for the shorter-chain-length phosphates. If the value, $\Delta[R_{app}]/\bar{n}$, is divided by the Na_2O/P_2O_5 ratio of the phosphate, the results are more nearly comparable. The members of the sodium polyphosphate system exhibit a nearly constant change of $\Delta[R_{app}]$ per $\bar{n}$ atoms per molecule per sodium ion per P atom. This is interpreted to mean that the sodium ions of a solution will cause about the same polarization in a phosphate group, irrespective of the size of the molecule-ion in which the phosphate group is found.

The orthophosphates and sodium tetrametaphosphate do not conform to the patterns exhibited by the other phosphates in this work. In Table I, disodium orthophosphate contributes slightly more to the refractive index of its solutions than tetrasodium pyrophosphate does when the salts are compared at concentrations of equal formulaweights of phosphorus.

Tetrametaphosphate contributes more to the refractive index of its solutions than does trimetaphosphate at the same concentration. The trimetaphosphate behaves normally (*i.e.*, as though it were very long chains). It may be seen from the data of Table IV that the contribution to molar refraction of each formula-weight of phosphorus in trimetaphosphate is smaller than any of the other phosphates studied.

Those compounds exhibiting high refractive properties also show high density-concentration relationships. In neither case are the differences large, but they are well beyond the limits of experimental error.

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Peroxydisulfuryl Difluoride

BY F. B. DUDLEY[1] AND G. H. CADY

The high temperature reaction between fluorine and sulfur trioxide, the latter being kept in excess, results in the formation of a substance having the empirical formula $S_2O_6F_2$.[1a] The evidence obtained from its chemical reactions and its infrared and nuclear magnetic resonance spectra suggests that it has the structure shown

$$O=\overset{\displaystyle O}{\underset{\displaystyle F}{\overset{\|}{S}}}-O-O-\overset{\displaystyle O}{\underset{\displaystyle F}{\overset{\|}{S}}}=O.$$

Strong infrared absorption bands occur at 755, 848, 1246 and 1495 cm.$^{-1}$. The substance is a colorless liquid at room temperature. It melts at $-55.4°$ and boils at $67.1°$.

During the preparation of some fluorine fluorosulfonate,[2] b.p. $-31.3°$ by the action of fluorine on sulfur trioxide, a small amount of a reactive byproduct, liquid at room temperature, was obtained. The object of this investigation was to vary the reaction conditions in an effort to obtain this new compound in sufficient quantity to permit identification. A decrease in temperature was found to decrease the yield of fluorine fluorosulfonate but to increase the yield of the higher boiling material.

Experimental

(a) Streams of sulfur trioxide and fluorine, each diluted with nitrogen, were allowed to mix in a silver difluoride catalytic reactor[3] heated to 100°. The fluorine was present in excess and the gases, after reaction, were led through two traps cooled with Dry Ice and liquid air, respectively. Practically the entire product was condensed in the Dry Ice trap, and was very largely a new compound with the empirical formula $S_2O_6F_2$. No fluorine fluorosulfonate was obtained at this temperature.

The reactants were then allowed to mix at successively higher temperatures, and it was not till a temperature of 170° was reached that fluorine fluorosulfonate was readily detected in the reaction products. At 190°, the amount of fluorine fluorosulfonate in the mixture of reaction products had increased to over 90%, the remainder being essentially $S_2O_6F_2$. At temperatures from 220 to 280° the amount of $S_2O_6F_2$ was negligible, the product being essen-

tially fluorine fluorosulfonate whilst fluorine was present in excess.

On two occasions, although the rate of flow of fluorine was unchanged, combustion of the metal packing apparently occurred, for no fluorine could be detected in the exit gases. Under these circumstances the product obtained was essentially $S_2O_6F_2$. The production of peroxydisulfuryl difluoride at high temperature thus appears to require an excess of sulfur trioxide.

(b) A mixture of nitrogen, fluorine and sulfur trioxide vapor was passed into a one inch diameter nickel tube 18 inches long and heated to 250°. The products, collected as before, consisted of a mixture of SO_3F_2 and $S_2O_6F_2$ in approximately equal amounts. The crude materials obtained by methods (a) and (b) were distilled to obtain $S_2O_6F_2$ of moderate purity.

(c) Sulfur trioxide and fluorine fluorosulfonate, the former in small excess, were mixed in a 500-cc. glass bulb, the total pressure in the bulb being about two thirds of an atmosphere. No reaction occurred at room temperature, but after holding the bulb at about 300° for a minute a substance, liquid at room temperature, was separated from the reaction products. Its boiling point, melting point and infrared spectrum showed that it was the same compound as that obtained by methods (a) and (b).

Analyses.—A weighed sample of the compound was caused to react with an excess of sodium hydroxide solution and the solution was then heated overnight on a steam-bath to ensure the complete hydrolysis of any fluorosulfonate ions formed initially. Separate aliquots of this solution were used in the analyses for sulfur and fluorine. The sulfur was determined gravimetrically as barium sulfate and the fluorine by titration with thorium nitrate using sodium alizarin sulfonate as indicator.[4] Prior to titration the fluoride was separated from interfering sulfate ions by steam distillation of SiF_4 from a perchloric acid solution.

Anal. Calcd. for $S_2O_6F_2$: S, 32.42; F, 19.2. Found: S, 32.15, 31.93; F, 18.5, 18.9.

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(1a) U. Wanngat and G. Mennicken (*J. anorg. allgem. Chem.*, **278**, 310 (1955)) have produced a peroxy-compound probably having the empirical formula $S_2O_6F_2$. It differs considerably in properties from peroxydisulfuryl difluoride. The two do not appear to be identical compounds

(2) F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., THIS JOURNAL, **78**, 290 (1956).

(3) K. B. Kellogg and G. H. Cady, *ibid.*, **70**, 3986 (1948).

(4) R. H. Kimball and L. E. Tufts, *Ind. Eng. Chem., Anal. Ed.*, **19**, 150 (1947).

Molecular Weight.—The molecular weight was obtained from vapor density measurements assuming ideal gas behavior. High values were obtained regularly until it was realized that the substance dissolved extensively in the fluorocarbon grease used on the stopcock of the bulb. By using a larger bulb, and a minimum of fluorocarbon grease on the stopcock, an average value of 199.5 g. per gram-molecular-volume, from six determinations, was obtained. The maximum deviation from this average value was less than 1%. The theoretical value for $S_2O_6F_2$ is 198 per g.m.v.

Temperature Dependence of Vapor Pressure.—The variation of the vapor pressure of the compound in the temperature range 9 to 68° was measured using apparatus previously described.[3] The temperature dependence of the vapor pressure is given by the equation

$$\log_{10} P(\text{mm.}) = 5.49916 - \frac{1.2925 \times 10^2}{T} - \frac{2.5921 \times 10^5}{T^2}$$

the deviation of observed values from those obtained by the use of the above equation being less than one per cent.

P(mm.)	T, °K.	P(mm.)	T, °K.
(50)	(278.7)	299.3	315.2
60.8	282.1	384.9	321.4
71.7	285.2	(400)	(322.3)
80.9	287.2	476.2	327.0
(100)	(291.3)	527.8	329.8
121.5	295.1	580.6	332.4
146.4	299.0	628.9	334.7
171.3	302.4	679.7	336.9
(200)	(305.6)	726	338.9
232.8	309.2	(760)	(340.3)
264.9	312.2	775.5	340.9

The values given in parentheses are not experimental but were calculated from the above equation.

The boiling point of the compound determined from the above data is 67.1°. The latent heat of vaporization calculated from the Clapeyron equation, assuming ideal gas behavior, is 7620 cal. per mole. This corresponds to a Trouton constant of 22.4.

Density.—The densities observed at 35.5, 40.9 and 45.9° were 1.6450, 1.6315 and 1.6192, respectively. In that temperature range, the density σ is given by the equation

$$\sigma = 2.3959 - 2.434 \times 10^{-3}\, T$$

where T is in degrees absolute. The volume coefficient of expansion, calculated from the above data, is 0.00152 at 40°.

Melting Point.—The melting point of the compound as obtained from a warming curve is −55.4°. The apparatus was similar to that described by Sturtevant.[5]

Infrared Spectrum.—The infrared absorption spectrum of the substance in the vapor phase was measured over the
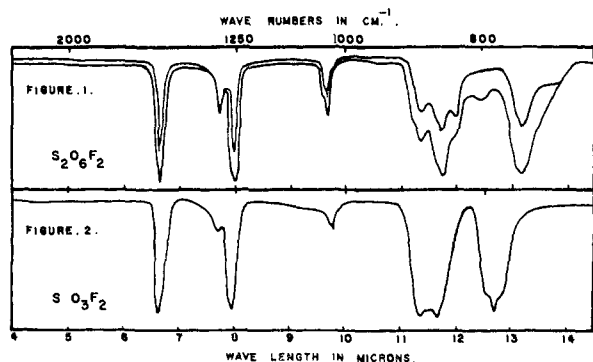
Figs. 1 and 2.

(5) J. M. Sturtevant, chapter X in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945.

range 2–15 μ by means of a double beam Perkin–Elmer spectrometer, Model 21, employing a rock salt prism and a specially prepared 10-cm. Pyrex glass cell with sodium chloride windows. The spectra obtained at 10 and 5 mm. pressure have been reproduced in Fig. 1. For comparison the spectrum of fluorine fluorosulfonate is included in Fig. 2. The S–O stretching frequencies of 1501 and 1248 cm.$^{-1}$, observed in the fluorine fluorosulfonate spectrum, have been displaced to slightly lower frequencies, viz., 1495 and 1246 cm.$^{-1}$, in the new compound.

The band at 848 cm.$^{-1}$ may be assigned to totally symmetric S–F stretch. The P and R branches are well defined in this band. Absorption bands due to totally symmetric S–F stretch occur at 848 cm.$^{-1}$ in sulfuryl fluoride, at 852 cm.$^{-1}$ in fluorine fluorosulfonate and at 840 cm.$^{-1}$ in methyl fluorosulfonate.

One other strong band occurs at 755 cm.$^{-1}$. The band at 1031 cm.$^{-1}$ is due to silicon tetrafluoride and that at 1300 cm.$^{-1}$, also present in the fluorine fluorosulfonate spectrum, is probably due to a product formed by reaction with glass, for it is equally strong at a lower gas pressure.

Nuclear Magnetic Resonance Spectrum.—The n.m.r. spectrum contained only the one fluorine peak at a negative field shift of 176 p.p.m. relative to the fluorine peaks of perfluorocyclobutane. The presence of only one peak shows that the two fluorine atoms have identical environments, and the fact that other molecules such as fluorine fluorosulfonate, pentafluorosulfur hypofluorite and thionyl tetrafluoride all show a fluorine peak due to S–F bonding at approximately the same field strength[6] confirms that both the fluorine atoms in the $S_2O_6F_2$ molecule are bonded directly to sulfur atoms.

Chemical Reactions.—With cold air-free water, this compound reacted in accordance with the equation

$$S_2O_6F_2 + H_2O \longrightarrow 2SO_3F^- + 2H^+ + \tfrac{1}{2}O_2$$
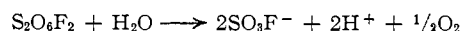
half a mole of oxygen being liberated per mole of reactant. By allowing the compound to react with an excess of sodium hydroxide solution, and waiting for the fluorosulfonate to hydrolyze completely to sulfate ion, it was found that six equivalents of base were consumed by one mole of the compound as shown by the equation

$$S_2O_6F_2 + 6OH^- \longrightarrow 2SO_4^{--} + 2F^{--} + 3H_2O + \tfrac{1}{2}O_2$$
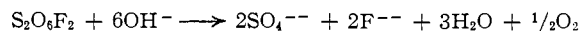
When the compound was allowed to react with cold neutral potassium iodide solution, iodine was liberated in accordance with the equation

$$S_2O_6F_2 + H_2O + 2I^- \longrightarrow$$
$$SO_3F^- + F^- + SO_4^{--} + 2H^+ + I_2$$
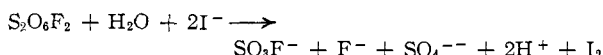
Titration with sodium thiosulfate showed that one mole of the reactant liberated one mole of iodine.

Probable Structure.—All of the above properties are consistent with a molecule having the peroxy type structure shown below

$$\begin{array}{ccccccc} & O & & & & O & \\ & \| & & & & \| & \\ O{=}S{-} & O & {-}O{-} & S{=}O \\ & | & & & & | & \\ & F & & & & F & \end{array}$$
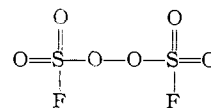
If this is the structure, the compound may be named peroxydisulfuryl difluoride.

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(6) F. B. Dudley, G. H. Cady and J. Shoolery, THIS JOURNAL, 78, 568 (1956).