Concurrent Oxygen Exchange and Racemization Reactions of Diaryl Sulfoxides in Phosphoric Acid*[1]

Norio KUNIEDA and Shigeru OAE

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka

(Received October 6, 1967)

Several works have been reported on the acid-catalyzed oxygen exchange and racemization reactions of sulfoxides.[1)]

In this note, we wish to report that phosphoric acid[2)] can also cause the concurrent oxygen exchange and racemization reactions of various diaryl sulfoxides while recovering of the sulfoxides is quantitative when quenched with a large amount of water.

For a typical run, 100 mg of ^{18}O-labeled[3)] (0.97 atom% ^{18}O) or optically active[4)] ($[\alpha]_D = +27.1°$, $c=3.6$ $l=1$, in ethanol) *p*-tolyl phenyl sulfoxide was dissolved in 5.0 m*l* of 85% phosphoric acid, and the solution was kept for 2 hr at 120°C; then the resulting pale blue solution was diluted with 30 m*l* of normal water or 30 m*l* of ^{18}O-enriched water (0.45 atom% ^{18}O). The sulfoxide can be recovered as crystalline solid almost quantitatively from the aqueous solution, and its melting point and IR spectrum were found to be identical to those of the starting sulfoxide. The sulfoxides thus recovered under the two different conditions were found to be racemized and also incorporated with ^{18}O of the same concentration of ^{18}O as shown in Table 1.

---

*[1] Paper XXI on "Sulfoxide."

1) a) In Sulfuric Acid: S. Oae, T. Kitao, Y. Kitaoka and S. Kawamura, This Bulletin, **38**, 546 (1965); S. Oae and N. Kunieda, *ibid.*, **41**, 696 (1968). b) In Hydrogen Chloride - Dioxane: K. Mislow, T. Simmons, J. Millow and A. L. Ternay, *J. Am. Chem. Soc.*, **86**, 1452 (1964). c) In Polychloroacetic Acid: S. Oae, M. Yokoyama and M. Kise, unpublished work.

2) Day and Cram have reported that (+)*p*-tolyl methyl sulfoxide was recemized in polyphosphoric acid; J. Day and D. J. Cram, *J. Am. Chem. Soc.*, **87**, 4398 (1965).

3) ^{18}O-Labeled sulfoxides were prepared by the oxidation of the corresponding sulfides with bromine complex of pyridine and ^{18}O-enriched water (1.63 atom%); S. Oae, Y. Onishi, S. Kozuka and S. Oae, This Bulletin, **39**, 364 (1966).

4) Optically active sulfoxides were prepared from (−)menthyl (−)-*p*-toluenesulfinate according to the method developed by Andersen; K. K. Andersen, *Tetrahedron Letters*, **1962**, 93.

Table 1. Oxygen exchange and racemization of p-tolyl phenyl sulfoxide in 85% phosphoric acid at 120°C

	^{18}O-Concentration (atom%)	Rotation $[\alpha]_D$ (in EtOH)
Starting sulfoxide	0.97	+27.1° (c=3.6 l=1)
Recovered sulfoxide		
Quenched with $H_2{}^{18}O$ (0.45 atom%)	0.28	
Quenched with H_2O	0.29	+3.8° (c=3.0 l=1)
Natural CO_2	0.21	

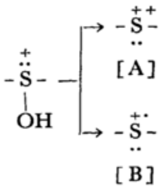
In order to understand the nature of these concurrent oxygen exchange and racemization reactions, we have compiled a substantial amount of kinetic data on the reactions of the diaryl sulfoxides. None of the sulfoxides used was found to undergo thermal racemization under the present condition. The kinetic data of both oxygen exchange and racemization are listed in Table 2.

Table 2. Rate constants of oxygen exchange and racemization of p-CH_3-C_6H_4-SO-R[3,4] in 85% phosphoric acid

No.	R[a)]	Temp. °C	$k_r \times 10^4$ sec^{-1}	$k_{ex} \times 10^4$ sec^{-1}
1	C_6H_5	110	0.871±0.046	
2[b)]	C_6H_5	120	1.98±0.11	1.93±0.11
3	C_6H_5	130	4.20±0.22	
4	m-CH_3-C_6H_4	120	1.91±0.08	
5[c)]	p-Cl-C_6H_4	120	1.25±0.05	1.27±0.06
6	o-Cl-C_6H_4	120	0.543±0.013	

a) Sulfoxide=0.1 mol/l
b) $k_{ex}/k_r=0.975$, $E_a=24.1$ kcal, $\Delta S^{\ne}=-15.7$ e.u.
c) $k_{ex}/k_r=1.02$

The rate of the oxygen exchange was identical to that of the racemization (See; Run No. 2 and 5 of Table 2), which is presumed to suggest that the reaction proceeds through a S_N1 like S–O bond cleavage of the sulfoxide.[5)] The whole pattern of substituent effects is quite similar to that of the concurrent oxygen exchange and racemization reactions of diaryl sulfoxides in sulfuric acid.[1a)] Apparently, the diaryl sulfoxide dissociates in phosphoric acid to form the hydroxysulfonium ion,[6)] and then the partial cleavage of the S–O bond will take place at the transition state. As for the cleavage of the S–O bond, two different ways are conceivable; the one is the heterolysis of the S–O bond to form the sulfidonium ion [A] and the other is the homolysis to form the radical cation [B].



The very small polar effects of substituents on the rates of both oxygen exchange and racemization reactions seem to suggest that the reaction follows the homolytic cleavage.

Diphenyl sulfone was found not to undergo these reactions under the same reaction condition.

The detailed studies of these reactions and ESR measurements now in progress in our laboratory will shed further light on these problems.

Experimental

Kinetic Procedures of the Oxygen Exchange and Racemization Reactions of Diaryl Sulfoxides. An aliquot of ^{18}O-labeled[3)] or an optically active[4)] sulfoxide was dissolved in 85% phosphoric acid, maintaining the concentration of the sulfoxide to be 0.1 mol/l, at a preset temparature. An aliquot portion (5.0 ml) of the solution was taken up from time to time for 5—7 times and was quenched with ice water. Then the sulfoxide was recovered for both the ^{18}O-analysis and the optical activity measurement by the same procedure described in our previous paper.[1a)]

---

5) D. Samuel and B. L. Silver, "Oxygen Isotope Exchange Reactions of Organic Compounds," in "Advances in Physical Organic Chemistry," Vol. 3, ed by V. Gold, Academic Press, London & N. Y. (1965), p. 129.

6) It is known that sulfoxides ionize in concentrated sulfuric acid to form the hydroxysulfonium ion: S. Oae, T. Kitao and Y. Kitaoka, This Bulletin, **38**, 543 (1965); R. J. Gillespie and R. C. Passerini, *J. Chem. Soc.*, **1956**, 3850.