These considerations indicate that the differences in the ratio of specific rate constants cannot be completely attributed to a diffusion activation energy for reaction 5, which is naively approximated by a viscosity activation energy. However, in view of the low precision to which the specific rate constant ratios are known, and the difficulties in estimating an activation energy for the diffusion of methyl radicals in these solvents, the agreement between these independent investigations is very satisfying.

**Comparison of Quantum Yields,**—It is interesting to note from Table II that water is least effective in reducing the quantum yields. Perfluorodimethylcyclobutane is singularly effective in reducing the quantum yields below those obtained in liquid acetone. This order of reduction is difficult to reconcile in terms of a "cage-effect" mechanism since water, possessing considerable structure in the liquid, would be expected to act as a very efficient "cage" for acetone. While these data are explainable in terms of solvent quenching concepts, the explanation requires that acetone be less effective than perfluorodimethylcyclobutane in quenching excited acetone molecules. Whether the quenching act places the photo-excited acetone molecule in its ground electronic state or in a low vibrational level of the excited singlet or lowest triplet state is not known. The order of variation of the quantum yields with solvent is not unreasonable if the solvent quenching involves the removal of vibrational energy. Neither the "cage-effect" nor solvent quenching offer very satisfying explanations of the observed trends.

A clue to the variation of the quantum yields in changing from one solvent to another is perhaps to be found in the material balance ratio $(1/2CH_4 +$ $C_2H_6)/CO$. It is evident from Table II that the material balance ratio, a measure of the carbon monoxide deficiency, increases in the same order that the quantum yields increase. This is understandable in terms of the "cage-effect" mechanism if once an acetyl and methyl radical escape geminate recombination they result in product formation. (This is a reasonable assumption at low radical concentrations where homogeneous recombination must compete with many other reactions.) Since the acetyl radical usually results in liquid products, the carbon monoxide deficiency is then a measure of the ability of the methyl and acetyl radical pair to escape geminate recombination. Alternately, in terms of the solvent quenching concepts, the carbon monoxide deficiency is a measure of the probability of the dissociation of A*, the photo-excited state of acetone, prior to solvent quenching. Since the variation is explainable from both a "cage-effect" viewpoint and a solvent quenching viewpoint, it contributes little to the present understanding of the primary photochemical process in solution. Furthermore, a possible relationship between the carbon monoxide deficiency and the liquid phase quantum yields of acetone photolysis, while interesting, can scarcely be considered established based upon the limited data presently available. Many more quantum yield studies seem necessary to gain some insight into the factors influencing the magnitude of the quantum yield in the liquid phase.

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# Bis-(pentafluorosulfur) Peroxide

By Claude I. Merrill and George H. Cady

Preparation of bis-(pentafluorosulfur) peroxide, $(SF_5)_2O_2$, has been achieved by allowing pentafluorosulfur hypofluorite $(SF_5OF)$ to react with thionyl fluoride $(SOF_2)$ or with thionyl tetrafluoride $(SOF_4)$ and by subjecting $SF_5OF$ to ultraviolet light. Bis-(pentafluorosulfur) peroxide is a dense, colorless liquid that boils at 49.4° and freezes at $-95.4°$. It reacts very slowly with base and shows oxidizing character by slowly producing free iodine when contacted with potassium iodide solution. Thermal decomposition of $S_2O_2F_{10}$ results ultimately in the products $SF_6$, $SO_2F_2$ and $O_2$, although $SOF_4$ is one of the materials produced initially. Chemical, mass spectrographic, infrared and nuclear magnetic resonance data contribute evidence consistent with a peroxide structure for this substance.

A small amount of bis-(pentafluorosulfur) peroxide, $SF_5OOSF_5$, was produced a few years ago by J. W. Dale and D. A. McLeod of the Defense Research Chemical Laboratories, Ottawa, Canada. They obtained the substance as one of the products of the reaction of fluorine with sulfur. The structure of the compound has been determined by Harvey and Bauer,[1] using the electron diffraction method, and found to consist of two $F_5SO$-octahedra joined by the two oxygen atoms. Some physical properties determined by Dale and McLeod are given in the paper of Harvey and Bauer.

Hypofluorites are known to be useful reagents for producing certain peroxides. For example, $CF_3OF$ combines with $COF_2$ to form $CF_3OOCF_3$[2]

$$CF_3OO\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{|}{\underset{|}{S}}}}\text{-}F$$

or with $SO_3$ to form $CF_3OO\overset{O}{\underset{O}{S}}\text{-F}$.[3] By analogy with

(1) R. B. Harvey and S. H. Bauer, This Journal, **76**, 859 (1954).

(2) R. S. Porter and G. H. Cady, *ibid.*, **79**, 5628 (1957).

(3) W. P. Van Meter and G. H. Cady, *ibid.*, **82**, 6005 (1960).

CF$_3$OF one may expect SF$_5$OF to combine with OSF$_4$ to form SF$_5$OOSF$_5$. This has been found to be true. The purpose of this paper is to describe the synthesis of bis-(pentafluorosulfur) peroxide and to report a few properties of the substance.

## Experimental

**Materials.**—Thionyl fluoride (SOF$_2$) was prepared by allowing thionyl chloride (SOCl$_2$) to react with antimony trifluoride (SbF$_3$) in the presence of antimony pentachloride (SbCl$_5$) as catalyst.[4] All materials used were of reagent grade. Fluorination of SOF$_2$ by nitrogen-diluted fluorine over a silver difluoride catalyst at 215° produced the compound SF$_5$OF[5] which was purified by fractional codistillation.[6] Although thionyl tetrafluoride was produced in the reaction between thionyl fluoride and fluorine, it was not obtained in high yield and was found to be very difficult to isolate from sulfuryl fluoride (SO$_2$F$_2$) which was one of the main products. For this work thionyl tetrafluoride was prepared by a new method in which SF$_5$OF and SOF$_2$ were placed in equimolar amounts over a AgF$_2$ catalyst at 190°. The reaction occurred rapidly producing nearly pure SOF$_4$.

**Preparation of Bis-(pentafluorosulfur) Peroxide.**—The compound, SF$_5$OOSF$_5$, has been produced in the following ways: (1) By combining SF$_5$OF with SOF$_4$ in the presence of N$_2$ as a diluent at a temperature of about 190° in a "catalytic reactor" of a type previously described[7] containing a mass of copper ribbon coated with fluorides of silver (yield, about 2% of theoretical); (2) By combining SF$_5$OF with SOF$_2$ in a ratio of 3 to 1 in the presence of N$_2$ as a diluent within the temperature range 190° to 233° in a "catalytic reactor." (This reaction probably involves the steps: SOF$_2$ + SF$_5$OF = 2 SOF$_4$; SOF$_4$ + SF$_5$OF = SF$_5$OOSF$_5$); (yield, 2 to 5% of theoretical); (3) By combining SF$_5$OF with SOF$_2$ in a ratio of 3 to 1 at about 225° in a "catalytic reactor"; the gas being removed from the reaction at 20 minute intervals and then returned after separating the SF$_5$OOSF$_5$ by condensation (yield, 21% of theoretical); (4) By combining SF$_5$OF with SOF$_2$ in a ratio 3 to 1 in a nickel vessel not containing "catalyst" within the temperature range 200 to 252°. (The reaction probably involved the steps given above under (2). It did not become apparent until a temperature of 200° was reached.) (yield, 8% of theoretical); (5) By combining SF$_5$OF with SOF$_2$ in a ratio of 3 to 1 under high pressure and at 25° in a copper vessel (yield after standing 50 days, 5% of theoretical); (6) By a procedure like (5) except that the temperature was 100° (yield after standing 16 hr., 20% of theoretical); (7) By a procedure like 5 except that the temperature was 168° (yield after 12 hr., 33% of theoretical); (8) By irradiation of SF$_5$OF by ultraviolet light.

More detailed descriptions of procedures 7 and 8 follow.

**Procedure 7.**—A 5.1 g. portion of a 3 to 1 mixture (by moles) of SF$_5$OF and SOF$_2$ was condensed in a copper cylinder having a volume of 5 ml. The vessel was heated in a constant temperature oven for 12 hr. at 168°. The product was then distilled yielding 1.69 g. of SF$_5$OOSF$_5$.

**Procedure 8.**—A one liter flask was filled with SF$_5$OF to one atmosphere pressure and the gas was irradiated for 3 hr. by a 350 watt mercury vapor lamp constructed of silica tubing. The lamp was cooled externally by water and it was located in a quartz-glass finger at the center of the flask. As the irradiated product was removed, it was pumped through a trap at −183° and then through a tube filled with soda-lime. The trap contained SiF$_4$, SF$_6$, SO$_2$F$_2$, SOF$_4$, SF$_5$OF and SF$_5$OOSF$_5$. Fluorine, formed by the reaction, passed through the trap but was absorbed by the soda-lime with the liberation of heat. Approximately 25% of the material in the trap was SF$_5$OOSF$_5$. Since much of the SF$_5$OF had not been consumed, the yield of the peroxide was well in excess of 25%. A longer period of irradiation failed to increase the yield of the peroxide. This was the result of establishing equilibrium in a reversible reaction

$$2SF_5OF \rightleftharpoons SF_5OOSF_5 + F_2$$
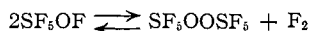
(4) H. S. Booth and F. C. Mericola, THIS JOURNAL **62**, 640 (1940).

(5) F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., *ibid.*, **78**, 1553 (1956).

(6) G. H. Cady and D. P. Siegworth, *Anal. Chem.*, **31**, 698 (1959).

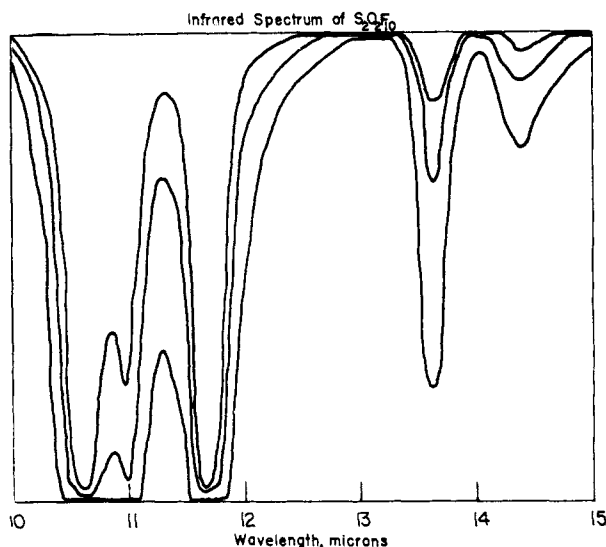(7) K. B. Kellogg and G. H. Cady, THIS JOURNAL, **70**, 3086 (1948).

Fig. 1.—Infrared spectrum of S$_2$O$_2$F$_{10}$ in the 2–15 $\mu$ region using a 10 cm. cell at 1, 2.5 and 10 mm. pressure.

It was also noted that SF$_5$OOSF$_5$ was decomposed slowly by ultraviolet light.

**Properties of Bis-(pentafluorosulfur) Peroxide.** (a) **Molecular Weight.**—Experimental molecular weights of S$_2$O$_2$F$_{10}$ fractions isolated by fractional codistillation were usually within one mass unit of the calculated value, 286.1. Measurements were made at pressures below 100 mm. to reduce the error caused by absorption of the vapor in Kel-F grease used to lubricate the stopcock of the gas-density bulb.

(b) **Freezing Point.**—The freezing point observed for S$_2$O$_2$F$_{10}$ was −95.4°. This agrees rather well with the value, −95°, of Dale and McLeod.[1]

(c) **Density.**—The density of S$_2$O$_2$F$_{10}$ has been determined at four different temperatures. The interpolated value of density at 20° is 1.968 g./ml.

### TABLE I

DENSITIES OF BIS-(PENTAFLUOROSULFUR) PEROXIDE

| Temp., °C. | −15.8 | 0.0 | 13.5 | 24.8 |
|---|---|---|---|---|
| Density, g./ml. | 2.082 | 2.033 | 1.991 | 1.950 |

(d) **Vapor Pressure.**—The values for the vapor pressure of S$_2$O$_2$F$_{10}$ given in Table II indicate a normal boiling point of 49.4°. This compares with a boiling point of 49° found by Dale and McLeod.[1] From the Clausius–Clapeyron equation the heat of vaporization is 7.45 kcal. per mole and the Trouton constant is 23.1.

### TABLE II

VAPOR PRESSURES OF BIS-(PENTAFLUOROSULFUR) PEROXIDE

| $T$, °K. | $P$, mm. | $T$, °K. | $P$, mm. |
|---|---|---|---|
| 212.9 | 1.3 | 300.7 | 329.8 |
| 226.3 | 4.5 | 308.3 | 454.1 |
| 242.0 | 14.4 | 315.9 | 602.4 |
| 259.2 | 42.4 | 322.5 | 757.6 |
| 274.4 | 104.4 | (322.6) | (760.0) |
| 289.2 | 208.1 | 323.5 | 803.8 |

(e) **Infrared Spectrum.**—The infrared spectrum of S$_2$O$_2$F$_{10}$ was measured over the range 2–15 $\mu$ by means of a double beam Perkin–Elmer spectrometer, Model 21, equipped with sodium chloride optics. A glass cell of 10 cm. length having silver chloride windows was used. Figure 1 shows the spectrum of S$_2$O$_2$F$_{10}$ obtained in the range 2 to 15 $\mu$ at 1 2.5 and 10 mm. pressure. There are strong absorption bands at 944 cm.$^{-1}$ (10.60 $\mu$), 913 cm.$^{-1}$ (10.97 $\mu$) and 857 cm.$^{-1}$ (11.68 $\mu$). A moderately strong band is located at 734 cm.$^{-1}$ (13.62 $\mu$) and a weak band appears at 694 cm.$^{-1}$ (14.40 $\mu$). The band at 944 cm.$^{-1}$ must be due to S–F stretching in the SF$_5$ group. A similar band appears at 935 cm.$^{-1}$ for SF$_5$OF and at 940 cm.$^{-1}$ for S$_2$F$_{10}$.

(f) **Mass Spectrum.**—Consolidated Model 21–103 mass spectrometer was used at an ionizing potential of 70 volts. The principal peaks in the spectrum for masses above 65 corresponded to the ions: $SOF^+$, $SF_2^+$, $SOF_2^+$, $SF_3^+$, $SOF_3^+$ and $SF_5^+$. No peaks for masses greater than that of $SF_5^+$ were observed.

(g) **Nuclear Magnetic Resonance Spectrum.**—The nuclear magnetic resonance spectrum of $S_2O_2F_{10}$ was obtained through the use of a Varian Model 4311 B high resolution spectrometer employing a sixty megacycle oscillator. The spectrum consisted of only one peak with some evidence for fine structure.

(h) **Thermal Decomposition of $S_2O_2F_{10}$.**—A sample of $S_2O_2F_{10}$ was placed in a nickel vessel like one described previously.[2] The temperature of the vessel was slowly increased from 51.2 to 338° with both temperature and pressure being recorded periodically. At about 200° a positive deviation of the pressure from perfect gas behavior was noticed. With increasing temperature beyond this point the pressure initially rose quite rapidly and then slowly approached asymptotically perfect gas behavior. When the reactor was slowly cooled, it was observed that the pressure in the vessel followed the behavior of a perfect gas but at a pressure 2.5 times as great as would be expected from the initial pressure. The products of the above reaction were $SF_6$, $SO_2F_2$, $SOF_4$ and $O_2$. In another run the temperature of the reaction vessel was maintained near 521° for a period of 12 hr. Only absorption bands for $SO_2F_2$ and $SF_6$ were observed in the infrared spectrum of the product.

(i) **Reaction with Hydroxide and Iodide Solutions.**—A sample of $S_2O_2F_{10}$ placed in a sealed bulb with 5 $N$ NaOH was only slightly attacked after a seven day period at 100°; the vast majority of the compound remaining unaffected. A sluggish reaction with a solution of potassium iodide was observed. Reaction was incomplete after a 48 hr. period at 100° but was complete after seven days at 100° producing 2 equivalents of iodine per mole of peroxide.

## Discussion

Although none of the preparative methods described above have given high yields of bis(-pentafluorosulfur) peroxide, it appears likely that the yields could be increased by removing the product as it is formed and by continuing the preparative reaction until the reactants have been consumed. This comment applies equally to the method of combining $SF_5OF$ with $SOF_2$. As things stand, the authors now prefer the method in which $SF_5OF$ combines with $SOF_2$ under pressure at about 170°.

In some of the preparations described above a "catalyst" was used. It is not clear from the results obtained that the "catalyst" accelerated the formation of bis-(pentafluorosulfur) peroxide or that it increased the yield.

When irradiation of pentafluorosulfur hypofluorite is used as the preparative method, it is probable that the yield of peroxide product can be increased by removing fluorine. Since the reaction

$$2\ SF_5OF\ =\ SF_5OOSF_5\ +\ F_2$$

is reversible, the removal of fluorine should favor the formation of the peroxide. This factor has been demonstrated by a run in which $SF_5OF$ was irradiated for 140 hr. by a ultraviolet lamp shining on the end of the quartz flask. At the end of this run about 70% of the product was $SF_5OOSF_5$. The flask also contained $O_2$, $SiF_4$, $SO_2F_2$ and a little $SF_5OF$ and $SOF_4$. Little if any fluorine was present. Apparently it had been consumed by reaction with the quartz flask.

The irradiation of pentafluorosulfur hypofluorite may involve the reaction

$$SF_5O \xrightarrow{u.v.} SF_5O \cdot\ +\ F\cdot$$
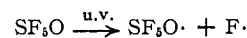
and this may be followed by recombination of the free radicals. The formation of peroxides by the combination of RO· radicals has been reported by Buncel and Davies.[8]

All of the properties of $S_2O_2F_{10}$ observed in this research are consistent with the structure found by Harvey and Bauer.[1] There is no reason to doubt that the substance is bis-(pentafluorosulfur) peroxide, $SF_5OOSF_5$.

(8) E. Buncel and A. G. Davies, *J. Chem. Soc.*, 1550 (1958).

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# Expansion of a Polyion in Salt Solutions[1]

BY MITSURU NAGASAWA[1b]

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It is known that the existing theories of polyion expansion, such as those of Hermans, Overbeek and Pals, Katchalsky and Lifson, Flory and Nagasawa and Kagawa, predict calculated values of the polyion volume much larger than those found experimentally. In this paper it is shown that the main reason for this discrepancy is the neglect of the electrostatic effect of the polyion on the counterions, *i.e.*, the neglect of the activity coefficient of the counterions. If the activity coefficient of the counterions, determined experimentally, is introduced into these theories, the calculated expansions correspond closely to the experimentally determined ones. Finally, it is demonstrated that the introduction of the counterion activity coefficient is equivalent to the use of an effective charge density and hence to the introduction of the site-binding model.

## Introduction

It is well known that linear polyions have very expanded forms in solution. The origin of the expansion is now accepted to be the electrostatic repulsive force between the fixed charges on the polyion. Many models have been suggested for the purpose of computing the electrostatic expansion; we cite Hermans and Overbeek[2a] and Pals[2b], Katchalsky and Lifson,[3] Flory,[4] Harris and Rice[5,6]

(1) (a) This work was supported by grants from the National Science Foundation and the National Institutes of Health. (b) On leave from Department of Applied Chemistry, Nagoya University, Nagoya, Japan.

(2) (a) J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948). (b) D. T. F. Pals and J. J. Hermans, *ibid.*, **71**, 433 (1952).

(3) A. Katchalsky and S. Lifson, *J. Polymer Sci.*, **11**, 409 (1953).