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# Mechanism of the Oxygen Exchange Reaction of Diaryl Sulfoxides in Hydrochloric Acid[1]

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Mislow *et al.*[2] showed that sulfoxides undergo stereomutation together with oxygen exchange in hydrochloric acid-dioxane media. While the rate of oxygen exchange of *p*-tolyl phenyl sulfoxide was equal to that of racemization, the rate of racemization was found to be affected markedly by the steric requirement of the group attached to the central sulfur atom. The rate-determining step of the reaction was assumed to be the interconversion of the enantiomorphic chlorosulfonium chloride to the other.

Landini *et al.*[3] studied the acid-catalyzed stereomutation of sulfoxides with chloride ion and found that the rate of racemization of *p*-tolyl methyl sulfoxide was accelerated by the increase of chloride ion concentration in aqueous perchloric acid media, while the logarithms of the rates of racemization were nicely correlated with the Hammett acidity function (*Ho*). They suggested that the rate-determining step of the reaction is the formation of chlorosulfonium salt.

The two investigations seem to deal with the same reaction system. However, there is a disagreement as to the rate-determining step of the reaction. In order to correlate the two investigations and to find the rate-determining step of the oxygen exchange and racemizations of sulfoxide with hydrochloric acid, and also to confirm the importance of the steric effect of this reaction, we have carried out a kinetic study on the oxygen exchange and racemization reactions of both $^{18}$O-labeled and optically active *p*-tolyl phenyl sulfoxide, and also a more sterically hindered *p*-tolyl mesityl sulfoxide in 3.93N HCl in 80% dioxane-water mixture. We also reinvestigated the correlation of the rates of racemization of both sulfoxides with the Hammett acidity function (*Ho*). The rates of racemization of both sulfoxides were determined in hydrochloric acid with various concentrations of hydrogen chloride in 80% dioxane-water solution, and the logarithms of $k_{\mathrm{rac}}/[\mathrm{HCl}]$ were plotted against the Hammett acidity function (*Ho*). Strainght lines with a slope 0.80 and 0.81 were obtained for *p*-tolyl phenyl and *p*-tolyl mesityl sulfoxides, respectively, as shown in Table 1.

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[1] Paper XL on Sulfoxides

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

[3] a) D. Landini and F. Montanari, *Chem. Commun.*, **1968**, 86 b) D. Landini, G. Modena, F. Montanari and G. Scorrano, *J. Amer. Chem. Soc.*, **92**, 7168 (1970)

TABLE 1. RATES OF RACEMIZATION OF $p$-Tol-S(O)-Ar[a] IN HYDROCHLORIC ACID OF VARIOUS CONCENTRATIONS

| HCl ($N$) | $-Ho$ | Temp (°C) | $10^6k_{rac}$(sec$^{-1}$) |  | $k_{ph}/k_{Mes}$ |
|---|---|---|---|---|---|
|  |  |  | Phenl | Mesityl |  |
| 3.16 | 1.07 | 25 | 104 |  |  |
| 3.55 | 1.30 | 25 | 169 | 0.798 | 212 |
| 3.93 | 1.49 | 25 | 276[b] | 1.25[c] | 216 |
| 3.93 | 1.49 | 30 | 430[b] | 2.03[c] | 212 |
| 3.93 | 1.49 | 35 | 645[b] | 2.98[c] | 216 |
| 4.51 | 1.84 | 25 | 510 | 2.29 | 222 |
| 4.89 | 1.96 | 25 | 798 |  |  |

a) Sulfoxide; 0.1 mol/$l$; $p$-Tol=$p$-$CH_3C_6H_4$

b) $E_a$=15.4 kcal/mol $\Delta S^{\ddagger}=-23.3$ $e.u.$

c) $E_a$=15.8 kcal/mol, $\Delta S^{\ddagger}=-30.9$ $e.u.$

This means that the protonated species are involved in the transition state of the reaction, indicating that the reaction is of the A-1 type mechanism according to Zucker-Hammett's hypothesis.[4]

The rates of oxygen exchange of both sulfoxides in 3.93N hydrochloric acid were determined. The results are listed in Table 2 together with rates of racemization.

TABLE 2. KINETIC DATA OF OXYGEN EXCHANGE AND RACEMIZATION REACTIONS OF $p$-Tol-S(O)Ar[a] AT 25°C

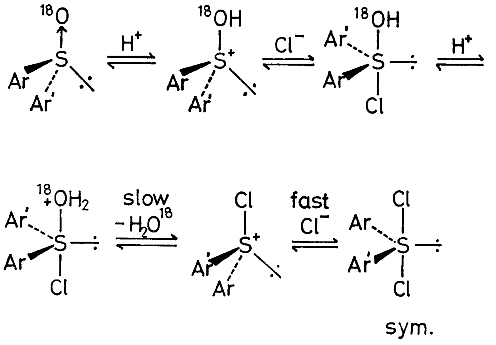
| Ar | $10^6k_{ex}$(sec$^{-1}$) | $10^6k_{rac}$(sec$^{-1}$) | $k_{ex}/k_{rac}$ |
|---|---|---|---|
| Phenyl | 326 | 276 | 1.18 |
| Mesityl | 1.55 | 1.25 | 1.24 |

a) Sulfoxide; 0.1 mol/$l$

The results reveal that the rate of oxygen exchange is nearly the same as that of racemization in both cases. This means that the two reactions share a common rate-determining step which is presumed to be the A-1 type S-O bond cleavage in view of the Hammett acidity correlation.

The rate of oxygen exchange of $p$-tolyl mesityl sulfoxide was about 210 times smaller than thet of $p$-tolyl phenyl sulfoxide. The marked rate retardation by the *ortho* substituents is for the most part due to the difference in the activation entropies of racemization reactions of both sulfoxides (Table 1). This is steric hindrance at either one of the two conceivable steps or both steps of the reactions; namely, the nucleophilic attack of chloride ion at the sulfur atom of the hydroxysulfonium salt to form the chlorosulfonium intermediate and the prior second protonation to form the diprotonated species. The steric hindrance for the double protonation was suggested to be responsible for the substantial retardation of the rates of racemization of $p$-tolyl mesityl sulfoxide in concentrated sulfuric acids.[5]

The fact that the rate of HCl-catalyzed racemization is markedly greater than that of $H_2SO_4$ catalyzed reaction suggests that the attack of chloride ion facilitates the S-O bond cleavage in the rate-determining step. We have found that the acid-catalyzed oxygen exchange and racemization reactions in concentrated sulfuric acids is markedly accelerated by the addition of chloride ion.[6] A plausible scheme of the oxygen exchange reaction of sulfoxide in hydrochloric acid can be illustrated as follows.



The reaction seems to proceed through the nucleophilic attack of chloride ion at the sulfur atom of protonated sulfoxide, followed by the rate-determining S-O bond cleavage to afford an unstable chlorosulfonium intermediate.

The subsequent step of either the formation of sulfonium dichloride or the hydrolysis of chlorosulfonium salt should be very fast.

## Experimental

*Optically Active Sulfoxides and $^{18}$O-Labeled* p-*Tolyl Phenyl Sulfoxide* were synthesized in the usual procedure as described.[5a]

*$^{18}$O-Labeled* p-*Tolyl Mesityl Sulfoxide* was prepared from the $^{18}$O-labeled methyl $p$-toluenesulfinate with the Grignard reagent of mesityl bromide in tetrahydrofuran. 55% yield mp 75—77°C.

*The Values of Ho* were determined with $p$-nitro, $o$-chloroaniline as an indicator in UV spectrometry by the method of Jorgenson and Harter.[7]

*Kinetic Procedures of Oxygen Exchange and Racemization Reaction.* The procedures were similar as those described previously.[8]

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[4] M. A. Paul and F. A. Long, *Chem. Revs.*, **51**, 935 (1957)

[5] a) S. Oae and N. Kunieda, This Bulletin, **41**, 696 (1968) b) S. Oae, *Quart. Rept. Sulfur Chem.*, **5**, 53 (1970)

[6] N. Kunieda and S. Oae, unpublished work.

[7] J. Jorgenson and D. R. Harter, *J. Amer. Chem. Soc.*, **85**, 878 (1963)

[8] T. Numata, K. Sakai, M. Kise, N. Kunieda, and S. Oae, *International J. Sulfur Chem.* **1**, 1 (1971).