoles}}{F_2S_2O_6} + \underset{14\ \text{mmoles}}{O_2F_2} \xrightarrow[1\ \text{hr.}]{-63^\circ} \underset{1.8\ \text{mmoles}}{F_2SO_2} \tag{5}$$

A total of 20.8 mmoles of $F_2S_2O_6$ was recovered.

When $F_2S_2O_6$ reacts with fluorine, the peroxy bond is easily broken (*2, 9*); however, $F_2S_2O_6$ was surprisingly stable, and no reaction was observed at temperatures below −63° C. These results show that the O—O bond is resistant to attack by O_2F_2 (and even by decomposing O_2F_2, which should yield fluorine atoms). When the reaction was carried out above −63° C., the S—O bond was broken and small amounts of F_2SO_2 were formed.

Reaction of O_2F_2 with H_2SO_4. Previous attempts (*2*) to obtain S—OF compounds by reacting fluorine with sulfuric acid (H_2SO_4) were unsuccessful. The reactivity of O_2F_2 was again demonstrated; when H_2SO_4 was allowed to react with O_2F_2 at −100° C., FSO_2OF was formed (although in small amounts). H_2SO_4 reacted slowly with O_2F_2; the reaction of 3 mmoles of H_2SO_4 with 3 mmoles of O_2F_2 at −130° C. for 6 hours yielded only 0.4 mmole of product. The reaction product contained FSO_2OF, $F_2S_2O_6$, $F_2S_2O_5$, and SiF_4. About one-half of the product was SiF_4; therefore, the primary reaction apparently is the fluorination of the O—H bond to form hydrogen fluoride (HF), which subsequently reacts with the glass. If both O—H groups react, the primary product expected would be $FOSO_2OF$. However, no evidence of this compound was found.

Reaction of O_2F_2 with H_2SO_5. The reaction of persulfuric acid (H_2SO_5) with O_2F_2 was similar to that of H_2SO_4 with O_2F_2; large amounts of HF were formed. H_2SO_5, however, reacted at a much faster rate. The reaction of 13 mmoles of H_2SO_5 with 21 mmoles of O_2F_2 at −100° C. was complete after 1 hour and produced approximately 6 mmole of SiF_4, 0.9 mmole of FSO_2OF, 0.5 mmole of FSO_2OOF, and 1.23 grams of $F_2S_3O_8$ and higher polymer.

Therefore, as in the case of H_2SO_4, the primary reaction seems to be the attack of the O—H bond and the S—O bonds. The small amount of FSO_2OOF formed probably means that the O—O bond is attacked slightly.

Reaction of O_2F_2 with F_2SO and F_4SO. It is also interesting to compare the reaction of thionyl fluoride (F_2SO) and thionyl tetrafluoride ($F_4S{=}O$) with fluorine to the reaction of these compounds with O_2F_2. Ruff and Lustig (*10*) have shown that metal fluoride catalysts play a large role in the fluorination of these compounds. Static fluorination of F_2SO at room temperature in the presence of cesium fluoride produces good yields of pentafluorosulfur hypofluorite, SF_5OF. If the fluorination is run in the absence of a catalyst, F_4SO is obtained. F_4SO is the only product when F_2SO is allowed to react with O_2F_2, and, as might be expected, F_2SO does not react further with—O_2F_2.

EXPERIMENTAL

Preparation of O_2F_2. O_2F_2 was prepared by using the method previously reported (*12*). A 1 to 1 gaseous mixture of fluorine and oxygen was passed through an electrical discharge apparatus that is cooled to −196° C. The discharge varies from 15 to 25 ma. at about 2500 volts.

Decomposition of O_2F_2. These experiments were monitored by passing the decomposition gases (O_2 and F_2) through a sodium chloride trap heated to 240° C.; the F_2 is quantitatively converted to Cl_2 by reaction with the sodium

Table II. Properties of Sulfur Oxyfluorides

Formula	Name	M.P., ° C.	B.P., ° C.	F^{19} NMR Chemical Shifts[a]
SO_2F_2	Sulfuryl fluoride	−120(?)	−52	−33.5
FSO_2OF	Fluorine fluorosulfonate	−158.5	−31.3	−249, −37
FSO_2OSO_2F	Pyrosulfuryl fluoride	−58	51	−48.5
FSO_2OOSO_2F	Peroxydisulfuryl difluoride	−55.4	67.1	−40.4
FSO_2OOF	Fluorosulfuryl hypofluorite	. . .	1	−291, −43.0

[a] Measured relative to $CFCl_3$.

chloride to convert the fluorine to chlorine. The chlorine was condensed at liquid nitrogen temperature and measured volumetrically. The oxygen was transferred by means of a Toepler pump to a standard volume and measured. Small but various amounts (as much as 10% of the total gas) of SiF_4 were found, and corrections were made when the amounts were appreciable.

Reactions of O_2F_2. The material to be reacted with O_2F_2 was placed in a small glass tube containing a magnetic stirrer. The O_2F_2 was then distilled into the tube, which was cooled to −196° C. Distillation usually resulted in a slight decomposition of O_2F_2. If a solvent was used in the reaction, it was then distilled into a reactor and used to wash down the O_2F_2 frozen on the side of the tube. The reaction was considered complete upon the disappearance of the red color of O_2F_2.

Separation and Identification of Products. Depending on the complexity of the products, trap-to-trap distillation or the Cady (*1*) codistillation method was used to separate the products. Both infrared and NMR analysis were used to characterize the products, but it was found that F^{19} NMR analysis was usually the best method, since the chemical shifts for all the compounds in question had previously been reported (*4*). The physical properties and NMR data for all of these compounds are given in Table II.

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λ-Type Thermal Anomaly in Triuranium Octaoxide at 482.7° K.

H. L. GIRDHAR and EDGAR F. WESTRUM, JR.
Department of Chemistry, University of Michigan, Ann Arbor, Mich. 48104

Heat capacities of U_3O_8 have been measured by adiabatic calorimetry from 300° to 555° K. A reversible λ-type thermal anomaly of uncertain origin, and with an enthalpy of transition of only 41 cal./(mole ° K.), was observed at 482.7° K.

APART from the potential importance of U_3O_8 as a nuclear fuel, its thermophysical properties are of interest because of its polymorphism. The heat capacity of the α-phase was investigated from 5° to 350° K. by Westrum and Grønvold (*12*). A λ-type thermal anomaly, which is presumed to be of magnetic origin, occurs at 25.3° K. Magnetic susceptibility data do indeed show a small anomaly at this temperature but do not reveal the primary nature of the anomaly (*8*). Heat capacity measurements have been made by other workers, covering the temperature regions 477° to 1254° K. (*3*) and 623° to 1273° K. (*7*). The temperature region 350° to 477° K., however, has remained unexplored. The present investigation endeavors to remedy this deficiency.

EXPERIMENTAL

The U_3O_8 sample was prepared in this laboratory eight years ago by purifying uranyl nitrate hexahydrate, A. R. by the well-known procedure of Hönigschmidt (*cf. 12*). This U_3O_8 was reduced to UO_2 by heating it in dry, purified hydrogen gas at 500° until the formation of water ceased. The temperature was raised to 1200° and the sample kept at this temperature for 4 hours before cooling to room temperature. It then was oxidized in air at 800° to constant weight, transferred to a vitreous silica tube which was evacuated and sealed, heated at 800° for seven days, and gradually cooled to room temperature over a period of two months.

Spectrographic analysis of the U_3O_8 sample showed the presence of these impurities (in parts per million): Al 60, B < 0.08, Cu 3, Fe 10, Mg 30, Ni 20, and Si 200. The weight increase upon oxidation of UO_2 to U_3O_8 corresponded to the theoretical value within 0.01 O/U atom, and x-ray powder photographs showed only the presence of the U_3O_8 phase with cell dimensions in accord with the literature (*12*) both before and after the heat capacity determinations.

Heat capacity was determined by the quasi-adiabatic technique using a silver calorimeter (laboratory designation W-22) and platinum resistance thermometer (A-8) in the previously described Mark IV (*11*) cryostat. The calorimeter was sealed after admitting 110 torr of helium gas