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 $\gamma$ -Ray Decomposition of Pure Liquid Sulfur Dioxide

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Pure liquid sulfur dioxide irradiated by  $\text{Co}^{60}$   $\gamma$ -rays at  $-17^\circ$  disproportionates essentially according to  $3\text{SO}_2 \rightarrow 2\text{SO}_3 + \text{S}$ . The elemental sulfur precipitates in the shape of long needles. Analyses of the permanent gases by combustion techniques and mass spectrometry indicate that small amounts of molecular oxygen are also formed. This oxygen does not arise by recombination of O atoms in the spurs but, most likely, by the attack of O atoms on sulfur trioxide. The rate of formation of sulfur and sulfur trioxide is constant with dose up to at least 0.5% conversion of  $\text{SO}_2$  to  $\text{SO}_3$ . The rate of formation of oxygen increases with dose. The  $G$ -values (100 e.v. yields) of the production of  $\text{SO}_3$ , S, and  $\text{O}_2$  are  $1.31 \pm 0.04$ ,  $0.65 \pm 0.02$ , and approximately 0.01, respectively. On the basis of a proposed reaction mechanism, which employs the species O and SO, the primary  $G$ -value of the decomposition of pure liquid sulfur dioxide is calculated to be 1.35. The ratio of the rate constants of the reaction steps  $\text{O} + \text{SO}_2$  and  $\text{O} + \text{SO}_2$  is estimated to be 10.

## Introduction

Up to the present time, the radiation chemistry of pure liquid sulfur dioxide has received no attention. Liquid sulfur dioxide is an important solvent for many covalent compounds<sup>1</sup>; it has been employed in radiation-induced polymerization reactions<sup>2,3</sup> and has been suggested as reactor coolant.<sup>4</sup>

The present paper reports some results on the radiation chemistry of pure liquid sulfur dioxide.

## Experimental

**Filling of Ampoules.**—A cylinder of commercial liquid sulfur dioxide (The Matheson Co., Inc., 99.98% min.) was attached to a metal-glass vacuum system incorporating a cartridge filled with freshly desiccated Drierite, a large glass vessel containing a few grams of  $\text{P}_2\text{O}_5$ , a stainless steel cylinder serving as final reservoir, and a manifold carrying five to ten glass ampoules of 20- to 32-ml. capacity. Some of the ampoules were equipped with break seals for gas analysis. After evacuation, interspersed by repeated bleedings of  $\text{SO}_2$  into the system, the glass vessel containing the  $\text{P}_2\text{O}_5$  was cooled to  $-80^\circ$  and approximately 300 ml. of  $\text{SO}_2$  was permitted to condense during the course of a few hours. The  $\text{SO}_2$  was transferred by trap-to-trap distillation into the stainless steel storage vessel and from there distilled into an ampoule. After  $\text{SO}_2$  had liquefied to about one-half of capacity, the ampoule was frozen with liquid nitrogen and sealed off with a torch. The vapor pressure during sealing varied between 5 and 15  $\mu$ . The ampoules were stored at  $-20^\circ$ .

**Irradiations.**—The ampoules were positioned, one at a time, inside a dewar vessel, which was filled with glycol and equipped with a cooling coil connected to an outside refrigerating bath. The dewar assembly then was lowered into the cobalt-60 source (5000-c. Gammacell, Canadian Atomic Energy Commission), and the temperature kept at  $-17^\circ$ . The dose rate, which varied between  $4.41 \times 10^{17}$  and  $4.63 \times 10^{17}$  e.v.  $\text{cm}^{-2}$   $\text{min}^{-1}$  depending on the size of the ampoules, was determined using the Fricke dosimeter, measured under the same geometry as encountered during sample irradiations. The energy absorbed in the liquid  $\text{SO}_2$  was assumed to be 1.295 times (= ratio of electron densities of liquid  $\text{SO}_2$  at  $-17^\circ$  to 0.8  $N$   $\text{H}_2\text{SO}_4$ ) the energy absorbed in the dosimetric solution.

**Analysis for Sulfur Trioxide.**—The irradiated ampoule was cooled to approximately  $-70^\circ$ , scratched with a file, broken, and the liquid carefully decanted off the sulfur crystals into a heavy-walled glass bottle equipped with a tightly fitting screw cap. The bottle contained a frozen mixture (at  $-80^\circ$ ) of, at least, a twofold excess of the required amount of a 5% aqueous  $\text{BaCl}_2$  solution and about 15 ml. of formalin.<sup>5</sup> With sporadic external cooling, the tightly closed bottle was gently shaken after the  $\text{BaCl}_2$  solution had thawed. Precipitation of  $\text{BaSO}_4$  is

quantitative after a few minutes of agitation. The bottle then was kept at temperatures below  $0^\circ$  at all times and the liquid  $\text{SO}_2$  was permitted to evaporate. After evaporation was complete, the pH of the solution was adjusted between 1.5 and 1.8 with concentrated  $\text{NaOH}$ , the solution boiled for about 1 hr., and the  $\text{BaSO}_4$  determined gravimetrically.

**Analysis for Sulfur.**—The ampoule containing the sulfur crystals was placed into a desiccator and dried *in vacuo* at room temperature to constant weight. The sulfur crystals were removed with sulfur-free  $\text{CS}_2$  and the ampoule redried and weighed. The crystals melted at  $119.4$ – $119.6^\circ$ .

**Gas Analysis by Combustion.**—The irradiated ampoule was cooled below  $-30^\circ$  and sealed to a high-vacuum system (pressure below 1  $\mu$ ) equipped with a Toepler pump and a McLeod gage. After cracking of the break seal, the  $\text{SO}_2$  was permitted to distil into a liquid nitrogen-cooled flask to ensure complete stripping of all permanent gases. After the  $\text{SO}_2$  had completely solidified in the flask, the permanent gases were quantitatively transferred through a liquid nitrogen-cooled trap into the McLeod gage with the help of the Toepler pump. The total amount of gas was measured and known quantities of purest hydrogen admitted. The gas mixture was quantitatively combusted with the help of an incandescent wire; the water was condensed in a cold finger. Small amounts of noncombustible, permanent gases were found in all ampoules. They were assumed to consist of nitrogen originating from air leaks. One-quarter of this nitrogen, the atmospheric equivalent of oxygen, was subtracted from the total amount of oxygen analyzed and the results given as net formation of oxygen. To check whether the radiation liberated gases from the glass, an empty, thoroughly evacuated ampoule was irradiated and analyzed. No significant amount of gases, particularly oxygen, was found.

**Gas Analysis by Mass Spectrometer.**—A Consolidated Engineering mass spectrometer equipped with a micro-inlet system<sup>6</sup> was used to scan for the peaks of  $\text{C}^+$ ,  $\text{N}_2^{+2}$ ,  $\text{O}_2^{+2}$ ,  $\text{N}_2^+$  or  $\text{CO}^+$ ,  $\text{O}_2^+$  or  $\text{SO}_2^{+2}$ ,  $\text{Ar}^+$ ,  $\text{CO}_2^+$ , and  $\text{SO}_2^+$ . The special ampoules for the mass spectrometer had a capacity of about 5 ml. and contained 2 to 3 ml. of liquid  $\text{SO}_2$ . The ampoules were kept at liquid nitrogen temperature during analysis. The intensities of the peaks of  $\text{C}^+$ ,  $\text{SO}_2^+$ , and  $\text{CO}_2^+$  were very small. This permitted the analysis to be based unambiguously on the  $\text{O}_2^+$  and  $\text{N}_2^+$  peaks, which had been calibrated with the pure gases. The ratio  $\text{Ar}^+/\text{N}_2^+$  was run as a check. It varied between 0.0147 and 0.0137.

**Test for Radiation-Induced Gas Phase Reactions.**—The partial vapor pressure of liquid  $\text{SO}_2$  at the irradiating temperature was about 0.7 atm.; therefore, gas phase radiation-induced reactions cannot be excluded *a priori*. To test this, two samples were irradiated with a lead shield of 2.5 cm. thickness (the maximum thickness which could be accommodated in the dewar vessel), screening the gas volume of the ampoules. Owing to scattering of the radiation, the theoretical shielding corresponding to the lead thickness was not realized and the energy incident on the gas space of an ampoule was only diminished by a factor of about two.

## Results

The major decomposition products in the irradiated liquid sulfur dioxide were elemental sulfur and sulfur

(1) H. H. Sisler, "Chemistry in Non-Aqueous Solvents," Reinhold Publishing Corp., New York, N. Y., 1961, p. 98.

(2) J. Herz, D. Hummel, and C. Schneider, *Makromol. Chem.*, **63**, 12 (1963).

(3) Z. Kuri and T. Yoshimura, *J. Polymer Sci.*, **1B**, 107 (1963).

(4) L. B. Borst, process for cooling a nuclear reactor, U. S. Atomic Energy Commission, U. S. Patent 3,068,159, Dec. 11, 1962.

(5) H. Steinle, *Z. Anal. Chem.*, **129**, 340 (1949).

(6) W. Burlant and J. Neerman, *J. Org. Chem.*, **26**, 3602 (1961).

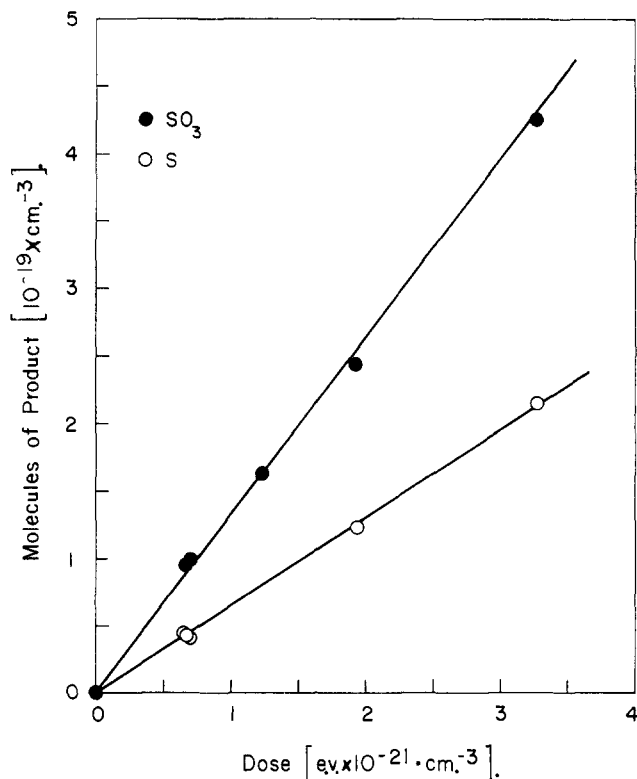


Fig. 1.—Yields of sulfur trioxide and sulfur as a function of dose in  $\text{Co}^{60}$   $\gamma$ -irradiated pure liquid sulfur dioxide at  $-17^\circ$ .

trioxide. The sulfur trioxide was not detected *per se* but was inferred from the appearance of sulfate and hydrogen ion (persistent to boiling) upon hydrolysis of the irradiated dioxide. When the irradiated sulfur dioxide was distilled *in vacuo* at  $-10^\circ$ , a white residue remained first on the interior wall of the ampoule and then slowly sublimed off in a behavior characteristic of a solid possessing a high vapor pressure, such as sulfur trioxide. The sulfur collected in the shape of long needles at the bottom of the ampoules. The supernatant dioxide and the walls of the ampoule remained completely clear.

The amounts of sulfur trioxide and sulfur formed during irradiation are proportional to the dose up to the longest exposures (equivalent to approximately 0.5% conversion of  $\text{SO}_2$  to  $\text{SO}_3$ ). Figure 1 shows a plot of the number of molecules formed as a function of the dose absorbed. The straight lines were calculated by the method of least squares. The  $G$ -values (yield of products expressed as number of molecules formed per 100 e.v. of energy absorbed) amount to  $G(\text{SO}_3) = 1.31 \pm 0.04$  and  $G(\text{S}) = 0.65 \pm 0.02$ . The error indicates the 95% confidence limit calculated from the imperfect fit of the data to a straight line.

Small but significant amounts of oxygen were detected as a minor product in the irradiated sulfur dioxide. The oxygen arises from decomposition of the liquid phase and not from the vapor phase since the yields obtained from the ampoules with shielded gas space agree with those of the unshielded ampoules. Figure 2 shows a plot of the net formation of oxygen as a function of dose. As will be explained below, the curve through the points was drawn with a continuous, increasing slope, which amounts to  $G(\text{O}_2) \approx 0.01$  at  $2 \times 10^{21}$  e.v.  $\text{cm}^{-3}$ .

The mass spectrographic determinations were

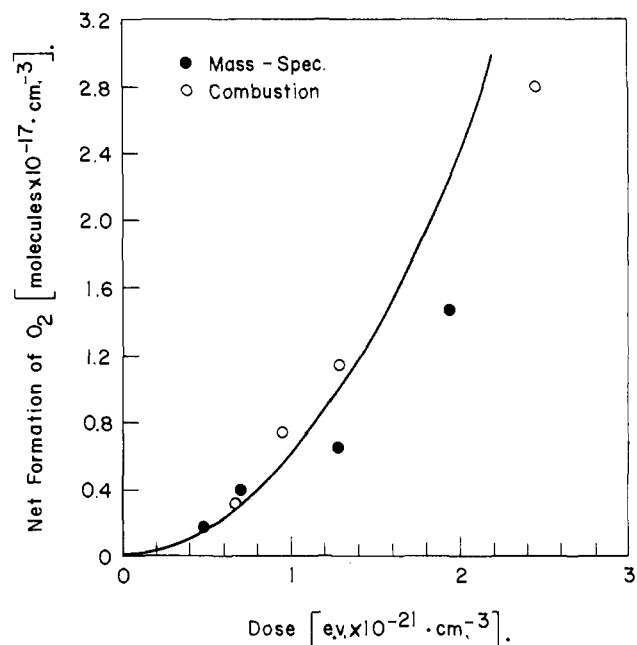


Fig. 2.—Yields of molecular oxygen as a function of dose in  $\text{Co}^{60}$   $\gamma$ -irradiated pure liquid sulfur dioxide at  $-17^\circ$ ; the notation indicates the method of oxygen analysis. The curve is calculated from the data using  $k_{\text{O}+\text{SO}_2}/k_{\text{S}-\text{SO}_2} = 10$ .

generally lower than those done by combustion. This may have been caused by calibration errors in the microsampling system of the mass spectrograph or by experimental difficulties in extracting the permanent gases as efficiently as could be done in case of the ampoules analyzed by combustion.

The equation of material balance among the three products  $\text{SO}_3$ ,  $\text{O}_2$ , and S is

$$G(\text{SO}_3) + 2G(\text{O}_2) = 2G(\text{S})$$

The data are in agreement with it. Since the yield of  $\text{O}_2$  is very low, the effect of the  $\gamma$ -radiation on pure liquid sulfur dioxide is essentially the disproportionation reaction  $3\text{SO}_2 = 2\text{SO}_3 + \text{S}$ , which obeys the same stoichiometry as the photolytic decomposition of gaseous sulfur dioxide.<sup>7</sup>

### Discussion

The data are insufficient to set up a unique reaction mechanism. However, a likely reaction mechanism is proposed which is simple, consistent with the data, and employs only definitely established species as possible reactive intermediates.

The  $\gamma$ -rays are assumed to break up a  $\text{SO}_2$  molecule into O and SO. This reaction has been proposed by Norrish and Oldershaw as a major step at a wave length smaller than 2200 Å. in the flash photolysis of gaseous  $\text{SO}_2$ .<sup>8</sup> The same authors propose the formation of sulfur to occur by mutual combination of SO. This reaction may proceed *via* unstable intermediates, such as  $\text{S}_2\text{O}_2$ . Markovich and Emanuel have shown that  $\text{S}_2\text{O}_2$  decomposes fairly rapidly into S and  $\text{SO}_2$ .<sup>9</sup> The existence of  $\text{S}_2\text{O}_2$  has been questioned by other authors.<sup>10</sup>

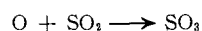
(7) A. Coehn, *Z. Elektrochem.*, **36**, 789 (1930).

(8) R. G. W. Norrish and G. A. Oldershaw, *Proc. Roy. Soc. (London)*, **A249**, 498 (1958).

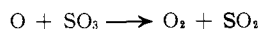
(9) V. G. Markovich and N. M. Emanuel, *Russ. J. Phys. Chem.*, **21**, 1351 (1947); see *Chem. Abstr.*, **42**, 5313f (1948).

(10) R. C. Brasted, "Comprehensive Inorganic Chemistry," Vol. 8, D. Van Nostrand Co., Inc., New York, N. Y., 1961, pp. 115-116.

The sulfur trioxide may be formed by



The small amount of molecular oxygen probably arises by attack of O on  $\text{SO}_3$ <sup>8</sup> according to



The alternate explanation that the  $\text{O}_2$  is formed by recombination of O atoms in the spurs (analogous to  $\text{H} + \text{H} = \text{H}_2$  in irradiated water) can be ruled out by the following argument: for gas phase reactions, the specific rate constant for  $\text{O} + \text{O} + \text{M} = \text{O}_2 + \text{M}$  is  $9.8 \times 10^8 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ ,<sup>11</sup> whereas for  $\text{O} + \text{SO}_2 + \text{M} = \text{SO}_3 + \text{M}$  it amounts to  $3 \times 10^{10} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ .<sup>12</sup> In the condensed phase, in analogy to the events in irradiated water, the O atoms are probably clustered a few ångstrom units apart within isolated volume elements,<sup>13,14</sup> each O atom being surrounded by  $\text{SO}_2$  molecules. Therefore, no significant amounts of  $\text{O}_2$  arising from recombination of O atoms can be expected.

The reaction  $\text{O} + \text{SO}_3 \rightarrow \text{SO}_2 + \text{O}_2$  is competitive with  $\text{O} + \text{SO}_2 \rightarrow \text{SO}_3$ . Applying the usual equations for such cases,<sup>15</sup> the following relations are obtained among  $G(\text{SO}_3)$ ,  $G(\text{O}_2)$ ,  $G_0$  (the primary yield of oxygen atoms), the specific rate constants  $k$  of  $\text{O} + \text{SO}_3 = \text{SO}_2 + \text{O}_2$  and  $\text{O} + \text{SO}_2 = \text{SO}_3$ , respectively, and the concentrations of  $\text{SO}_2$  and  $\text{SO}_3$

(11) R. R. Reeves, G. Manella, and P. Harteck, *J. Chem. Phys.*, **32**, 632 (1960).

(12) F. Kaufman, *Proc. Roy. Soc. (London)*, **A247**, 123 (1958).

(13) A. O. Allen, "The Radiation Chemistry of Water and Aqueous Solutions," D. Van Nostrand Co., Inc., Princeton, N. J., 1961, p. 7.

(14) C. J. Hochanadel, "Comparative Effects of Radiation," John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter VIII.

(15) See ref. 13, p. 29.

$$\frac{G_0}{1 + \frac{k_{\text{O}+\text{SO}_3}[\text{SO}_3]}{k_{\text{O}+\text{SO}_2}[\text{SO}_2]}} = G(\text{SO}_3) \quad (1)$$

$$\frac{G_0}{1 + \frac{k_{\text{O}+\text{SO}_2}[\text{SO}_2]}{k_{\text{O}+\text{SO}_3}[\text{SO}_3]}} = G(\text{O}_2) \quad (2)$$

Equations 1 and 2 show that at low doses ( $[\text{SO}_3] \approx 0$ )  $G(\text{SO}_3) \approx G_0$  and  $G(\text{O}_2) \approx 0$ . With increasing accumulation of  $\text{SO}_3$ , the rate of oxygen production increases whereas the rate of sulfur trioxide formation decreases. Equation 2 is integrated to give the concentration of oxygen molecules as a function of the dose. Noting that  $G(\text{O}_2) = d[\text{O}_2]/d \text{ dose}$ ,  $[\text{SO}_2] \approx \text{constant}$ ,  $(k_{\text{O}+\text{SO}_2}/k_{\text{O}+\text{SO}_3})([\text{SO}_2]/[\text{SO}_3]) \gg 1$ ,  $G_0 \approx G(\text{SO}_3)$ , and  $[\text{SO}_3] \approx G(\text{SO}_3) \times \text{dose}$ , one obtains

$$[\text{O}_2] \approx \frac{(G(\text{SO}_3) \times \text{dose})^2}{2[\text{SO}_2] \frac{k_{\text{O}+\text{SO}_2}}{k_{\text{O}+\text{SO}_3}}} \quad (3)$$

where concentrations are in number of molecules per  $\text{cm.}^3$  and dose is in units of  $100 \text{ e.v. cm.}^{-3}$ . Figure 2 shows the curve according to eq. 3 with  $k_{\text{O}+\text{SO}_2}/k_{\text{O}+\text{SO}_3} \approx 0.1$ . From eq. 1 follows  $G_0 = 1.35$ . According to the proposed mechanism,  $G_0$  equals  $G_{\text{SO}}$ ; therefore, the net decomposition of pure liquid sulfur dioxide proceeds with a primary  $G$ -value of 1.35.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

## Spectral Properties of Chlorophyllin *a*<sup>1</sup>

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The infrared and visible absorption spectra and the fluorescence spectrum of chlorophyllin *a* were determined and compared with those of chlorophyll *a*. The infrared spectrum showed the absence of a carbonyl group except when chlorophyllin *b* was present as an impurity. This provides the basis of a convenient method of analysis of the chlorophyll *b* content of a given chlorophyll preparation. Since the cyclopentanone ring is absent in chlorophyllin, the observed infrared bands help to clarify those observed in the case of chlorophyll. The visible absorption spectrum of chlorophyllin *a* has features in common with that of chlorophyll *a*. In particular, the formation of colloidal aggregates is shown by the appearance of an absorption band at  $735 \text{ m}\mu$  just as is observed for microcrystals of chlorophyll *a*. The appearance of a pronounced absorption maximum at  $688 \text{ m}\mu$  attributed to dimer formation is analogous to that observed by difference spectra in the case of concentrated solutions of chlorophyll *a*. In stretched polymer films chlorophyllin *a* and chlorophyll *a* exhibit a positive dichroism which is greater for the blue absorption maximum than for the red. The fluorescence spectrum of chlorophyllin *a* is markedly dependent on the wave length of excitation.

### Introduction

Because of the oleophilic character of chlorophyll, photochemical and spectral studies of this pigment have of necessity been carried out in organic solvents. In the chloroplast, however, some of the chlorophyll

molecules are in contact with an aqueous medium. We have therefore undertaken a study of the water-soluble chlorophyll derivative chlorophyllin, in aqueous solution. Chlorophyllin, the product of saponification of chlorophyll in air, has been known for more than 50 years,<sup>3</sup> yet the photochemical and spectral properties of this interesting pigment have not been studied extensively. A preliminary account of our

(1) (a) Supported by the United States Air Force through the Air Force Cambridge Research Laboratories under Contract No. AF19(628)-475 and by the National Institutes of Health under Research Grant No. C6351. (b) Taken in part from the dissertation of Suse B. Broyde, submitted June, 1963, to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Public Health Service Research Career Awardee.

(3) (a) R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Springer-Verlag, Berlin, 1913; (b) S. Aronoff in "Handbuch der Pflanzenphysiologie," Vol. 5, Part 1, W. Ruhland, Ed., Springer-Verlag, Berlin, 1960.