Sulfoxides. V.[1] The Ionization of Sulfoxides in Sulfuric Acid[2]

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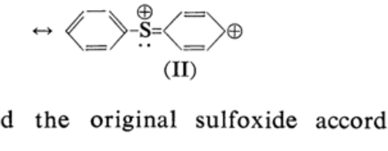
Some years ago, Szmant and Brost[3] investigated the cryoscopic behaviors of several organic sulfur compounds in sulfuric acid and presented, among other things, the interesting observation that diphenyl sulfoxide gave a large and reproducible freezing point depression with an *i*-factor of 4.7 with the formation of a brilliant green solution. They theorized that diphenyl sulfoxide ionizes in 100% sulfuric acid according to the following Eq. 1:

$$(C_6H_5)_2\text{–}SO + 3H_2SO_4 \rightleftarrows \underset{(I)}{(C_6H_5)_2\overset{\oplus\oplus}{S}:} + H_3\overset{\oplus}{O} + 3HS\overset{\ominus}{O}_4 \ (i=5) \qquad (1)$$

The green color of the double positive species, "diphenyl sulfidonium ion," I, was assumed to result from the contribution of such resonance structures as II. They also indicated that this species, I, in the presence of water restored the original sulfoxide according to Eq. 2:


(II)

$$(C_6H_5)_2\text{–}\underset{\cdot\cdot}{\overset{\oplus\oplus}{S}} + 3H_2O \rightarrow (C_6H_5)_2\text{–}SO + 2H_3\overset{\oplus}{O} \qquad (2)$$

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[1] a) Paper I: S. Oae, T. Kitao and Y. Kitaoka, *Chem. & Ind.*, **1961** 291; b) II: S. Oae and S. Kawamura, This Bulletin, **36**, 163 (1963); c) III: S. Oae, T. Kitao, S. Kawamura and Y. Kitaoka, *Tetrahedron*, **19**, 817 (1963); b) IV: S. Oae, T. Kitao and S. Kawamura, ibid., **19**, 1783 (1963).

[2] a) Preliminary Communication; see Ref 1a; d) The early part of this work was performed at the Department of Chemistry, Brookhaven National Laboratory, under the auspices of the U. S. Atomic Energy Commission, while S. O. was a visiting chemist there. We wish to thank Dr. David R. Christman for some of the ^{18}O analyses. Appreciation is also expressed to Mr. Motoyoshi Hatada for his generous collaborations in the mass-spectroscopic analyses.

[3] H. H. Szmant and G. A. Brost, *J. Am. Chem. Soc.*, **73**, 4175 (1951).

This conclusion was later challenged,[4] and it was claimed that the *i*-factor of this green solution was 2.0, that this gradually changed to about 3 when the solution was left standing and that the original sulfoxide could not be recovered after some time when its freezing point had become approximately constant.[5]

A convenient way to test the rather attractive Szmant & Brost's hypothesis of the presence of the doubly-charged "sulfidonium ion" I in sulfuric acid is to determine the ^{18}O incorporation into the resulting sulfoxide recovered by quenching the green solution by ^{18}O-enriched water. When diphenyl sulfoxide was dissolved in 97% sulfuric acid and this brilliant green solution was diluted with a large excess of ^{18}O-enriched water (0.6 atom % ^{18}O), the original sulfoxide was recovered in almost a quantitative yield. However, the sulfoxide recovered was found to be incorporated with no excess of ^{18}O, contrary to what one would expect from the conclusion by the previous workers.[3]

^{18}O for Ph–SO–Ph	0.208%
^{18}O for tank CO_2	0.211%

Since this ^{18}O tracer experiment clearly excludes the hypothesis of the presence of the "diphenyl sulfidonium ion" in sulfuric acid, the other alternative would be that the ionization of the sulfoxide in sulfuric acid takes place according to Eq. 3, as was suggested by Gillespie *et al.*[4] Accordingly, the cryoscopic determinations were made on diphenyl sulfoxide and

$$(C_6H_5)_2S \rightarrow O + H_2SO_4$$

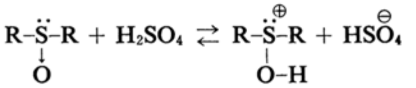
$$\rightleftarrows (C_6H_5)_2\overset{\oplus}{S}\text{-OH} + HS\overset{\ominus}{O}_4 \quad (i=2) \qquad (3)$$

other related sulfoxides with about 99% sulfuric acid. Although some of the sulfoxides, e. g., phenyl benzyl sulfoxide and phenyl methyl sulfoxide, gradually decomposed in sulfuric acid, others were recovered in satisfactory yields when treated within an hour. Even the unstable sulfoxides could be recovered in satisfactory yields when the solutions were treated within ten to fifteen minutes. Therefore, with these compounds, the cryoscopic determinations were carried out in such short periods. The results obtained are shown in Table I.

An inspection of the results in Table I indicates that none of the sulfoxide measured gave an *i*-factor as large as 4 or 5; all the values fall around two, within the range of experimental error, suggesting that the sulfoxide in general ionizes according to Eq. 4, possibly with only the exception of thianthrene monoxide.[6]

TABLE I. CRYOSCOPIC *i*-FACTORS AND COLORS OF VARIOUS SULFOXIDES IN 99.5% SULFURIC ACID

Compound	*i*-Factor	Color of solution
Ph-SO-Ph	2.15	Deep green
4-MeC_6H_4-SO-C_6H_4-NH_2-4′	2.15	Deep green
Ph-SO-CH_2Ph	1.95	Red
Ph-SO-CH_3	2.10	Pale orange
CH_3-SO-CH_3	1.90	None


$$\text{R-}\underset{\substack{\downarrow\\ \text{O}}}{\ddot{\text{S}}}\text{-R} + H_2SO_4 \rightleftarrows \text{R-}\underset{\substack{|\\ \text{O-H}}}{\overset{\oplus}{\text{S}}}\text{-R} + HS\overset{\ominus}{O}_4$$
(4)

Although we cannot offer any satisfactory explanation for the different colors associated with different compounds in sulfuric acid, these colors are probably related to the ease of charge-transfer. The sulfoxides bearing a π-electron system of a benzene ring at the α-position appear to give deeper colors.

Earlier, it was suggested that the *i*-factor changes in value from 2 to 3 when diphenyl sulfoxide was kept in sulfuric acid for hours. We also confirmed this. It should be mentioned here also that the recovery of diphenyl sulfoxide was better from the green solution of less concentrated sulfuric acid, while the recovery became negligible and a large amount of a gummy, brown substance was formed when the sulfoxide was dissolved in over 100% of sulfuric acid. Even with 100% sulfuric acid, however, the yield of the recoverable sulfoxide was very small.

Experimental

Materials. — *Diphenyl sulfoxide* purchased from K and K Laboratories, Inc., was recrystallized from a mixture (1 : 1) of benzene and ligroin. White crystals (m. p. 70.5—71°C) were used.

Dimethyl Sulfoxide.—The oxidation of dimethyl sulfide was performed by the method reported by R. L. Shriner et al.,[7] using 30% hydrogen peroxide in an acetone solution. The fraction boiling at 90—91°C/26 mmHg was used.

Benzyl Phenyl Sulfoxide. — The oxidation of benzyl phenyl sulfide was carried out in a similar way.[7] To the sulfide (52 g., 0.26 mol.) in 250 ml. of acetone 40 g. of 30% H_2O_2 was added. The

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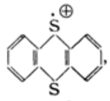
[4] R. J. Gillespie and J. A. Leisten, *Quart. Rev.*, **8**, 40 (1954).

[5] R. J. Gillespie and R. C. Passerini, *J. Chem. Soc.*, **1956**, 3850.

[6] H. J. Shine and L. Piette have reported (*J. Am. Chem. Soc.*, **84**, 1798 (1962)) that thianthrene monoxide dissociates to form an ion radical, , in 96—97% sulfuric acid. This view seems to be favored by our preliminary ^{18}O-tracer experiment, a full account of which will be reported shortly.

[7] R. L. Shriner, H. C. Struck and W. J. Jorison, *J. Am. Chem. Soc.*, **52**, 2060 (1930).

mixture was shaken and allowed to stand at room temperature for 72 hr. After the acetone had been removed, the oil which remained immediately solidified upon cooling. The solid was recrystallized from 60% ethanol. The yield was 40 g. (70%). After repeated recrystallization, white crystals m. p. 122—123°C were used.

Phenyl Methyl Sulfoxide.[8]—Phenyl methyl sulfide was prepared by treating thiophenol with dimethyl sulfide under alkaline conditions. Phenyl methyl sulfoxide was obtained by an oxidation similar to that described above, and the fraction boiling at 91—92°C/12 mmHg was collected and used.

d,l-4-Amino-4′-methyldiphenyl Sulfoxide.[9]—A mixture of *p*-toluenesulfinic acid (1 part) and aniline (4 parts) was heated at 110—115°C for 30 hr. The excess of aniline was removed by steam distillation, and the non-volatile residue was filtered, washed with ether, and recrystallized from ethanol. Pure d, l-4-amino-4′-methyldiphenyl sulfoxide m. p. 169.5—170.5°C was obtained in a 45% yield.

Cryoscopic Measurements.—The apparatus used for the cryoscopic measurements was essentially the same as that reported by Newman et al.[10]

Near 100% sulfuric acid was prepared by mixing extra pure concentrated sulfuric acid and fuming sulfuric acid. The concentration of sulfuric acid was checked by measuring the freezing point, which was determined by a Beckmann-type thermometer. The thermometer was calibrated each time by a standard thermometer. All the determinations were carried out in an air-conditioned room which was kept at around 20°C with a humidity of slightly less than 40%. In all the runs, the freezing points of the acids were in the 9.80—10.20°C range. The samples taken to lower the freezing point of the solution were about (1.0—2.0)×10⁻² mol./l.; they were kept in very thin glass ampules. After the acid had been kept in the apparatus for a few hours, the freezing point of the solvent was determined; then the solute in the ampule was put in as rapidly as possible through one of the three necks of the apparatus, and the apparatus was closed with a glass stopper. The ampule was broken with a glass-rod stirrer, and the solute was thoroughly dissolved by stirring it at room temperature. The system was then cooled in an ice-salt bath. The temperature of the solution was read every minute, and the freezing point was graphically recorded. The calculation of the van't Hoff factor was made by the equation where Δm is the molarity of the solute, $\Delta\theta$ is the freezing point depression, and θ is the total freezing point depression:

$$i=\frac{\Delta\theta}{\Delta m\times 6.154\ (1-0.0047\theta)}$$

The average *i*-values of three to five runs are shown in Table II.

TABLE II. *i*-FACTORS OF THE SULFOXIDES IN SULFURIC ACID

Compound	Initial f. p. °C	Δw, g.	Δm (mol./l.) $\times 10^2$	$\Delta\theta$ °C	i
Ph-SO-Ph	10.15	0.1134	1.404	0.186	2.15
4-MeC_6H_4-SO-C_6H_4-NH_2-4′	10.00	0.1033	1.118	0.148	2.15
Ph-SO-CH_2Ph	10.20	0.1070	1.242	0.149	1.95
Ph-SO-CH_3	9.82	0.08224	1.468	0.190	2.10
CH_3-SO-CH_3	9.95	0.0542	1.737	0.203	1.90

The Oxygen Exchange Reaction of Diphenyl Sulfoxide.—Diphenyl sulfoxide (1.0 g.; 5 mmol.) was dissolved in 10 ml. of 98.99% sulfuric acid, prepared by adding fuming sulfuric acid to c. p.-grade 93.5% sulfuric acid under ice-cooling. A brilliant blue-green color formed immediately. After this ice-cooled solution had been kept for from five to ten minutes, the solution was poured into 25 ml. of frozen ^{18}O-enriched water (0.6 atom% ^{18}O). The pale yellow precipitate which formed was collected on a sintered-glass filter, washed once with 5 ml. of a cold, diluted, alkaline solution of the same ^{18}O-enriched water, washed three times with 5 ml. of the same ^{18}O-enriched water, and then dried. The dried sample (0.95 g.), recovered in nearly a quantitative yield, was recrystallized from ethanol to give colorless crystals with a m. p. of 70—71°C; the mixed melting point with an authentic sample was 70—71°C. This sample was subjected to ^{18}O analysis.

Isotopic Analysis.—The analysis of the ^{18}O content of the sulfoxide was performed by an adaptation of the method of Rittenberg and Ponticorvo.[11] The compound (50 mg.) was introduced, together with a 1 : 1 mixture (300 mg.) of mercuric chloride and mercuric cyanide, in to an 8 mm. A-top tube (27 cm.) with a break off-seal at one end and a seal-off construction at the other. The tube was vacuum-sealed and then heated at 500°C for 3—5 hr. After it had then been cooled, the tube was opened in a vacuum line and the hydrogen chloride which had formed was removed by adding a few drops of quinoline, while the hydrogen sulfide which had formed was removed by passing the gas through a glass-wool-packed tube absorbing a small amount of lead acetate. The gases which had formed were condensed by cooling the gas with liquid nitrogen, and the non-condensable gases which had formed were pumped off. After repeated fractionations, the carbon dioxide was collected and subjected to mass-spectrometric analysis. The atom % ^{18}O was calculated from the peak of mass 44 and 46 according to the following equation:

$$\text{Atom \% }^{18}\text{O}=\frac{\text{Peak 46/Peak 44}}{2+\text{Peak 46/Peak 44}}$$

Summary

Contrary to the earlier claim that diphenyl sulfoxide ionizes in nearly 100% sulfuric acid to give a "diphenyl sulfidonium" ion, which

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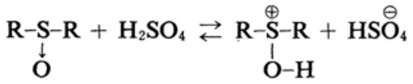
[8] van Hove, *Bull. soc. chim. Belg.*, **36**, 556 (1927).

[9] P. W. B. Harrison, J. Kenyon and H. Phillips, *J. Chem. Soc.*, **1926**, 2079.

[10] M. S. Newman, H. G. Kuivila and A. B. Garrett, *J. Am. Chem. Soc.*, **67**, 704 (1945).

[11] D. Rittenburg and L. Ponticorvo, *J. Appl. Rad. Isotopes*, **I**, 208 (1956).

can then return to the original sulfoxide when quenched with water, the ^{18}O tracer experiment and a new set of cryoscopic determinations of a few sulfoxides have revealed that the dissociation of the sulfoxide takes place in a concentrated sulfuric acid in the following manner:



$$\mathrm{R{-}\underset{\overset{\downarrow}{O}}{S}{-}R} + \mathrm{H_2SO_4} \rightleftarrows \mathrm{R{-}\underset{\overset{|}{O{-}H}}{\overset{\oplus}{S}}{-}R} + \mathrm{HS\overset{\ominus}{O}_4}$$

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