Sulfoxides. VI.[1] The Oxygen Exchange Reaction of Sulfoxides in Sulfuric Acid[2]

By Shigeru OAE, Teijiro KITAO, Yoshinori KITAOKA and Shunichi KAWAMURA

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Unlike those in sulfone groups, the sulfur-oxygen links in sulfoxides are known to be considerably weak. A number of reactions are known to involve the facile cleavage of the S-O bonding.[3] A typical illustration of the weaker S-O bonding in sulfoxide than that in sulfone can be seen in the following ^{35}S-tracer experiment. Diphenyl sulfone reacts sluggishly with sulfur above 300°C to give diphenyl sulfide, with a replacement of the sulfur atom of the sulfone group involving the cleavage of the C-S bond, while diphenyl sulfoxide is reduced quantitatively to the sulfide via the cleavage of the S-O bond by heating it with sulfur at 280°C.[4]

Another marked difference between the sulfoxide group and the sulfone group is that the former still retains a lone electron pair on the sulfur atom. Because of this lone electron pair, the sulfur atom of the sulfoxide is still nucleophilic in nature in spite of the positive charge. Thus, dimethyl sulfoxide is known to react with methyl iodide to yield trimethylsulfoxonium iodide.[5]

An interesting reaction in this connection is the oxygen exchange reaction of sulfoxides in sulfuric acid;[2] this paper will present detailed accounts of this rather unusual reaction.

Results and Discussion

It was shown in the previous paper[1] that diphenyl sulfoxide ionized in concentrated sulfuric acid in the following manner, giving a deep green solution:

$$(C_6H_5)_2\ddot{S}\rightarrow O + H_2SO_4 \rightleftarrows (C_6H_5)_2\overset{\oplus}{\ddot{S}}—OH + HS\overset{\ominus}{O}_4 \qquad (1)$$

When diphenyl sulfoxide was dissolved in a large excess of concentrated ^{18}O-enriched sulfuric acid for five to ten minutes at around 0°C, and the resulting green solution was diluted with normal water and ^{18}O-enriched water (0.6 atom% ^{18}O), and it was found that

TABLE I. ^{18}O CONCENTRATIONS OF DIPHENYL SULFOXIDES RECOVERED FROM THE GREEN SOLUTION WITH ^{18}O-ENRICHED H_2SO_4

Ph-SO-Ph (Quenched with ^{18}O-enriched water, 0.6 atom% ^{18}O)	0.412%
Ph-SO-Ph (Quenched with normal water)	0.426%
H_2SO_4	0.480%
Natural CO_2	0.212%

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[1] Part V; S. Oae, T. Kitao and Y. Kitaoka, This Bulletin, **38**, 543 (1965).

[2] a) Preliminary Communication; see S. Oae, T. Kitao and Y. Kitaoka, *Chem. & Ind.*, **1961**, 291. b) 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 ammission, when S. O. was a visiting chemist there. We wish to thank Dr. David R. Christman of the B. N. L. for some ^{18}O analysis. We are also grateful to Mr. Motoyoshi Hatada and Dr. Keiji Kuwata for their generous collaborations in mass spectric and ESR analyses.

[3] For details see Chapter 4 of "Sulfur Bonding," by C. C. Price and S. Oae, Ronald Press., N. Y. (1962), or S. Oae, *Chemistry (Kagaku)*, **19**, 220—229 (1964).

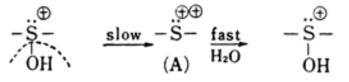
[4] S. Oae and S. Kawamura, This Bulletin, **36**, 164 (1963).

[5] R. Kuhn and H. Tischmann, *Ann.*, **611**, 117 (1958).

the recovered diphenyl sulfoxide was incorporated with a similar concentration of ^{18}O. A typical run is shown in Table I.

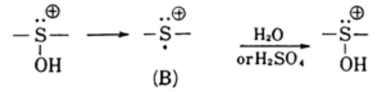
Among a number of mechanisms that could be considered, the following are a few mechanisms that are conceivable for this ^{18}O exchange reaction:

a) SN_1-Type:



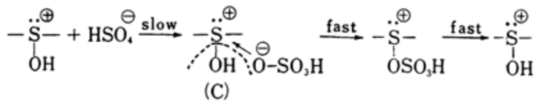
(2)

b) Free Radical Type:



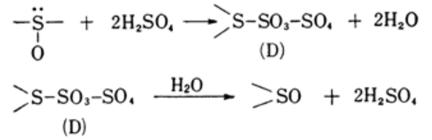
(3)

c) SNi-Type:



(4)

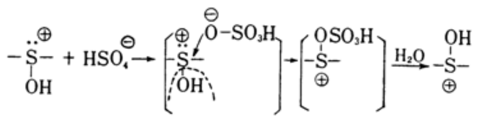
d) Oxidative Adduct Formation and Subsequent Hydrolysis:



(5)

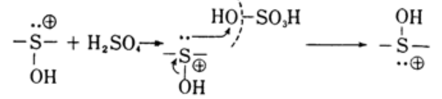
e) SN_2-type:

1) Nucleophilic Attack on Sulfoxide by Sulfate Ion:



(6)

2) Nucleophilic Attack on Sulfuric Acid by Sulfoxide:



(7)

SN_1-Type Mechanism. — Although Szmant's hypothesis of the formation of the diphenyl sulfidonium ion in the deep green solution was excluded by the ^{18}O tracer experiment¹⁾ and by the careful determination of the i-factor¹⁾, the SN_1-type mechanism still remains acceptable if one assumes that the formation of the sulfidonium ion (A) is the slow, rate-determining step and that the sulfidonium ion hydrolyzes to give the sulfoxide in the subsequent fast step. Here, the facile ^{18}O exchange of diphenyl sulfoxide can be explained on the basis of the resonance stabilization of the incipient sulfidonium ion, just as in the case of the facile solvolysis of benzhydryl compounds. The replacement of a phenyl group by an alkyl or an aralkyl substituent would retard the ^{18}O exchange. However, such was not found to be the case. Especially, the facile ^{18}O exchange of dimethyl sulfoxide, where the formation of the corresponding sulfidonium ion would be very difficult, does not seem to favor the mechanism. (See Table II).

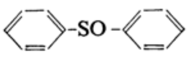
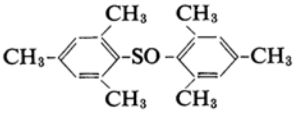
It is known that SN_1 reactivity increases if the starting substance has a steric strain and the strain is relieved in going to the transition state. Thus, 2, 4, 6-trimethyl-α-phenethyl chloride reacts far faster (ca. 2000 fold.) than α-phenethyl chloride in ethanolysis.⁶⁾

A similar steric acceleration in the SN_1 reaction was observed in the ethanolyses of substituted benzhydryl chlorides⁶⁾.

TABLE II. ^{18}O-EXCHANGE OF VARIOUS SULFOXIDES WITH 97% ^{18}O-LABELED SULFURIC ACID AT 0°C FOR FIVE MINUTES

Compound	Color of solution	^{18}O Incorporation
C_6H_5-SO-C_6H_5	Deep green	0.42
C_6H_5-SO-$CH_2C_6H_5$	Red	0.42
C_6H_5-SO-CH_3	Pale orange	0.42
CH_3-SO-CH_3	Colorless	0.45
H_2SO_4		0.48
Tank CO_2		0.21

TABLE III. RATES OF ^{18}O EXCHANGE OF DIARYL SULFOXIDES WITH ^{18}O-LABELED 94.5% SULFURIC ACID AT 0°C

	3.4×10^{-4} sec^{-1}
	1.0×10^{-5} sec^{-1}

A similar comparison of rates between diphenyl sulfoxide and dimesityl sulfoxide has therefore been carried out; the results are shown in Table III. An inspection of the data clearly excludes the SN_1-type mechanism for this ^{18}O exchange, since in this case the sterically-strained dimesityl sulfoxide was found to be much less reactive than diphenyl sulfoxide this is contrary to what one would expect from the SN_1-type mechanism.

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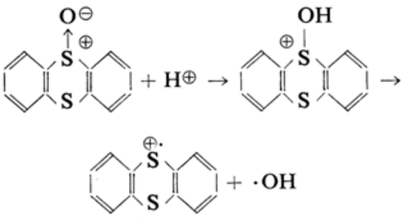
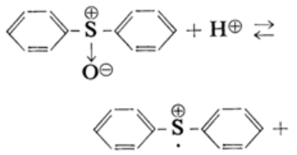
6) E. L. Eliel, "Substitution at Saturated Carbon Atoms," in "Steric Effects in Organic Chemistry," Ed. by M. S. Newman, John Wiley and Sons, N. Y. (1965), pp. 88—89.

Free Radical Mechanism.—Hirshon, Gardner and Fraenkel[7] have reported that the sulfuric acid solutions of certain sulfur-containing aromatic compounds show electron spin resonance and contain free radicals in substantial concentrations. German workers have reported recently[8] that the sulfuric acid solutions of aryl sulfoxides are paramagnetic. Especially well-studied are the solutions of diphenyl disulfide, thianthrene and thianthrene oxides.[9,10] It has been suggested that the species present in the sulfuric acid solution of thianthrene oxide on thiantrene is the positive ion-radical (B′), as is shown below:



(B′) (8)

A similar mechanism could be adopted in this case. If the hydroxyl radical thus formed would transfer with either water or sulfuric acid to regenerate an alternative hydroxyl radical, the recombination between the positive ion-radical (B) and the hydroxyl radical will give rise to the sulfoxide in which the original oxygen atom is exchanged. However, it is unlikely that a substantial amount of radical transfer takes place between the hydroxyl radical and water or sulfuric acid, or both. If there were the following dissociation (Eq. 9),

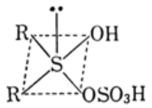


(B) (9)

the presence of the radical ion (B) could be detected by a conventional electron spin-resonance spectroscopy. When diphenyl sulfoxide was dissolved in 93 — 98% sulfuric acid at various concentrations and the solutions were subjected to ESR spectroscopic analysis, however, no noticeable signal was detected, contrary to the early claim by German workers.[11] None of the other sulfoxides, used for this ^{18}O exchange study, showed a noticeable ESR signal. Therefore, it is not likely that such a free radical dissociation takes place in sulfuric acid.

Another remaining possibility in the free radical mechanism is the process which involves a rate-determining dissociation of protonated diphenyl sulfoxide into the radical ion (B) and the hydroxyl radical, followed by the subsequent recombination of the two radicals. This is also rather unlikely, since the hydroxyl radical so formed would attack not only the sulsur atom but also benzenoid carbon atoms, usually giving some rearranged products,[12] if there were any radical transfer of the hydroxyl radical during the process. Moreover, the radical ion would accept an electron to be reduced back to the sulfide more easily than it would one to recombine to yield the original sulfoxide. In fact, thianthrene monoxide, which is believed to give the radical ion, B′, in sulfuric acid, showing clear ESR signals, is reduced back to thianthrene chiefly when the solution is quenched with water.[10,13] Obviously, a different reaction is taking place in the case of thianthrene.

SN$_\mathrm{i}$-Type Mechanism Involving 3d Orbitals of Sulfur Atom.—Since the sulfur atom can utilize its 3d orbitals for forming an extra bond, expanding its valence shell beyond the octet, especially when the central sulfur atom bears positive charge, such as in the sulfoxide or sulfonium group,[14] the formation of an incipient intermediate, (C), is possible. If the intermediate (C) has a square pyramidal structure, stereochemical considerations will predict a net retention of the original configuration:



(C)

In fact, retention was found to be the case in some of the various nucleophilic substitutions involving tetracovalent phosphorous compounds,[15] and moreover, a similar nucleophilic addition-elimination process was suggested in the reaction of sulfonium compounds with phenyllithium.[16]

This mechanism can be readily tested by using

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[7] J. M. Hirshon, K. M. Gardner and G. K. Fraenkel, *J. Am. Chem. Soc.*, **75**, 4115 (1953).

[8] V. Schmidt, K. Kabitze and K. Markau, *Angew. Chem.*, **72**, 708 (1960).

[9] A. Fava, P. B. Sogs and M. Calvin, *J. Am. Chem. Soc.*, **79**, 1078 (1957).

[10] H. J. Shine and L. Piette, ibid., **84**, 4798 (1962).

[11] See Footnote 18 of Ref. 10.

[12] A similar reaction can be found in the photochemical rearrangement of azoxybenzene to 2-hydroxyazobenzene. S. Oae, T. Fukumoto and M. Yamagami, This Bulletin, **36**, 601 (1963).

[13] A detailed study is now under way in these laboratories.

[14] C. C. Price and S. Oae, " Sulfur Bonding," Chapters 4 and 5.

[15] a) W. E. McEwen et al., *J. Am. Chem. Soc.*, **82**, 2396, 2646, 5503 (1960); b) F. Ramirez et al., ibid., **82**, 2651, 2652, 5703 (1960); **82**, 429 (1961); **84**, 4588 (1962).

[16] a) V. Franzen and C. Mertz, *Angew. Chem.*, **72**, 416 (1960); b) J. Bornstein and J. H. Supple, *Chem. & Ind.*, **1960**, 1333.

an optically-active sulfoxide. Thus, an optically-active sulfoxide, *d*-4-methyl-4-amino-diphenyl sulfoxide,17) $[\alpha]_D^{30}$ $+105.9$ ($c=1.10$, $l=2.0$) in 98% ethanol, was synthesized and subjected to the ^{18}O-exchange. When the blue green solution of the *d*-isomer sulfoxide ^{18}O-enriched sulfuric acid was diluted with water, the compound recovered was found to be racemized completely to the *d*, *l*-isomer, while there was a usual amount of ^{18}O incorporation in the racemized sulfoxide, as Table IV shows.

TABLE IV. ^{18}O EXCHANGE OF *d*-4-AMINO-4′-METHYLDIPHENYL SULFOXIDE IN 97% ^{18}O-ENRICHED SULFURIC ACID AT 0°C FOR FIVE MINUTES

^{18}O for $4\text{-}NH_2\text{-}C_6H_4\text{-}SO\text{-}C_6H_4\text{-}CH_3\text{-}4'$	0.45%
^{18}O for H_2SO_4	0.48%
^{18}O for tank CO_2	0.21%

This data clearly excludes the possibility of a $S_{N}i$-type process involving the incipient nucleophilic adduct intermediate, C.

The Oxidative Formation of Adduct and Subsequent Hydrolysis.—Very recently, it has been reported by Mislow, Simmons, Melillo and Ternay that sulfoxides are readily racemized in the presence of hydrochloric acid accompanied by oxygen exchange with solvent water. The mechanism suggested for this reaction involves the initial oxidative adduct formation (Eq. 10) and the subsequent hydrolysis of the adduct (Eq. 11), as is shown below:18)

$$R_2SO + 2HCl \rightleftarrows R_2SCl_2 + H_2O \qquad (10)$$

$$R_2SCl_2 + H_2{}^{18}O \rightleftarrows R_2S^{18}O + 2HCl \qquad (11)$$

The reversible formations of dibromo compounds19) or dichloro compounds20) from the corresponding sulfoxides by the treatment of hydrobromic acid or hydrochloric acid have been known for some time. In fact, some dibromo compounds were successfully isolated, and the subsequent treatment of the dibromo compounds with ^{18}O-enriched water was found to give the corresponding sulfoxides labeled with ^{18}O.21) However, unlike hydrohalous acid, sulfuric acid is not a good nucleophile and cannot be oxidized so readily by such a weak oxidizing agent. Meanwhile, it has been suggested that concentrated sulfuric acid dissociates to form sulfur trioxide and water.22) Sulfur trioxide is a powerful electrophile and possibly coordinates with the sulfur atom of sulfoxide, replacing oxygen, as is shown by Eq. 5, to form perhaps the incipient intermediate (D), which would immediately react with water to give the original sulfoxide. If this were the case, then sulfides, being more nucleophilic in nature, would react more readily with sulfur trioxide to form the corresponding sulfoxides, as in the case of the bromine oxidation of sulfides and their corresponding sulfoxides.21) However, the reaction of diphenyl sulfide in concentrated sulfuric acid or in oleum is very sluggish; only when the red solution of the sulfide was kept in sulfuric acid for a long time, was the formation of a small amount of the sulfoxide observed.23) On the other hand, the ^{18}O exchange reaction of the sulfoxide is very fast in concentrated sulfuric acid; it is usually completed within a few minutes at 0°C. Therefore, it is likely that the ^{18}O exchange reactions of sulfoxides in concentrated sulfuric acid do not follow a path — oxidative adduct formation and subsequent hydrolysis — similar to that of the reactions with hydrohalous acids.

The Nucleophilic Attack on Sulfoxide by the Hydrogen Sulfate Ion or Water. — Since both sulfate and hydrogen sulfate ions are known to be very weak nucleophiles, it is difficult to accept the mechanism involving the nucleophilic attack of hydrogen sulfate or sulfate ion. Recently, however, Leonard and Johnson24) have

TABLE V. RATES OF THE ^{18}O EXCHANGE OF DIPHENYL SULFOXIDE AND DIMESITYL SULFOXIDE WITH ^{18}O-LABELED SULFURIC ACID

	Atom% ^{18}O of recovered sulfoxide					
Time, sec.	300	600	1800	3600	7200	
Diphenyl sulfoxide	0.26	0.31	0.45	0.60	—	$k_{ex}=3.4\times10^{-4}\,\text{sec}^{-1}$
Dimesityl sulfoxide	0.206*	0.21	—	0.22	0.24	$k_{ex}=1.0\times10^{-5}\,\text{sec}^{-1}$

* The Natural abundance of ^{18}O was 0.204 atom%.

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17) P. W. B. Harrison, J. Kenyon and H. Phillips, *J. Chem. Soc.*, **1926**, 2079.

18) K. Misolow, T. Simmons, J. T. Melillo and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

19) T. Zincke and W. Frohneberg, *Ber.*, **43**, 837 (1909).

20) a) K. Fries and W. Vogt, *Ann.*, **381**, 337 (1911); b) E. Fromm, ibid., **396**, 75 (1913); c) K. Issleib, M. Tschach, *Z. anorg. u. allegem. Chem.*, **305**, 198 (1960).

21) Unpublished works in our laboratories.

22) T. C. Hoering and J. W. Kennedy, *J. Am. Chem. Soc.*, **79**, 56 (1957).

23) R. J. Gillespie and R. C. Passerini, *J. Chem. Soc.*, **1956**, 3850.

24) N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).

presented a case in which the sulfur atom of a cyclic sulfoxide, 1-thiacycloocta-5-one, was presumed to be attacked by a water molecule in the presence of 2, 2-dimethoxypropane and 70% perchloric acid. When diphenyl sulfoxide was treated with 70% perchloric acid, however, it was found not to exchange with oxygen, but to be oxidized to the sulfone when it was kept at 0°C for four hours. Therefore, it appears that this nucleophilic attack of water on the sulfur atom is limited to the reactions of the particular thiacyclooctanone and possibly some related ones, and that it is not a general reaction to ordinary sulfoxides.

Moreover, if one assumes the nucleophilic attack of hydrogen sulfate or water on the sulfur atom of sulfoxides, the same nucleophilic attack may also be considered to take place on the nitrogen atom of *N*-oxides as well as on the phosphor atom of tertiary phosphine oxides, since these semipolar linkages are known to have a magnitude of force constants similar to that of diphenyl sulfoxide, 7×10^5 dyn./cm. Thus, phenazine *N*-oxides, whose force constant of the N-O bond is 7.0×10^5 dyn./cm. and triphenylphosphine oxide (8×10^5 dyn./cm.) were subjected to the ^{18}O exchange experiment. However, neither phenazine *N*-oxide nor triphenyl phosphine oxide was found to exchange oxygen in concentrated sulfuric acid. Diphenyl sulfone, which bears a double positive charge to attract nucleophilic attack[25] but has a stronger S-O bond (force constants 9.6×10^5 dyn./cm.), also failed to exchange oxygen. Furthermore, a more nucleophilic hydroxide ion also failed to attack the sulfur atom of diphenyl sulfoxide to exchange oxygen in a dioxane-water solution under prolonged refluxing. Thus, the mechanism involving the nucleophilic attack of the hydrogen sulfate ion or the water molecule on the sulfur atom of the sulfoxide cannot be accepted either as likely for this ^{18}O exchange reaction.

The Nucleophilic Attack on Sulfuric Acid by Sulfoxide.—One noteworthy fact which characterizes the sulfoxide bond is that the sulfur atom still bears a lone electron pair for nucleophilic reactions, unlike the hetero atoms in phenazine *N*-oxide, triphenylphosphine oxide and sulfones. Therefore, one can safely assume that the sulfur atom would undergo a nucleophilic attack on sulfuric acid, as is shown by Eq. 7. Meanwhile, this nucleophilic attack is considered to be suppressed by bulky substituents around the neighborhood of the reaction center. In fact, it was found that the rate of the ^{18}O exchange of dimesityl sulfoxide was 34 times slower than that of diphenyl sulfoxide. The extremely facile ^{18}O exchange of other sulfoxides tested can also be explained on the basis of the nucleophilic nature of the sulfur atoms of these sulfoxides, whose lone pair electrons are less delocalized and thus more nucleophilic than that of diphenyl sulfoxide. Therefore, this appears to be the only surviving, and hence the most favorable, mechanism for the ^{18}O exchange reactions.

As an outcome of the stereochemical considerations of this nucleophilic mechanism, one would expect that the rate of ^{18}O exchange will be exactly half of that of the racemization. Unfortunately, however, the kinetic control is very difficult with the optically-active sulfoxide, namely *d*-4-amino-4-methyldiphenyl sulfoxide, and only very crude, not very reproducible results were obtained. In several runs with different concentrations of sulfuric acid, it was found that the ratio of the rate of exchange (k_e) vs. that of racemization (k_r), k_e/k_r, fluctuates between 1/2—1/3.5, but that it is always less than 1/2 and never comes to 1. Although the k_e/k_r value lies in the right direction and is close to the 1/2 which is predicted from this mechanism, this cannot serve as foolproof evidence for this mechanism, since it was thought that a kind of acid-catalyzed racemization[26] was taking place independently. Thus, the optically-active sulfoxide was dissolved in 50% sulfuric acid and kept at 0°C for five hours and a half; however, there was no racemization in the recovered sulfoxide. In more concentrated acids in which oxygen exchange occurs, however, it seems that an independent process of racemization takes place to cause a rate of racemization twice as fast as that of ^{18}O exchange. More careful kinetic studies with less reactive systems are necessary for more accurate evaluations of both rates of ^{18}O exchange and rates of racemization.[27]

Experimental

Materials.—The manners of preparing the sulfoxides were similar to those previously reported. *Phenazine N-oxide*[28] was prepared by reacting aniline and nitrobenzene in the presence of sodium hydroxide. Yellow crystals with a m. p. of 221—222°C were used. *Triphenylphosphine oxide*[29] was prepared by reacting phenyl magnesium bromide with phosphorus oxychloride. The sample was repeatedly recrystallized from ethyl acetate to obtain colorless crystals with a m. p. of 157—157.5°C.

The Preparation of Dimesityl Sulfoxide. — A mixture of mesitylene (155 g.) and thionyl chloride (33 g.) was cooled in an ice-salt bath. To this

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[25] D. R. Christman and S. Oae, *Chem. & Ind.*, **1959**, 1251.

[26] H. F. Herbrandson and R. T. Dickerson, Jr., *J. Am. Chem. Soc.*, **81**, 4102 (1959).

[27] Studies are now underway in these laboratories.

[28] A. Wohl and W. Aue, *Ber.*, **34**, 2442 (1901).

[29] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **64**, 2984 (1942).

mixture anhydrous aluminum chloride (60 g.) was added in portions over a period of two hours. Then mesitylene (60 g.) was added and the solution refluxed until no further hydrochloric acid gas was evolved. After the mixture had been allowed to stand at room temperature for one or two hours, it was poured slowly onto 600 g. of ice. After a vigorous reaction had taken place, the white solids which had separated were collected and washed with water. Recrystallization from acetone gave 64 g. (25%) ; m. p. 153.5—154°C.

Found : C, 75.57 ; H, 7.67. Calcd. for $C_{18}H_{22}OS$: C, 75.52 ; H, 7.69.

^{18}O-Enriched Sulfuric Acid. — The apparatus shown in Fig. 1 was used for the preparation of ^{18}O-enriched sulfuric acid. An aliquot of sulfur trioxide distilled in a vacuum line was placed in one of the containers (A) and an equimolar amount of ^{18}O-enriched water in the other (B). Both were first repeatedly frozen and degassed. Then the vessel (A) was warmed in a water bath at 50—60°C, while the other vessel (B) was cooled with dry-ice-acetone. By this procedure sulfur trioxide was introduced into the ^{18}O-enriched water. After about twenty minutes, the introduction was stopped and the cooled trap was removed. The system was gradually warmed up to room temperature. After it had stood for a few minutes at room temperature, the vessel (A) was cooled once more and the other system (B) was warmed. By repeating this procedure, the introduction of sulfur trioxide into water was achieved. The concentration of the resulting sulfuric acid was determined by measuring the freezing point.

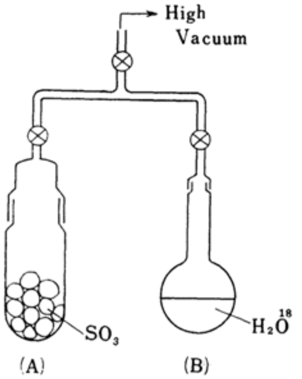

Fig. 1.

The Resolution of *d*, *l*-4-Amino-4′-methyldiphenyl Sulfoxide[17]. — The *d*, *l*-sulfoxide was prepared by reacting *p*-toluenesulfinic acid and aniline.[1] The *d*, *l*-sulfoxide (55 g.) was dissolved in 100 ml. of a hot water solution containing 60 g. of *d*-camphor sulfonic acid. Upon cooling, crude *d*-4-amino-4′-methyldiphenyl sulfoxide *d*-camphorsulfonate came out. After twenty recrystallizations (with 2% fresh *d*-camphor sulfonic acid added each time), the resolved salt was decomposed by ammonia and the sulfoxide obtained was recrystallized from ethanol. The *d*-isomer of the sulfoxide was thus obtained ; m. p. 150.5—151°C, with $[\alpha]_D^{30°}$ +105.9° in a 98% ethanol solution (c=1.10, l=2.0), +80.5° in a chloroform solution (c=1.15, l=2.0).

^{18}O-Exchange Reactions in ^{18}O-Enriched Sulfuric Acid. — *Diphenyl Sulfoxide.* — Diphenyl sulfoxide (0.53 g.) was dissolved in 5.95 g. of 97% ^{18}O-enriched sulfuric acid while the mixture was being cooled with ice, and the deep green solution was kept for fifteen minutes. From the deep green solution, about a half was quenched with 20 ml. of ^{18}O-enriched water (ca. 0.6 atom% ^{18}O), while the rest was quenched with 25 ml. of ordinary water. The precipitates were collected, washed with dilute alkali and water, and dried as usual. The two crude sulfoxide samples thus obtained were recrystallized from ethanol, and the samples with a m. p. of 70—71°C were subjected to ^{18}O analysis.

Sulfoxides in General.—An aliquot amount of sulfoxide was dissolved in a 10 molar equivalent of ^{18}O-enriched sulfuric acid, and the solution was kept at the desired temperature for the desired period. Then the solution was poured into a large excess of ice-water, and the precipitate was washed with dilute alkali and then water. Solid samples were collected and recrystallized from either ethanol or benzene, while liquid samples were extracted with ether, and from the ether layer the samples were collected either by crystallization or by distillation. The samples thus collected, identified by their correct m. p.(s) or b. p.(s), were subjected to ^{18}O-analysis.

Phenazine N-Oxide.—Phenazine *N*-oxide (200 mg.) was dissolved in 1.5 ml. of ^{18}O-enriched 97% sulfuric acid (0.70 atom% ^{18}O) ; the red solution was then allowed to stand at 0°C for 20 min. This solution was neutralized with 28% ammonia under cooling and then poured into 30 g. of ice-water. The precipitates were filtered and recrystallized from 99% ethanol, and the crystals m. p. 221—222°C were subjected to ^{18}O analysis.

Triphenylphosphine Oxide. — The oxide (1.0 g.) was dissolved in 5.0 ml. of ^{18}O-enriched sulfuric acid (0.70 atom% ^{18}O) and allowed to stand at 0°C for 10 minutes. The solution was then poured onto ice-water, and the resulting precipitates were collected and recrystallized repeatedly from ethyl acetate m. p. 157°C. They were used for the usual oxygen-18 analysis.

Diphenyl Sulfone.—Diphenyl sulfone (0.5 g.) was dissolved in 5 ml. of ^{18}O sulfuric acid (0.70 atom% ^{18}O) ; the solution was kept at room temperature for 20 min. and then poured onto ice-water. The precipitate was collected and dried. Recrystallization from benzene gave colorless crystals with a m. p. of 128°C ; they were subjected to ^{18}O-analysis.

Analysis :	Ph-SO_2-Ph	0.209%
	Tank CO_2	0.211%

The Reaction of Diphenyl Sulfoxide With 70% Perchloric Acid.—Diphenyl sulfoxide (0.5 g.) was dissolved in 10 ml. of 70% perchloric acid. The mixture was allowed to stand at 0°C for 4 hr. Then the mixture was poured into water, and the resulting solid was separated. Repeated recrystallizations from a mixture of benzene and ligroin gave a product the m. p. of which agreed with that of diphenyl sulfone. A mixed melting point determined with an authentic sample of diphenyl sulfone was not depressed.

^{18}O-Exchange of Diphenyl Sulfoxide in an Alkaline Solution. — Diphenyl sulfoxide (1.01 g.) was dissolved in 60 ml. of a 70% dioxane solution, made by diluting 42 ml. of absolute dioxane with ^{18}O-enriched water (0.61 atom% ^{18}O) to 60 ml. of the solution. To this solution was added 0.28 g. of ^{18}O-enriched potassium hydroxide (0.61 atom% ^{18}O). Then the whole mixture was sealed in an ampoule and heated at 90°C for 8 hours and a half. After the ampoule had been broken and neutralized with hydrochloric acid, the solvent was distilled off. The precipitate was recrystallized from benzene, and the sample of sulfoxide m. p. 71°C was subjected to ^{18}O-analysis.

Analysis:		
	Ph-SO-Ph	0.214%
	Tank CO_2	0.212%

ESR Spectra. — Sulfuric acid solutions (93.6%) containing 1.0×10^{-2}—1.0×10^{-4} mol./l. of the compounds, such as diphenyl sulfoxide, diphenyl sulfone, 4-amino-4′-methyldiphenyl sulfoxide and phenazine *N*-oxide, were subjected to ESR spectroscopy. However, none of the solutions of these compounds except phenazine *N*-oxide gave any sign of the presence of a free radical.

Kinetic Studies of the Oxygen Exchange Reactions of Diphenyl Sulfoxide and Dimesityl Sulfoxide.—To compare the rate constants of diphenyl sulfoxide and dimesityl sulfoxide, exchange reactions of both the sulfoxides were carried out under the same conditions. Both sulfoxides (4.0×10^{-2} mol.) were dissolved in 40 g. of ^{18}O-enriched 94.5% sulfuric acid (0.57 atom% ^{18}O) at 0°C. Aliquot portions (5.0 ml.) of the solutions were taken up after 5, 10, 30, 60 and 120 min., and each portion was quenched with ice-water. The precipitates were collected, recrystallized, and then subjected to ^{18}O analyses. From the incorporation values of ^{18}O in the recovered compounds, the rate constants of the oxygen exchange reactions were calculated.

The Rate Constants of the Racemization and ^{18}O-Exchange Reaction of *d*-4-Amino-4′-methyldiphenyl Sulfoxide in ^{18}O-Enriched Sulfuric Acid. —The kinetic studies of the rates of ^{18}O exchange reaction and racemization were carried out in ^{18}O-enriched 93% sulfuric acid (0.76 atom% ^{18}O). The reaction conditions and the procedure of the separation were similar to those used with the diphenyl sulfoxide. However, in this case a portion of the sample was decomposed to give colored substances. In a separate experiment, it was confirmed that no change in the optical activity was observed when the *d*-isomer was treated with activated charcoal. Therefore, the recovered substance was refluxed with activated charcoal in order to purify it. The samples taken for ^{18}O-analysis and for measuring the optical activity were repeatedly recrystallized from ethanol until the correct m. p. values were obtained. A solution containing 0.11 g. of the sample in 10 ml. of 98% ethanol was used for each measurement of the optical rotation. The same experiment was performed three times, but the rate constant of the racemization fluctuated from 2.5×10^{-5} sec^{-1} to 4.2×10^{-5} sec^{-1}. Meanwhile, the ^{18}O analyses of the same sample were done by the usual methods, and the rate constant, $k_{ex}=1.2\times10^{-5}$ sec^{-1}, was obtained.

Sulfoxides in general have been shown to exchange oxygen very readily in concentrated sulfuric acid. On the other hand, sulfones, *N*-oxides and phosphine oxides, with no lone electron pair, have been shown not to exchange oxygen with concentrated sulfuric acid. This oxygen exchange was accompanied by racemization and retarded by adjacent bulky substituents. All these observations seem to indicate that the oxygen exchange reaction proceeds by the nucleophilic attack of sulfoxide on sulfuric acid, as is depicted by Eq. 7.

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Kita-ku, Osaka (S. O.)

Department of Chemistry
Radiation Center of Osaka Prefecture
Sakai, Osaka (T. K. & Y. K.)