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

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Dioxygen difluoride (O_2F_2) is considerably less stable than previously reported. The reaction of O_2F_2 with SO_2 at $-160^\circ C.$ 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 $-160^\circ C.$ 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 $-100^\circ C.$ or lower. Temperatures of 200° to $300^\circ C.$ are necessary for the formation of these products by conventional fluorination reactions.

RESULTS

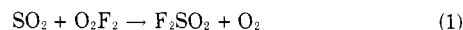
Stability of O_2F_2 . It was necessary to understand the decomposition of O_2F_2 before studying its chemistry so that decomposition would not be confused with actual reaction. The completeness of a reaction was usually assessed by the disappearance of the red color of the O_2F_2 .

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 $-78^\circ C.$ and that its half-life at $-50^\circ C.$ is 220 minutes. The authors found, however, that O_2F_2 is considerably less stable than previously reported and observed a 4% per day decomposi-

tion at $-160^\circ C.$ 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 $-160^\circ C.$ 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 $-160^\circ C.$ 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.



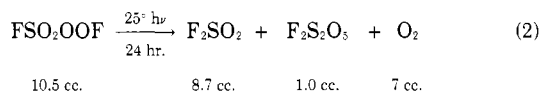
The main product of this reaction is the same as that reported for the reaction of fluorine with SO_2 (3), however pentafluorosulfur hypofluorite was a minor product in the latter reaction.

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 sta-

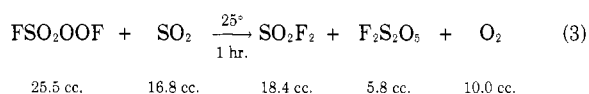
ble at room temperature, it decomposes rapidly in the presence of ultraviolet light. Neumayr and Vanderkooi (7) found that FSO₂OOF was quite unstable when exposed to ultraviolet light; it decomposed to F₂S₂O₅, F₂SO₂, and noncondensable gas. The mole ratio of F₂S₂O₅ to F₂SO₂ was approximately 2.

The authors also confirmed the fact that FSO₂OOF is quite unstable when exposed to ultraviolet light; however, a somewhat different product distribution was observed, and the noncondensable gas was oxygen:

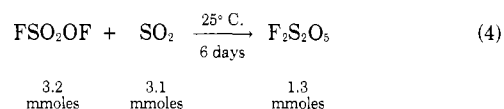


No reactant was recovered.

We found that F₂S₂O₅ is also formed by the reaction of FSO₂OOF with SO₂:



Roberts (8) reported that F₂S₂O₅ is also formed by the reaction of FSO₂OF with SO₂ at 195° C. The reaction occurs at room temperature, but it is quite slow:



A total of 1.6 mmoles of FSO₂OF and 1.2 mmoles of SO₂ was recovered. Small amounts of (F₂S₃O₈) and higher polymers were also detected in the products of Equations 2, 3, and 4.

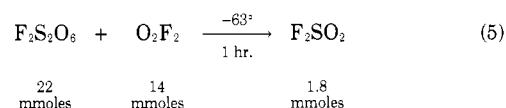
Thus F₂S₂O₅ can be produced in various ways, but it is difficult to predict exactly how it is formed in the reaction of SO₂ with O₂F₂. However, because of its ease of formation, it probably occurs via all the above routes.

Reaction of O₂F₂ with SO₃. The reaction of SO₃ and O₂F₂ is very vigorous, and explosions occur if the reaction is carried out in the absence of a solvent. The results of the reaction of O₂F₂ and SO₃ in two solvents are given in Table I. In each case, SO₃ was fluorinated to give nearly equimolar amounts of FSO₂OF and F₂S₂O₆. Essentially all of the oxygen and half of the fluorine from the original O₂F₂ 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 SO₃ with O₂F₂ is similar to the catalytic fluorination of SO₃ (2) in which F₂S₂O₆ is favored when the reaction is carried out below 170° C., and FSO₂OF

is favored above 170° C. Apparently, F₂S₂O₆ is fluorinated only at higher temperatures; this fact was further demonstrated in the following experiment.

Reaction of O₂F₂ with F₂S₂O₆. To define further the chemistry of O₂F₂, the reaction of F₂S₂O₆ with O₂F₂ was studied:



A total of 20.8 mmoles of F₂S₂O₆ was recovered.

When F₂S₂O₆ reacts with fluorine, the peroxy bond is easily broken (2, 9); however, F₂S₂O₆ 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 O₂F₂ (and even by decomposing O₂F₂, which should yield fluorine atoms). When the reaction was carried out above -63° C., the S—O bond was broken and small amounts of F₂SO₂ were formed.

Reaction of O₂F₂ with H₂SO₄. Previous attempts (2) to obtain S—OF compounds by reacting fluorine with sulfuric acid (H₂SO₄) were unsuccessful. The reactivity of O₂F₂ was again demonstrated; when H₂SO₄ was allowed to react with O₂F₂ at -100° C., FSO₂OF was formed (although in small amounts). H₂SO₄ reacted slowly with O₂F₂; the reaction of 3 mmoles of H₂SO₄ with 3 mmoles of O₂F₂ at -130° C. for 6 hours yielded only 0.4 mmole of product. The reaction product contained FSO₂OF, F₂S₂O₆, F₂S₂O₅, and SiF₄. About one-half of the product was SiF₄; 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 FOSO₂OF. However, no evidence of this compound was found.

Reaction of O₂F₂ with H₂SO₅. The reaction of persulfuric acid (H₂SO₅) with O₂F₂ was similar to that of H₂SO₄ with O₂F₂; large amounts of HF were formed. H₂SO₅, however, reacted at a much faster rate. The reaction of 13 mmoles of H₂SO₅ with 21 mmoles of O₂F₂ at -100° C. was complete after 1 hour and produced approximately 6 mmole of SiF₄, 0.9 mmole of FSO₂OF, 0.5 mmole of FSO₂OOF, and 1.23 grams of F₂S₃O₈ and higher polymer.

Therefore, as in the case of H₂SO₄, the primary reaction seems to be the attack of the O—H bond and the S—O bonds. The small amount of FSO₂OOF formed probably means that the O—O bond is attacked slightly.

Reaction of O₂F₂ with F₂SO and F₄SO. It is also interesting to compare the reaction of thionyl fluoride (F₂SO) and thionyl tetrafluoride (F₄S=O) with fluorine to the reaction of these compounds with O₂F₂. Ruff and Lustig (10) have shown that metal fluoride catalysts play a large role in the fluorination of these compounds. Static fluorination of F₂SO at room temperature in the presence of cesium fluoride produces good yields of pentafluorosulfur hypofluorite, SF₅OF. If the fluorination is run in the absence of a catalyst, F₄SO is obtained. F₄SO is the only product when F₂SO is allowed to react with O₂F₂, and, as might be expected, F₂SO does not react further with—O₂F₂.

Table I. Reactions of SO₃ with O₂F₂

Reaction Conditions	Results, Solvent	
	F ₂ SO ₂	C ₂ F ₄ Cl ₂
Temperature, ° C.	-80	-80
Time, hr.	56	56
SO ₃ used, mmoles	11	52
O ₂ F ₂ used, mmoles	17	52
Results, mmoles		
F ₂ released	1.5	23.0
O ₂ released	13.0	48.7
F ₂ S ₂ O ₆ formed	2.6	5.5
FSO ₂ OF formed	2.8	5.6

EXPERIMENTAL

Preparation of O₂F₂. O₂F₂ 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 O₂F₂. These experiments were monitored by passing the decomposition gases (O₂ and F₂) through a sodium chloride trap heated to 240° C.; the F₂ is quantitatively converted to Cl₂ 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 ₂ F ₂	Sulfuryl fluoride	-120(?)	-52	-33.5
FSO ₂ OF	Fluorine fluorosulfonate	-158.5	-31.3	-249, -37
FSO ₂ OSO ₂ F	Pyrosulfuryl fluoride	-58	51	-48.5
FSO ₂ OOSO ₂ F	Peroxydisulfuryl difluoride	-55.4	67.1	-40.4
FSO ₂ OOF	Fluorosulfuryl hypofluorite	...	1	-291, -43.0

^a Measured relative to CFCI₃.

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 SiF₄ were found, and corrections were made when the amounts were appreciable.

Reactions of O₂F₂. The material to be reacted with O₂F₂ was placed in a small glass tube containing a magnetic stirrer. The O₂F₂ was then distilled into the tube, which was cooled to -196°C. Distillation usually resulted in a slight decomposition of O₂F₂. If a solvent was used in the reaction, it was then distilled into a reactor and used to wash down the O₂F₂ frozen on the side of the tube. The reaction was considered complete upon the disappearance of the red color of O₂F₂.

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 F¹⁹NMR 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.

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Heat capacities of U₃O₈ 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 U₃O₈ 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 Grønvdal (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 U₃O₈ 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 U₃O₈ was reduced to UO₂ 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 U₃O₈ 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 UO₂ to U₃O₈ corresponded to the theoretical value within 0.01 O/U atom, and x-ray powder photographs showed only the presence of the U₃O₈ 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