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The Reaction of Diphenyl Sulfoxide with Bromine in Aqueous Acetic Acid[1),*]

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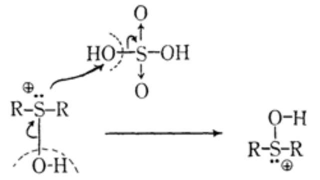
When diphenyl sulfoxide was allowed to react with bromine in a mixture of acetic acid and ^{18}O-enriched water, the sulfoxide was recovered, together with a small amount of diphenyl sulfone. The sulfoxide recovered incorporated a very small amount of ^{18}O from the water. Meanwhile, diphenyl sulfoxide was found to undergo a facile oxygen exchange reaction with water in the presence of hydrobromic acid. Possible mechanisms for these reactions have been discussed.

Previously, we found that oxygen exchange takes place when sulfoxide is dissolved in ^{18}O-enriched concentrated sulfuric acid.[2)] The mechanism suggested, on the basis of the several observations, was the nucleophilic attack of the sulfur atom of sulfoxide on sulfuric acid (Eq. 1). A similar oxygen exchange reaction is conceivable between sulfoxides and other acids, such as hypobromous acid. Hypobromous acid is known to be an equilibrium species in a bromine-water solution. Therefore, it seems that it would be interesting to examine the possibility of the oxygen exchange reaction of sulfoxide in a bromine-water mixture, although the reaction in this mixture may be expected to be somewhat complex, as will be explained later.

This paper will describe a preliminary investigation of the reactions of diphenyl sulfoxide in a bromine - water - acetic acid solution; the products were analyzed, and the oxygen exchange reaction was studied.



(1)

Reaction Products.—Diphenyl sulfoxide was found to be recovered almost quantitatively when the reaction mixture was quenched with water after the solution of diphenyl sulfoxide had been kept for 24 hr. in bromine - water - acetic acid at around room temperature (Table I). It is interesting to note, however, that a small amount of diphenyl sulfone (1—0.5%) was always isolated. Since the starting sulfoxide was prepared by the oxidation of diphenyl sulfide with hydrogen peroxide, the inclusion of a trace of sulfone in the starting sulfoxide is conceivable; in fact, the presence of a trace of sulfone was always shown by the characteristic infrared spectra near 1150 cm^{-1}, even in a pure diphenyl sulfoxide which had been obtained after repeated recrystallizations and which had the constant m. p. of 70°C. However, such a trace of the sulfone could be completely removed by purification through alumina-column

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1) This work was supported by the Petroleum Reseasch Fund, administered by the American Chemical Society.

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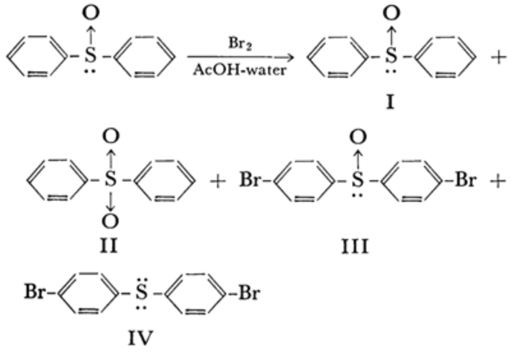
2) a) S. Oae, T. Kitao and Y. Kitaoka, *Chem. & Ind.*, **1961**, 291; b) S. Oae, T. Kitao, Y. Kitaoka and S. Kawamura, This Bulletin, **38**, 546 (1965).

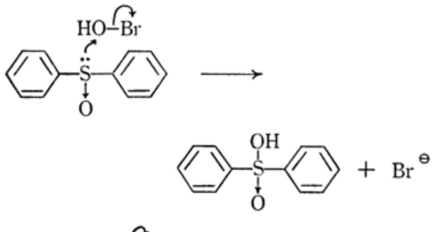
TABLE I. THE PRODUCTS OBTAINED IN THE REACTION OF DIPHENYL SULFOXIDE WITH BROMINE IN WATER - ACETIC ACID (1 : 15, v/v)



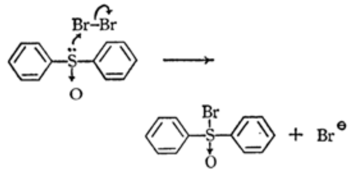
Reaction temp., °C	Yield of the products, %			
	I	II	III	IV
25	98.5—99	1—0.5	—	—
60	98—99	1—0.5	trace	—
100	—	—	—	90

chromatography using a mixture of *n*-hexane and benzene as the solvent. When the sulfoxide thus purified was used, a small amount of the sulfone was found in the quenched product described above. Therefore, the oxidation of the sulfoxide to the sulfone undoubtedly took place in this bromine - water - acetic acid solution. The yield of diphenyl sulfone increased up to 5% when the reaction mixture was quenched with aqueous sodium carbonate.

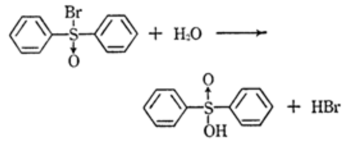
Two pathways are conceivable for the oxidation of the sulfoxide to the sulfone. One is the direct oxidation of sulfoxide by hypobromous acid (Eq. 2); the other involves the incipient formation of the bromosulfonium intermediate, which is subsequently hydrolyzed by water to give the sulfone (Eqs. 3a and 3b).



(2)



(3a)



(3b)

At a higher temperature, the bromination of the benzene ring and the reduction of S–O bond were observed (Table I). Thus practically all the diphenyl sulfoxide was quantitatively converted to bis-(*p*-bromophenyl) sulfide (IV) by the action of a one-mole equivalent of bromine at around 100°C.

The Oxygen Exchange Reaction of Diphenyl Sulfoxide.—The oxygen exchange reactions were carried out at 25°C for two different systems. In one system diphenyl sulfoxide with a natural oxygen- and ^{18}O-enriched water were used, while in the other the ^{18}O-labeled sulfoxide and the natural water were applied. The solvent was the same as that shown in Table I. The ^{18}O-enriched sulfoxide was prepared by the oxidation of diphenyl sulfide with *N*-bromosuccinimide in ^{18}O-enriched water,[3] since the sulfoxide thus prepared is known to be completely free from the sulfone. The results of oxygen exchange are shown in Table II.

It is interesting to note that there was a definite incorporation of ^{18}O in the recovered sulfoxide, though the amount of incorporation was very small, as can be seen from the runs 1—5 in Table II. The small decrease in ^{18}O content (except in the run 4) observed when the "crude sulfoxide" was purified to "pure sulfoxide" by alumina column chromatography, is due to the removal of the sulfone. Since at least one of the two oxygen atoms of the sulfone originates in the ^{18}O-enriched water, the ^{18}O content of the sulfone should be higher than that of the sulfoxide when the extent of the exchange reaction is low. The same conclusion can be derived more definitely by the use of the ^{18}O-labeled sulfoxide (run 6). Here, contrary to the cases in the runs 1—5, the removal of the sulfone increased the ^{18}O content of the pure sulfoxide.

The mechanism of the oxygen exchange reaction by bromine water is not clear. Although the oxygen exchange could take place between the sulfoxide and hypobromous acid much as with sulfuric acid (cf. Eq. 1), there is no definite evidence to substantiate the mechanism, nor is there any concrete evidence to exclude other possibilities. However, if one assumes that hypobromous acid causes the oxygen exchange, the accompanying oxidation of the sulfoxide to the sulfone can be nicely fit in the same reaction scheme. Another likely possibility is that the exchange reaction is due to hydrobromic acid, since hydrobromic acid is formed during the formation of diphenyl sulfone, as is illustrated in Eqs. 2 and 3. Although hydrogen chloride was recently found to be an effective catalysis for the concurrent oxygen exchange and racemization reaction of sulfoxides,

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[3] W. Tagaki, K. Kikukawa, K. Ando and S. Oae, *Chem. & Ind.*, **1964**, 1624.

TABLE II. OXYGEN EXCHANGE REACTIONS OF DIPHENYL SULFOXIDE IN A BROMINE - ACETIC ACID - WATER MIXTURE

^{18}O-concentration (atom.%) of the starting sulfoxide	Run No.	Reaction temp., °C	^{18}O-concentration (atom.%) of	
			Crude sulfoxide[b]	Pure sulfoxide[c]
0.21[a]	1	25	0.27	0.25
	2	25	0.28	0.26
	3	25	0.35	0.32
	4	60	0.25	0.28
	5	60	0.25	0.24
0.85	6	25	0.71	0.77

a) 1.5% ^{18}O-enriched water.
b) The recovered sulfoxide containing a trace of sulfone.
c) The sulfoxide completely free from the sulfone.

hydrobromic acid was found to cause the decomposition of sulfoxide.[4] However, we have found that, in a low concentration in aqueous acetic acid, hydrobromic acid can cause the oxygen exchange of diphenyl sulfoxide with a quantitative recovering of the sulfoxide, as is shown in Table III. In this alternative mechanism, the sulfone formation is an independent process, probably caused by the oxidation with hypobromous acid.

TABLE III. OXYGEN EXCHANGE REACTIONS OF DIPHENYL SULFOXIDE IN AN AQUEOUS HYDROBROMIC ACID - ACETIC ACID MIXTURE

(22°C, 24 hr.)

Run No.	Sulfoxide	^{18}O-Concentration (atom.%)
	Starting sulfoxide	0.98
	from the solutions: HBr[a]: water (v/v)	
1	1:3	0.83
2	1:7	0.76
3	1:15	0.84

a) Commercial hydrobromic acid solution, 47.9%.

Experimental

Diphenyl Sulfoxide. — This was prepared by the oxidation of diphenyl sulfide with hydrogen peroxide in acetic acid.[5] The product was recrystallized from *n*-hexane - benzene to give the sulfoxide with a constant m. p. of 70—71°C. This sulfoxide, however, was shown by the infrared spectral band near 1150 cm^{-1} to include a trace of the sulfone. Therefore, this apparently pure sulfoxide was further purified by alumina column chromatography using *n*-hexane - benzene (1 : 9 v/v) as the developing solvent. Diphenyl sulfone was eluted first; then, after the elution of a few fractions of the mixture of the sulfone and the sulfoxide, the fractions of pure sulfoxide were eluted. Usually one or two chromatographic purifications were enough to obtain the spectroscopically-pure sulfoxide.

The Reaction of Diphenyl Sulfoxide with Bromine Aqueous Acetic Acid.—Diphenyl sulfoxide (1.4 g.) (0.0069 mol.) was dissolved in 15 ml. of glacial acetic acid; to this there were added 1.0 ml. of water and an equimolar amount of bromine (1.1 g.). The reaction mixture was then left at 25°C for 24 hr. in a constant temperature bath. The initial orange color of the reaction mixture did not disappear within 24 hr. The reaction mixture was then dissolved in benzene (15—20 ml.), washed with water containing sulfur dioxide to remove free bromine, washed with a dilute sodium carbonate solution, and dried. The benzene was removed to give a colorless product (1.27 g.). The product was analyzed by the alumina column chromatography described above. In the case of the reaction at 100°C, over 90% of the product was bis-(*p*-bromophenyl) sulfide, m. p. 111—112°C (lit., 109—111°C)[6]; it was difficult to detect other products. At 60°C, a minute but definite formation of bis-(*p*-bromophenyl) sulfoxide was observed in the last fractions of the elution chromatography; this showed the melting point of 150—151°C (lit., 151°C)[7] here, and the same melting point when mixed with an authentic sample. All these results are sohown in Table I.

The Preparation of ^{18}O-Labeled Diphenyl Sulfoxide.—The method of labeling was based on our previous communication,[3] where the experimental details were not, however, described.

Diphenyl sulfoxide (5 g.) (0.027 mol.) was suspended in a solution of 5 ml. of methanol and 1 g. of ^{18}O-enriched water. Into this there was vigorously stirred, portion by portion, 5 g. (0.028 mol.) of *N*-bromosuccinimide over a 10 min. period. The reaction was very rapid and over within 10 min. When *N*-bromosuccinimide was added, a red color appeared and then faded very rapidly. The reaction mixture was stirred for an additional 20 min. and then taken up in ether. The ether solution was washed with water, dilute aqueous sodium carbonate, and water, and then dried. The ether was removed, and the residue was recrystallized from *n*-hexane - benzene to give ^{18}O-labeled diphenyl sulfoxide, 3 g.; m. p. 70—71°C; atom% of ^{18}O: 0.85 (Table II), and 0.98 (Table III). Further purification by alumina column chromatography was found to be unnecessary.

The Oxygen Exchange Reaction of Diphenyl Sulfoxide.—*With Bromine in Aqueous Acetic Acid.*—The reaction conditions and the procedures for the isolation of the products were the same as have been described for the reactions in Table I. The crude sulfoxide

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[4] K. Mislow, T. Simmons, J. T. Melillo and L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

[5] S. Oae and S. Kawamura, This Bulletin, **36**, 163 (1963).

[6] F. Kraft, *Ber.*, **7**, 1164 (1874).

[7] G. Leandri, A. Mangini and R. Passerini, *J. Chem. Soc.*, **1957**, 1386.

was obtained by the recrystallization of the crude product from *n*-hexane - benzene. The pure sulfoxide was obtained by the purification of the crude sulfoxide by alumina column chromatography, as has been described above. In a separate experiment, it was confirmed that the chromatography did not change the ^{18}O content of the sulfoxide. Analyses of ^{18}O content were made by the same procedure as has been reported elsewhere. The results are shown in Table II.

With Hydrobromic Acid in Aqueous Acetic Acid.— Volumes of commercial hydrobromic acid (48%) were diluted with 3, 7 and 15 volumes of water respectively. Each 5 ml. of these hydrobromic acid solutions was dissolved in 10 ml. of glacial acetic acid, and to this diphenyl sulfoxide (0.001 mol.) was added. The reaction mixtures were then left at room temperature (22°C) for 24 hr., poured into benzene, and washed with water, dilute aqueous sodium carbonate and water; the benzene layer was then dried over anhydrous sodium sulfate. The benzene was then removed to give the recovered sulfoxide. The yield of the sulfoxide was over 95% in each case, and the purity of the sulfoxide after one recrystallization from *n*-hexane - benzene was enough for the ^{18}O-analyses. The results are shown in Table III.

Summary

The reactions of diphenyl sulfoxide in dilute solutions of bromine in acetic acid - water mixtures have been investigated. The formation of diphenyl sulfone, bis-(*p*-bromophenyl) sulfoxide or bis-(*p*-bromophenyl) sulfide has been observed, depending on the reaction temperatures. Minutely but definitely, the oxygen exchange has been observed for the recovered diphenyl sulfoxide from this bromine solution. The oxygen exchange of diphenyl sulfoxide has also been found to take place in a dilute solution of hydrobromic acid in an acetic acid - water mixture. The mechanisms of these oxygen exchange reactions have been discussed.