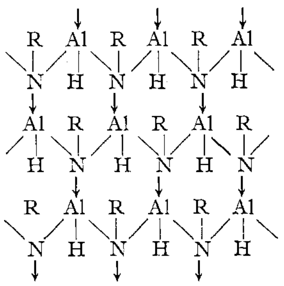
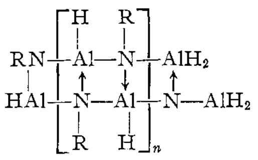


X



XI

latter type of structure has so far not been found in nitrogen–aluminum compounds. It is much more likely that the aluminum is tetracoordinate by virtue of cross linking with other chains through the free pair of electrons on the nitrogen. Such cross-linked polymers could be built up into systems forming cyclic networks such as X or XI,[14] or in a random manner.

A cyclic network probably would be preferred because of its inherently greater stability. Six-membered coordinated Al–N rings have been suggested as the structure for the trimer of dimethylaminoalane, $(CH_3)_2NAlH_2$,[8] for $C_2H_5Al(Cl)NHCH_3$, and for the polymer derived from this compound.[4] A three-dimensional cubic Al–N compound has been prepared recently[15] and the type of cross-linked network present in this material is also possible for the polyiminoalanes.

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[14] We are indebted to one of the referees for the suggestion of this folded-chain structure (XI).

[15] J. I. Jones and W. S. McDonald, *Proc. Chem. Soc.*, 366 (1962).

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Reactions of Peroxodisulfuryl Difluoride with Organic Halides

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The preparation of the new compounds, chlorotrifluorobis(fluorosulfato)ethane and octafluorobis-2,3-(fluorosulfato)butane, from peroxodisulfuryl difluoride, $S_2O_6F_2$, and chlorotrifluoroethylene and *cis-trans*-perfluoro-2-butene, respectively, is reported and some of their chemical and physical properties are given. Reactions of $S_2O_6F_2$ with several other organic halides have been examined.

Peroxodisulfuryl difluoride ($S_2O_6F_2$) has been shown to add readily across the carbon–carbon double bond in tetrafluoroethylene and perfluorocyclopentene and to react slowly with carbon tetrachloride.[1] Addition reactions have not been attempted with other than perfluoroolefins nor have the reactions with other halomethanes been examined. This present work is concerned with the reactions of $S_2O_6F_2$ with olefins containing other halogens in addition to fluorine, with olefins containing hydrogen, and with halomethanes containing other halogens in addition to fluorine.

Reaction of $S_2O_6F_2$ with carbon tetrachloride gives rise to carbonyl chloride, and if the $S_2O_6F_2$ is present in excess, carbon dioxide is obtained. With phosphorus trifluoride, phosphoryl fluoride is the product. It now has been shown that if the halomethane contains one other halogen, in addition to the trifluoromethyl group (*e.g.*, CF_3Cl, CF_3Br), oxygenation does not occur but rather the nonfluorine halogen is replaced by a fluorosulfate group. This reaction is similar to that of iodine monochloride and potassium chloride with $S_2O_6F_2$ where chlorine is replaced by fluorosulfate groups to give $I(SO_3F)_3$ and KSO_3F, respectively.[1]

Preliminary examination of the products of the reaction of $S_2O_6F_2$ and chlorodifluoromethane showed carbonyl fluoride, chlorine, fluorosulfuric acid, pyrosulfuryl fluoride ($S_2O_5F_2$), and unidentified volatile materials which could contain one or more fluorosulfate groups. Pyrosulfuryl fluoride is a product when $S_2O_6F_2$ acts as an oxygenating agent. Apparently, in this case, both the carbon–hydrogen and carbon–chlorine bonds were broken to allow formation of the carbon–oxygen double bond contained in COF_2.

Experimental

Reagents.—All gaseous reactants were obtained from the Matheson Company, Inc., and were used without further purification. Reagents used for analyses were of analytical reagent grade. Peroxodisulfuryl difluoride was obtained by the catalytic fluorination of sulfur trioxide.[2]

Vapor pressure measurements were obtained through the use of an apparatus similar to that described previously.[3] Vapor densities were determined by using Regnault's method with a glass flask of 253.4 ml. volume. A codistillation apparatus[4] was utilized to separate reaction products. Identification of previously known reaction products, after separation, was made using vapor density and infrared determinations. Infrared spectra were obtained by using a Perkin-Elmer Model 138 Infracord spectrophotometer. Cells were of Pyrex glass with a 5-cm. path length and sodium chloride windows or with a 10-cm. path

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[1] J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).

[2] J. M. Shreeve and G. H. Cady, *Inorg. Syn.*, **7**, 124 (1963).

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

[4] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

length and silver chloride windows. High pressure reaction vessels were constructed of 10-mm. o.d. Monel tubing. One end was closed with silver solder and the other end was soldered to a brass Hoke valve connected to a brass 10/30 inner standard taper joint. Reactions at pressures up to 300 atm. were carried out in these vessels without any noticeable effect on the tubing. Vessels with volumes between 5 and 8 ml. were used for the reactions. Pyrex glass reaction vessels of volumes ranging from 0.1 to 3 l. were used for all other reactions.

Procedure for the reaction of $S_2O_6F_2$ with a slight excess of the reacting olefin was as follows: (a) $S_2O_6F_2$ was added to a 3-l. Pyrex glass bulb to give a pressure of about 130 mm. (b) The reacting compound was introduced slowly at room temperature until present in slight excess. (The reactions were rapid and exothermic and, in the area of mixing, were accompanied by a fleeting, dark brown color which is due most likely to fluorosulfate free radicals.[5]) (c) Separation of unreacted olefin from the product was effected by holding the mixture at −23° and by pumping on it for an extended period of time.

Reactions with Olefins

Reaction with Chlorotrifluoroethylene to Give Chlorotrifluorobis(fluorosulfato)ethane.—Peroxodisulfuryl difluoride reacted vigorously with chlorotrifluoroethylene according to the equation

$$CF_2CFCl + S_2O_6F_2 \longrightarrow CF_2(OSO_2F)CFCl(OSO_2F)$$

Nearly pure chlorotrifluorobis(fluorosulfato)ethane was obtained by prolonged pumping at −23°.

Properties of Chlorotrifluorobis(fluorosulfato)ethane.—(a) The molecular weight was difficult to obtain due to the low vapor pressure of the compound at room temperature. Experimental measurements gave a molecular weight of 313 ± 4 compared to a calculated value of 315.5 for $C_2F_3Cl(SO_3F)_2$. (b) The density of $C_2F_3Cl(SO_3F)_2$ is 1.810 g./cc. at 25°; 1.854 at 2.9°; 1.829 at 14.3°; and 1.786 at 31.0°. (c) The melting point of the compound could not be determined accurately since attempts to crystallize it resulted in a glass. (d) The vapor pressure values, measured over the temperature range from 35.1 to 132.6°, are given in Table I. These data indicate a boiling point of 405.1°K. and a molar heat of vaporization of 8.9 kcal. (e) The infrared spectrum was obtained at 3 mm. pressure with a 5-cm. cell. Strong bands at 1496 and 1252 cm.$^{-1}$ may be attributed to S–O stretch, at 843 cm.$^{-1}$ to S–F stretch, and the one at 1150 cm.$^{-1}$ to C–F stretch. Weaker bands at 1090, 1060, and 995 cm.$^{-1}$ were not identified. (f) A carefully purified sample was sent to Galbraith Laboratories, Inc., for elemental analyses. *Anal.* Calcd. for $C_2F_3Cl(SO_3F)_2$: C, 7.64; S, 20.35; F, 30.20. Found: C, 8.80; S, 18.87; F, 28.72. (h) Peroxodisulfuryl difluoride added across the carbon–carbon double bond of chlorotrifluoroethylene in a rapid, nearly stoichiometric reaction at room temperature to form a clear, colorless liquid, $CF_2(OSO_2F)CFCl(OSO_2F)$, which reacts slowly with glass and is inert toward mercury.

TABLE I

VAPOR PRESSURE OF $C_2F_3Cl(SO_3F)_2$

P, mm.	T, °K.	P, mm.	T, °K.
11.6	308.1	422.0	383.5
23.9	317.1	514.2	389.0
32.3	322.0	599.0	395.1
55.7	328.1	608.0	395.7
107.8	346.9	692.1	401.1
136.0	351.5	727.9	403.0
212.5	361.9	744.0	404.4
219.7	364.0	754.9	404.5
268.3	368.1	760.0	405.1
323.1	373.0	764.0	405.6
378.1	377.1		

TABLE II

VAPOR PRESSURE OF $C_4F_8(SO_3F)_2$

P, mm.	T, °K.	P, mm.	T, °K.
11.3	302.6	435.2	385.0
29.5	317.1	496.1	389.5
44.7	328.0	543.3	393.0
82.4	339.5	616.0	398.1
120.0	349.0	680.0	403.0
168.0	358.9	724.2	406.0
267.9	370 0	767.1	409.5
357.5	379.0	775.0	410.6
405.0	383.0		

Reaction with *cis-trans*-Perfluoro-2-butene to Form Octafluoro-2,3-bis(fluorosulfato)butane.—When a mixture of *cis-trans*-perfluoro-2-butene was allowed to react with $S_2O_6F_2$, a colorless liquid gradually collected on the bottom of the flask. The reaction

$$C_4F_8 + S_2O_6F_2 \longrightarrow CF_3CF(OSO_2F)CF(OSO_2F)CF_3$$

was rapid and exothermic. After extended pumping at −23°, the compound was found to be essentially free of contaminants as was indicated by the observation of only a single peak when a sample was allowed to pass through a vapor phase chromatograph.

Properties of Octafluoro-2,3-bis(fluorosulfato)butane.—(a) Experimental measurements gave an average molecular weight of 399 ± 6 compared to a calculated value of 399. Poor reproducibility was attributed to the low vapor pressure of the compound at room temperature. (b) The density of $C_4F_8(SO_3F)_2$ has an interpolated value of 1.835 g./cc. at 25.0°; other values obtained include: 1.893 at 7.6°; 1.856 at 17.6°; 1.832 at 26.2°; 1.811 at 33.0°. (c) A melting point was not determined due to failure of all attempts to crystallize the compound. (d) A normal boiling point of 409.0°K. is obtained from the vapor pressure data given in Table II, and the molar heat of vaporization is 8.7 kcal. (e) The infrared spectrum obtained for this compound was run at 4 mm. pressure in a 5-cm. cell. Strong bands at 1501 and 1256 cm.$^{-1}$ may be attributed to S–O stretch, the one at 845 cm.$^{-1}$ to S–F stretch, and the one at 1140 cm.$^{-1}$ to C–F stretch. Weaker bands at 1090, 1050, 950, and 736 cm.$^{-1}$ were not identified. (f) *Anal.* Calcd. for $C_4F_8(SO_3F)_2$: C, 12.06; F, 47.75. Found: C, 14.25; F, 46.57. (g) Octafluoro-2,3-bis(fluorosulfato)butane is a clear, colorless liquid, is found to dissolve Kel-F stopcock grease, to react slowly with glass, to be nonreactive with mercury, and to be stable toward appreciable hydrolysis on contact with dilute, warm sodium hydroxide solution.

Reaction with Vinyl Fluoride.—Since the reactions of $S_2O_6F_2$ with unsaturated perfluorocarbons have been

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

shown to be rapid and exothermic, the reaction with vinyl compounds could be even more vigorous in the absence of protective fluorine atoms. However, under sufficiently mild conditions the addition of SO_3F groups across the double bond apparently occurs.

When vinyl fluoride entered the vacuum system, a thin coating of an unidentified brown-black polymerization product was produced immediately. This effect was probably caused by small amounts of $S_2O_6F_2$ adhering to the glass line. After this initial reaction, large amounts of the compound could be admitted without further reaction. Addition of 2-ml. aliquots of vinyl fluoride at a pressure of 150 mm. to a 1-l. reaction flask containing $S_2O_6F_2$ resulted in a fine white mist which condensed to give a colorless liquid of low volatility. The reaction was found to proceed with similar results at −23 and −78°, but no reaction was observed at −100°. The presence of an excess of either reactant did not affect the reaction products.

Infrared spectra of the materials volatile at −20° indicated only unreacted reactants to be present. The infrared spectrum of the slightly volatile liquid was compared with that of vinyl fluoride.[6] A doublet at 1670 and 1640 cm.$^{-1}$, which is assigned to C=C stretch, is missing in the product. New peaks are present at 1480, 1250, and 945 cm.$^{-1}$. While the first two may be attributed to S–O stretch, the latter cannot be assigned. The S–F band, characteristic of the SO_3F group, which normally appears in the 850 cm.$^{-1}$ region, was not observed in the spectrum of the new compound. Reaction of the compound with the windows of the infrared cell caused the region of the spectrum between 1000 and 700 cm.$^{-1}$ to be partially blanked out. Therefore, a weak S–F peak would have been masked.

Although the colorless liquid could be stored under vacuum at −78° with no apparent decomposition, it was unstable at room temperature as was indicated by a gradual darkening to give a black oil. Experimental measurements on the freshly distilled colorless liquid gave a molecular weight of 244.5 compared to a calculated value of 244 for $C_2H_3F(OSO_2F)_2$.

The reaction is most likely the addition of fluorosulfate groups across the carbon–carbon double bond according to

$$C_2H_3F + S_2O_6F_2 \longrightarrow CH_2(OSO_2F)CHF(OSO_2F)$$

This is also indicated by the infrared data. However, unsuccessful attempts to stabilize the compound prevented any further investigation of its properties.

Reaction with Vinyl Chloride.—Vinyl chloride, upon entering the vacuum system, brought about the formation of a purplish black polymeric coating on the glass line. Reaction of vinyl chloride and $S_2O_6F_2$ at −78° was accompanied by a brown flash and the subsequent formation of a colorless, essentially nonvolatile liquid. The liquid darkened when warmed to room temperature and, on standing, gradually was converted to a purple-black oil. An attempt to prepare larger quantities of the colorless liquid at −100° resulted in a violent explosion. Further investigation of this reaction was not attempted. However, it is probable that an unstable addition product is formed according to

$$C_2H_3Cl + S_2O_6F_2 \longrightarrow CH_2(OSO_2F)CHCl(OSO_2F)$$

Reactions with Halomethanes

Reaction with Chlorotrifluoromethane (Freon 13).—Peroxodisulfuryl difluoride did not react with chlorotrifluoromethane at room temperature. By maintaining the reactants, with $S_2O_6F_2$ in excess, at 300 atm. pressure and at 150° for 5 days, the reaction went essentially to completion. Volatile products were separated and identified as $S_2O_6F_2$,[7] SiF_4 (from reaction with glass apparatus), and a single substitution product, CF_3SO_3F.[8] A nonvolatile red liquid was also obtained. Physical appearance and vapor pressure indicated this compound to be chlorine fluorosulfate and its decomposition product as reported by Gilbreath and Cady.[9] The reaction

$$S_2O_6F_2 + CF_3Cl \longrightarrow CF_3SO_3F + ClSO_3F$$

requires very vigorous conditions in order to obtain satisfactory product yields.

Reaction with Bromotrifluoromethane (Freon 13-B1).—The reaction of $S_2O_6F_2$ with CF_3Br would be expected to proceed with greater ease than the reaction with the chloro analog because of the lower carbon–bromine bond energy. Equimolar amounts of the two reactants were mixed without reaction in a 1-l. glass bulb at room temperature. However, on standing at room temperature, a brown gas began to appear. Within 3 hr. the flask contained both a dark brown gas and a red-black liquid. Reaction with excess CF_3Br gave similar results.

When the reaction was allowed to proceed at room temperature with a slight excess of $S_2O_6F_2$, an increased quantity of the red-black liquid and lesser amounts of the brown gas were obtained. A large excess of $S_2O_6F_2$ gave a small amount of an orange solid, also.

The reaction products were held at −23° and the volatile materials removed. These were identified as bromine (vapor pressure), CF_3SO_3F (infrared as above), and unreacted CF_3Br. From physical appearance, freezing characteristics, and vapor pressure measurements, the red-black liquid was identified as $BrSO_3F$.[10] The orange solid was found to be $Br(SO_3F)_3$ which, according to Roberts and Cady, is formed by reaction of bromine with an excess of $S_2O_6F_2$ at room temperature. The following reactions occur

$$3CF_3Br + 2S_2O_6F_2 \longrightarrow 3CF_3SO_3F + BrSO_3F + Br_2$$

$$2CF_3Br + \text{excess } 3S_2O_6F_2 \longrightarrow 2CF_3SO_3F + BrSO_3F + Br(SO_3F)_3$$

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[6] H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 236 (1945).

[7] F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 513 (1957).

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[9] W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2**, 496 (1963).

[10] J. E. Roberts and G. H. Cady, *J. Am. Chem. Soc.*, **82**, 353 (1960).