drogen and sulfur dioxide are claimed to be catalysts at 273-325° for the hydrogenation of sulfur dioxide to sulfur.[7]

Rhenium heptasulfide catalyzed the hydrogenation of sulfur dioxide at ≦100° (10-30 atm.). Hydrogen sulfide was the major product although some sulfur was formed. Tungsten-nickel sulfide was also tested but found to be ineffective at 360° (10-30 atm.).

Acknowledgment.—Appreciation is expressed to G. W. Schoenthal for technical assistance.

[7] M. C. Boswell, U. S. Patent 1,880,741 (1932).

CONTRIBUTION FROM GENERAL CHEMICAL RESEARCH
LABORATORY, ALLIED CHEMICAL CORPORATION,
MORRISTOWN, NEW JERSEY

Reaction of Oxygen Difluoride with Sulfur Dioxide, Sulfur Trioxide, and Peroxydisulfuryl Difluoride

BY GERHARD FRANZ AND FRANZ NEUMAYR

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Recently Schumacher and co-workers reported the results of their photochemical decomposition studies of oxygen difluoride[1] and of the kinetics of the sulfur trioxide–fluorine interaction.[2] On the basis of their photodecomposition experiments using light of 365 mμ wave length, they postulated an O–F radical species as a reaction intermediate. The subsequent synthesis[3] of peroxysulfuryl difluoride (I) from sulfur trioxide and oxygen difluoride supported the existence of such a radical. In the present work, a gaseous mixture of the reactants was irradiated with light of 365 mμ wave length, giving I in a nearly quantitative yield. Ultraviolet light with a wave length of 365 mμ was used in order to exclude the activation of molecules other than oxygen difluoride.[4]

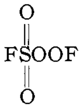
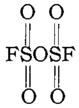
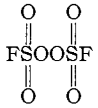
We studied the reaction of sulfur trioxide, sulfur dioxide, and peroxydisulfuryl difluoride (IV) with oxygen difluoride by irradiating the gaseous reaction mixtures with unfiltered ultraviolet light, permitting the excitation of sulfur trioxide, sulfur dioxide, and peroxydisulfuryl difluoride molecules also.

When sulfur trioxide and oxygen difluoride were allowed to react under these conditions only traces of compound I could be detected. The major reaction products were pyrosulfuryl fluoride (II) and sulfuryl fluoride (III). When ordinary window glass was used as a filter, compound I was obtained in a good yield. This glass absorbs below 350 mμ thus preventing the activation of sulfur trioxide.

Infrared and F^{19} n.m.r. analyses proved to be the best methods for differentiating compounds I, II, and III. The F^{19} n.m.r. spectrum of I indicated two different types of fluorine (see Table I) which interact with each other giving rise to spin–spin splitting. Multiplicity, intensity, chemical shift, and coupling constant data strongly support the structure given for compound I. A new synthesis for I was found by irradiating a gaseous mixture of peroxydisulfuryl difluoride (IV) and oxygen difluoride in a Pyrex vessel.

TABLE I

F^{19} CHEMICAL SHIFTS OF SOME S–O–F COMPOUNDS

No.	Structure	Name	Shift, p.p.m.[a]
I	 FSO_2OOF	Peroxysulfuryl difluoride	−291, −43.0
II	 FSO_2OSO_2F	Pyrosulfuryl fluoride	−48.5
III	 SO_2F_2	Sulfuryl fluoride	−33.5
IV	 FSO_2OOSO_2F	Peroxysulfuryl difluoride	−40.4
V	 FSO_2OF	Fluorine fluorosulfonate	−249, −37

[a] Measured relative to $CFCl_3$.

Even at room temperature, peroxydisulfuryl difluoride is known to be in equilibrium with its radical form.[5] Irradiation of compound IV and oxygen difluoride yielded peroxysulfuryl difluoride and fluorine fluorosulfonate (V) in accordance with Schumacher's proposed mechanism involving the activation of oxygen difluoride.

The photolysis of a sulfur dioxide–oxygen difluoride reaction mixture yielded compounds II and III only. Fluorine fluorosulfonate, the expected reaction product, could not be found.

Experimental

Preparation of Peroxysulfuryl Difluoride.—A previously reported[3,6] method was modified by substitution of a filter combination by ordinary window glass. Approximately 100 mm. (0.95 g., 0.012 mole) of SO_3, which was distilled from 60% oleum, and 600 mm. of OF_2 (General Chemical Division, Allied Chemical Corp.) were added to a 2-l. Pyrex flask, covered partially with aluminum foil to reflect the radiation.

A plate of window glass large enough to shield the entire flask was placed between a 360-watt high pressure mercury ultraviolet

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[1] R. Gatti, E. Staricco, J. E. Sicre, and H. J. Schumacher, *Z. physik. Chem.* (Frankfurt), **35**, 343 (1962).

[2] E. Staricco, J. E. Sicre, and H. J. Schumacher, *ibid.*, **35**, 122 (1962).

[3] R. Gatti, E. H. Staricco, J. E. Sicre, and H. J. Schumacher, *Angew. Chem.*, **75**, 137 (1963).

[4] A. Glissmann and H. J. Schumacher, *Z. physik. Chem.*, **24**, 328 (1934).

[5] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **85**, 3375 (1963).

[6] H. J. Schumacher, private communication.

lamp and the reaction vessel, which remained connected to a vacuum gage during the irradiation and was cooled by an air blower. After about 6 hr., the pressure had dropped to the theoretical value and the reaction mixture was separated by pumping on it at −183°, thus removing excess OF_2. No further purification of the product was necessary.

Reaction of SO_3 with OF_2 without a Filter.—Using the same vacuum apparatus 0.145 g. (0.0018 mole) of SO_3 was transferred into a 1-l. Pyrex flask resulting in about 40 mm. pressure. Then, OF_2 was added, bringing the total pressure to approximately 650 mm. The mixture was irradiated for 45 min. with ultraviolet light, transferred *in vacuo* to an n.m.r. tube,[7] and dissolved in a threefold excess of trichlorofluoromethane. A F^{19} n.m.r. analysis (Varian Model V-4302 spectrometer) of the mixture showed very small doublets at $\delta_{CCl_3F} = -291$ and -43 p.p.m., indicating the presence of a minute amount of I. The mixture also showed strong signals at -48.5 and -33.5 p.p.m. which were assigned to II and III, respectively.

Reaction of SO_2 and OF_2.—With the same apparatus used above, 0.54 g. (0.01 mole) of OF_2 and 0.64 g. (0.01 mole) of SO_2 (Matheson Co.) were condensed into a 1-l. Pyrex flask resulting in a 170 mm. partial pressure of each component at room temperature. It was exposed to ultraviolet radiation at room temperature for 18 hr. The reaction mixture was then separated by bulb-to-bulb fractionation and yielded 0.566 g. (0.0031 mole = 62%) of pyrosulfuryl fluoride and a small portion of sulfuryl fluoride. Pyrosulfuryl fluoride was identified by its infrared spectrum[8] and by comparing its F^{19} n.m.r. spectrum with that of a sample which was prepared by another method.[9] The F^{19} spectrum consists of a signal at $\delta_{CCl_3F} = -48.5$ p.p.m. Sulfuryl fluoride was identified by its infrared spectrum[10] and its F^{19} n.m.r. spectrum which showed a single signal at $\delta_{CCl_3F} = -33.5$ p.p.m.

Reaction of Peroxydisulfuryl Difluoride[11] with OF_2.—A 2-l. Pyrex flask was filled with IV (purity monitored by infrared analysis) at a pressure of 60 mm. using a Pyrex glass vacuum apparatus; then OF_2 was added until the total pressure was 200 mm. and the mixture was irradiated for 6 hr. at room temperature with a 360-watt high pressure mercury ultraviolet lamp. After a crude bulb-to-bulb distillation, the middle fraction was further separated by fractional codistillation[12] and consisted of silicon tetrafluoride, sulfuryl fluoride, fluorine fluorosulfonate (V), and peroxysulfuryl difluoride. The latter was identified by its infrared spectrum, which showed peaks at 6.7, 8.0 (S–O stretch), 11.7 (S–F stretch), 12.7, and 13.8 μ, as well as by F^{19} n.m.r. spectroscopy. The compound showed two doublets at $\delta_{CCl_3F} = -291$ and -43 p.p.m. with a coupling constant $J_{FF} = 10.5$ c.p.s. These spectra were identical with those of the compound made according to Schumacher.[1] Mass spectra were obtained with a Consolidated Electrodynamics Corporation Model 21-102 mass spectrometer, with an ionizing current of 52.2 μa. and an ionizing potential of 70 volts. The spectrum showed major peaks corresponding to SO_3F^+, SO_2F^+, SO_3^+, FSO^+ SO_2^+, SF^+, SO^+, and OF^+ and a number of minor peaks. The parent peak at mass number 134 was missing in all spectra.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS

The Fluorination of Nitrides

BY WALTER C. SCHUMB AND ROBERT F. O'MALLEY[1]

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Moissan[2] observed the reactions of the nitrides of boron and titanium with elementary fluorine but did not characterize the volatile products. Coates, Harris, and Sutcliffe[3] reported that boron trifluoride and nitrogen were the products of the direct fluorination of boron nitride. They also stated that magnesium nitride did not react with fluorine even at 400°. Glemsler and Haesler[4] obtained boron trifluoride and nitrogen from the reaction of boron nitride with fluorine and with silver(II) fluoride.

Ruff and Geisel[5] reported that fluorine did not react with ammonium fluoride or ammonium bifluoride.

Following a plan of study of the reactions of fluorine with carbides, previously reported,[6] the fluorination of a variety of types of nitrides was carried out to determine if any observable relationship exists between the structure possessed by a given nitride and the formation of nitrogen trifluoride as one of the products of its direct fluorination. Lithium nitride (Li_3N), beryllium nitride (Be_3N_2), magnesium nitride (Mg_3N_2), boron nitride (BN), silicon nitride (Si_3N_4), titanium nitride (TiN), vanadium nitride (VN), and copper(I) nitride were fluorinated with elementary fluorine.

When it became apparent that the action of fluorine upon the nitrides in general yields only small quantities of nitrogen trifluoride, ammonium fluoride and hydrazinium difluoride were added to the list of reactants.

Experimental

Lithium, magnesium, and copper(I) nitrides and ammonium and hydrazinium fluorides were prepared by known methods. The other nitrides, Be_3N_2, BN, Si_3N_4, TiN, and VN were obtained from commercial sources. The fluorine employed in these studies was the commercially available compressed gas.

The fluorinations were carried out in a general-purpose type reactor made largely of monel metal and resembling that described by Priest.[7] The solid to be fluorinated was placed in a nickel boat or reactor tray made from a section of 0.5-in. nickel pipe, split lengthwise.

A monel tube, containing a tray of soda lime, which had been preheated in an oven at 110–120° for several hours, followed the reactor. The purpose of this material was to react with any free fluorine which had passed through the reactor. The development of heat in this tube indicated when the reaction with the nitride was complete. A Dry Ice trap, a tube filled with sodium fluoride, and sodium hydroxide bubblers were introduced when necessary to remove hydrogen fluoride, silicon tetrafluoride, and

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