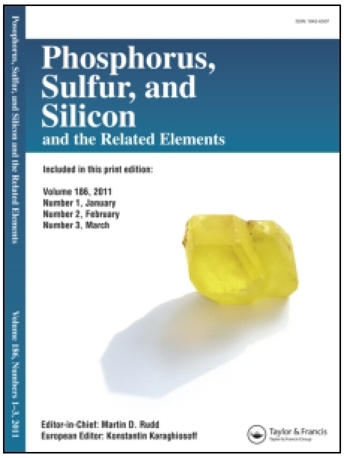

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OXYGEN EXCHANGE AND RACEMIZATION REACTIONS OF DIARYL SULFOXIDES IN SULFURIC ACID IN THE PRESENCE OF POTASSIUM CHLORIDE

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OXYGEN EXCHANGE AND RACEMIZATION REACTIONS OF DIARYL SULFOXIDES IN SULFURIC ACID IN THE PRESENCE OF POTASSIUM CHLORIDE†

by

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ABSTRACT

The mechanism of the concurrent oxygen exchange and racemization reactions of sulfoxides with chloride ion in sulfuric acid 64.7-80.2% has been studied. We have found that the rate of oxygen exchange of ^{18}O-labeled and optically active phenyl *p*-tolyl sulfoxide becomes identical to that of racemization by the addition of at least 0.08 mol/l potassium chloride to sulfuric acid media. The rate of the racemization cannot be correlated with H_A, and the steric effect of substituent is not very large. Based on these observations, a mechanism (Scheme II) which does not include the rate-limiting formation of the chlorosulfonium ion intermediate may be suggested as most plausible for the reaction.

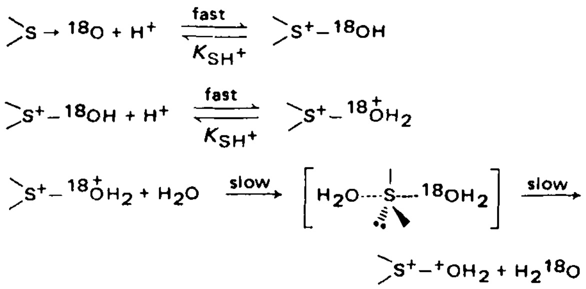
Introduction

The acid-catalyzed concurrent oxygen exchange and racemization reactions of sulfoxides are important for the study of the nature of nucleophilic substitution on trivalent sulfur atoms.

During the course of our studies on the oxygen exchange reaction of sulfoxides in sulfuric acid,[1] we suggested,[1a,c] that the reaction in sulfuric acid at a concentration of less than 75% proceeds through an SN_2 type Walden inversion process. This process involves both the entering and the displacement of water molecules on the sulfur atom at axial-axial positions of a trigonal bipyramidal transition, in the rate-limiting step (see Scheme I).

The racemization reaction of sulfoxides in hydrochloric acid[2] and the reduction and racemization reaction of sulfoxides with halide ion in acid media[3] have also been studied extensively. These reactions are considered to proceed *via* a nucleophilic attack of halide ion on the protonated sulfoxide to form a halosulfonium ion intermediate in the rate-limiting step.

The apparent difference between the mechanisms of the two acid-catalyzed reactions has prompted us to examine the oxygen exchange and racemization reactions of sulfoxides in less concentrated sulfuric acid in the presence of potassium chloride. We have compiled substantial amounts of kinetic data on the oxygen exchange and racemization reactions of ^{18}O-labeled and optically active sulfoxides in sulfuric acid ranging from 64.7% to 80.2% concentration and containing potassium chloride up to 0.16 mol/ ℓ.



(with oxygen exchange and racemization)

SCHEME I

Mechanism of oxygen exchange and racemization reactions of diaryl sulfoxides in less concentrated sulfuric acid[1a,c]

Results

The sulfoxide employed mainly in this study was optically active and ^{18}O-labeled phenyl *p*-tolyl sulfoxide, $[\alpha]_D^{19}$ + 21.0° (acetone), 1.06 atom %– ^{18}O, (1).

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† *Oxygen Exchange Reaction of Sulfoxides in Sulfuric Acid. Part VIII (paper 49 on Sulfoxides); Part VII, N. Kunieda and S. Oae, Bull. Chem. Soc. Japan,* **46**, *1745 (1973).*

TABLE I

Influence of potassium chloride on the oxygen exchange and Racemization reactions of (+) phenyl *p*-tolyl sulfoxide-^{18}O

H_2SO_4 (wt%)	KCl (mol/ℓ)	$10^5 k/sec^{-1}$ k_{rac}	$10^5 k/sec^{-1}$ k_{ex}	Method of kinetics
64.7	0	1.19 ± 0.03		A
64.7	0	3.47 ± 0.05^a		A
64.7	0	6.84 ± 0.08^b		A
64.7	0.02	3.60 ± 0.12		A
64.7	0.08	5.05 ± 0.08		A
64.7	0.08	13.8 ± 0.4^a		A
64.7	0.08	30.3 ± 0.2^a		A
64.7	0.16	6.35 ± 0.11	7.08 ± 0.41	A(rac) B(ex)
66.3	0	1.39 ± 0.01	0.691 ± 0.005	B
66.3	0.001	2.05 ± 0.03		A
66.3	0.005	2.80 ± 0.10		A
66.3	0.01	4.05 ± 0.19		A
66.3	0.02	4.77 ± 0.10		A
66.3	0.05	5.65 ± 0.16		A
66.3	0.08	6.20 ± 0.20		A
69.5	0	2.30 ± 0.05		A
69.5	0.02	7.02 ± 0.13		A
69.5	0.05	8.81 ± 0.21		A
69.5	0.08	9.66 ± 0.20	9.10 ± 0.50	B
74.4	0	4.08 ± 0.03	2.00 ± 0.03	B
74.4	0.01	11.6 ± 0.1		A
74.4	0.02	14.3 ± 0.2		A
74.4	0.05	16.5 ± 0.3		A
74.4	0.08	17.8 ± 0.3		A
80.2	0	9.00 ± 0.21		A
80.2	0.08	44.6 ± 2.5		A

Sulfoxide = 0.16 mol/ℓ, at 30°C.

^{a} at 40°C. ^{b} 47°C.

When the sulfoxide was dissolved in sulfuric acid containing potassium chloride, it was recovered quantitatively by quenching the reaction mixture with an excess of cold water.

The rates of both oxygen exchange and racemization reactions of **1** in sulfuric acid in the presence of a small amount of potassium chloride were measured by means of two methods A and B (see Experimental Section). Table I summarizes the kinetic conditions and the pseudo first order rate constants (k_{ex} and k_{rac}) for **1**. To cite an example, addition of 0.16 mol/ℓ of potassium chloride to 64.7% sulfuric acid accelerates the rate of the racemization of **1** about six times.

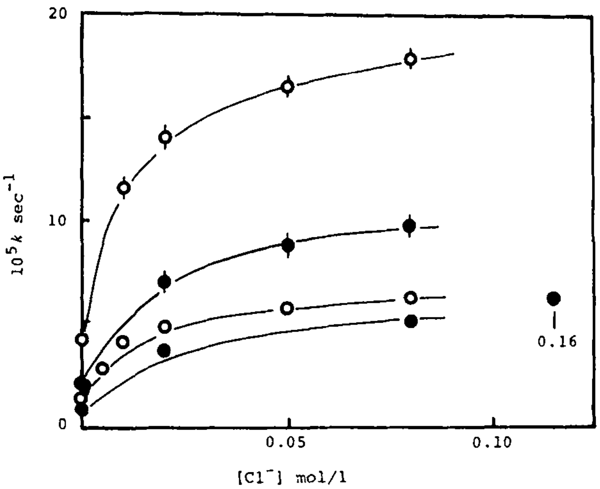

FIGURE I

Rate constants of racemization of (+) phenyl *p*-tolyl sulfoxide plotted against mole concentrations of KCl added in 64.7% (●), 66.3% (○), 69.5% (●) and 74.4% (○) sulfuric acid, at 30°C.

The dependence of the rate on the concentration of potassium chloride is complex. The plot of the rate constants against [Cl$^-$] does not give a straight line as shown in Figure I, thus the reaction is by no means first order in [Cl$^-$].

k_{ex}/k_{rac} Values and Activation Parameters

Since the oxygen exchange reaction accompanies the racemization, this reaction must include the cleavage of S–O bond of the sulfoxide. The change of mechanism by the addition of Cl$^-$ to sulfuric acid media will be reflected directly on the values of k_{ex}/k_{rac} and the activation parameters of the reaction. The k_{ex}/k_{rac} values and the activation parameters (E_a and $\Delta S^{\ne}$) of the reaction for **1** in several KCl-H_2SO_4 media were estimated. These values are listed in Table II. The k_{ex}/k_{rac} values obtained in 66.3% to 74.4% sulfuric acids and the $\Delta S^{\ne}$ value obtained in 64.7% sulfuric

TABLE II

Activation parameters and k_{ex}/k_{rac} values of (+) phenyl *p*-tolyl sulfoxide-$^{18}O^a$ in sulfuric acid-KCl system

H_2SO_4 (wt%)	Added KCl (mol/ℓ)	k_{ex}/k_{rac}	E_a (kcal/mol)	$\Delta S^{\ne}$ (e.u.)
64.7	0		19.7	−18.1
64.7	0.08		19.9	−15.0
64.7	0.16	1.11		
66.3	0	0.497		
69.5	0.08	0.932		
74.4	0	0.490		

^{a} Sulfoxide = 0.16 mol/ℓ.

acid were about 0.5 and −18.1 e.u., respectively, which are consistent with the finding in our previous work.[1c] However, the addition of at least 0.08 mol/ℓ of potassium chloride to the acid medium results in a drastic change of the k_{ex}/k_{rac} value from 0.5 to about 1, while there are no distinct variations on the activation parameters.

Correlation of Rate Constants with Acidity Functions

Since the sulfoxide is practically all-pronated in the range of sulfuric acid concentration used here, the rate of the reaction can be expressed as a function of the concentration of the protonated sulfoxide [$>S^+{-}OH$], and the rate constant, k_1, as the function of protonated sulfoxide is known to be formulated as follows with the aid of the H_A function.[1c,3f,4] However, an accurately determined value

$$k_1 = k_{obs}(h_A + K_{SH^+})/h_A$$

of acidity function of the sulfuric acid medium containing potassium chloride is most desirable. We have measured the effect of potassium chloride (up to 0.2 mol/ℓ) on H_0 function in 66.3% sulfuric acid by means of the uv method[5] by using 2,4-dinitroaniline as the Hammett indicator, and found the slope of the plots of ΔH_0 *vs.* [KCl] is less than 0.1. Thus the effect is very small, and in the range 0–0.16 mol/ℓ of concentration of potassium chloride it may be negligible. Therefore, we have used the published values of H_0[6] and H_A[7] without any correction for the salt effect.

The dependence of the racemization rates of 1 on the acidities of the media with and without potassium chloride, *i.e.*, the slopes given by plotting log k_1 *vs.* H_A and the Bunnett-Olsen's Φ-parameters[8] given by plotting (log k_{obs} + H_0) *vs.* (H_0 + log [H^+]), were evaluated.

TABLE III

Correlation between acidity functions and racemization rates of (+) phenyl *p*-tolyl sulfoxide in sulfuric acid-KCl system

H_2SO_4 (wt%)[a]	Added KCl (mol/ℓ)	log k_1[b] *vs.* H_A Slope	(log k_{obs} + H_0) *vs.* (H_0 + log [H^+]) Slope (*r*)[c]
64.7–74.4	0	0.684	0.685 (0.999)
64.7–74.4	0.08	0.689	0.680 (0.999)

[a] Range of sulfuric acid concentration.

[b] The pK_{SH^+} value for 1 used for the calculation of k_1 is −2.39 evaluated by Landini *et al.*[4]

[c] *r*; Correlation coefficient.

These data are collected in Table III. By either treatment, there is no difference between the dependences of the rates on the acidities with and without Cl^- ion.

Polar Effects of Substituents

We have also synthesized a series of para-substituted and ^{18}O-labeled diphenyl sulfoxides and studied the polar effects of the substituents on the rates of oxygen exchange in 64.7% sulfuric acid containing 0.15 mol/ℓ potassium chloride at 30°C. The results obtained are summarized in Table IV together with our previous data.

TABLE IV

Rate constants of oxygen exchange of $C_6H_5{-}S^{18}O{-}C_6H_4{-}R{-}p$

	$10^4 k$/sec^{-1}		
R;	64.7% H_2SO_4–KCl (0.15 mol/ℓ)[a]	75.4% H_2SO_4[b]	95.3% H_2SO_4[c]
CH_3	0.890 ± 0.005	1.45	2.92
H	1.04 ± 0.01	1.85	1.15
Cl	1.09 ± 0.03	1.98	1.53
NO_2	1.36 ± 0.05	2.48	1.13

[a] This work; sulfoxide = 0.05 mol/ℓ, at 30°C (method B).

[b] Sulfoxide = 0.1 mol/ℓ, at 50°C.[1a]

[c] Sulfoxide = 0.12 mol/ℓ, at 5°C.[1b]

The polar effects of *p*-substituents on the rates are very small, and log k_{ex} values are nicely correlated with Brown-Okamoto's σ^+ values[9] and give a positive ρ value (ρ = 0.164, correlation coefficient r = 0.994) as in the case of the reaction in 75.4% sulfuric acid without potassium chloride (for σ^+-log k_{ex}; ρ = 0.185, r = 0.980) (see second column in Table IV).

Sterical Effects of Substituents

The steric effects of substituents on the rates of racemization reaction in sulfuric acid containing potassium chloride were evaluated using optically active *p*-tolyl–SO–R type sulfoxides which have various sized R groups. The results obtained are listed in Table V together with the data observed for the reaction in 64.7% sulfuric acid without potassium chloride.

The racemization reaction of sulfoxides in aqueous hydrochloric acid has been known to show a large steric effect on the rates by bulky substituents. This has been attributed to the tightness of the intermediate (see below) which is considered to form at the rate

TABLE V

Sterical effects on the rates of the racemization of sulfoxides (*p*-Tolyl–S*O–R)

	10^5k/sec^{-1}			
R;	H_2SO_4 (64.7%)[a]	H_2SO_4 (64.7%)–KCl (0.16 mol/ℓ)[a]	H_2SO_4 (96.0%)[b]	HCl[c]
Me	4.20 ± 0.40	193 ± 3		3700
Et	2.30 ± 0.15	92.0 ± 1.3		975
Ph	1.19 ± 0.03	6.35 ± 0.11	23.8 ± 0.1	8.00
o-Tolyl	0.557 ± 0.018•	4.07 ± 0.02•		4.53
Mesityl		0.08 ± 0.01†	2.68 ± 0.13	0.042

[a] This work (Method A); Sulfoxide = 0.16 mol/ℓ, • 0.05 mol/ℓ, † 0.02 mol/ℓ, at 30°C.

[b] Sulfoxide = 0.1 mol/ℓ, at 0°C.[1b]

[c] In a 1:2 v/v mixture of 12 *M* aqueous HCl and dioxane at 25°C; data of Mislow *et al.*[2]

limiting step of the reaction.[2] (See fourth column in Table V.)

As shown in Table V, a similar trend of the steric effect was observed in our present reaction, though the magnitude is smaller than that of Mislow *et al.*[2]

Discussion

Mislow *et al.*[2] have reported that the rate of oxygen exchange of phenyl *p*-tolyl sulfoxide equals that of racemization in a 2:1 v/v mixture of dioxane and 12*M* aqueous hydrochloric acid. The rate of racemization is affected markedly by the steric requirements of the groups attached to the asymmetric sulfur atom. (The results are consistent with our previous finding.[10])

Landini *et al.*,[3e,f] in a study of the racemization reaction of methyl *p*-tolyl sulfoxide with chloride ion in perchloric acid, found that the reaction is first order in $[Cl^-]$. The rate is nicely correlated with H_A, and the Bunnett-Olsen's Φ parameter is 0.06. The two reactions dealing with the similar systems have been considered to proceed through the same chlorosulfonium ion intermediate in the rate-limiting steps.

A rough glance at the kinetic behavior of our system also seems to suggest that chloride ion appears to accelerate the rate as in the case of the above two reactions. However, the careful analysis of the kinetic results shows that this reaction is not similar to the above reactions. Namely, by the addition of a small amount of potassium chloride to sulfuric acid media, the slope of the plots of $\log k_1$ *vs.* H_A does not become unity and the Φ parameter shows a large positive value, though the k_{ex}/k_{rac} value for **1** becomes about 1. Moreover, the dependence of the rates on the acidities of the media is practically identical to that in the reaction without Cl^- (see Table III).

A plausible mechanism which does not include the rate-limiting formation of the chlorosulfonium intermediate is illustrated by Scheme II.

The initial step of the reaction begins with the rapid protonation equilibrium (eq. 1), followed by the slow attack of a Cl^- ion on the sulfur atom to form an α-chlorohydrin type intermediate (A) (eq. 2) and then the subsequent rapid second protonation takes place (eq. 3). Step (5) shows a rapid water exchange reaction which causes the oxygen exchange of sulfoxides. The mechanism involving the water exchange on the tetravalent sulfur atom† is quite reasonable since the activity of water in the range of sulfuric acid concentration used here is fairly large.[1c] The racemization can take place at the steps (4) and (6) due to the symmetry of the intermediate (B) formed. The steps (4), (5), and (6) are considered to take place competitively, while the subsequent step (7) should be very fast. Because of the low thiophilicity and the low

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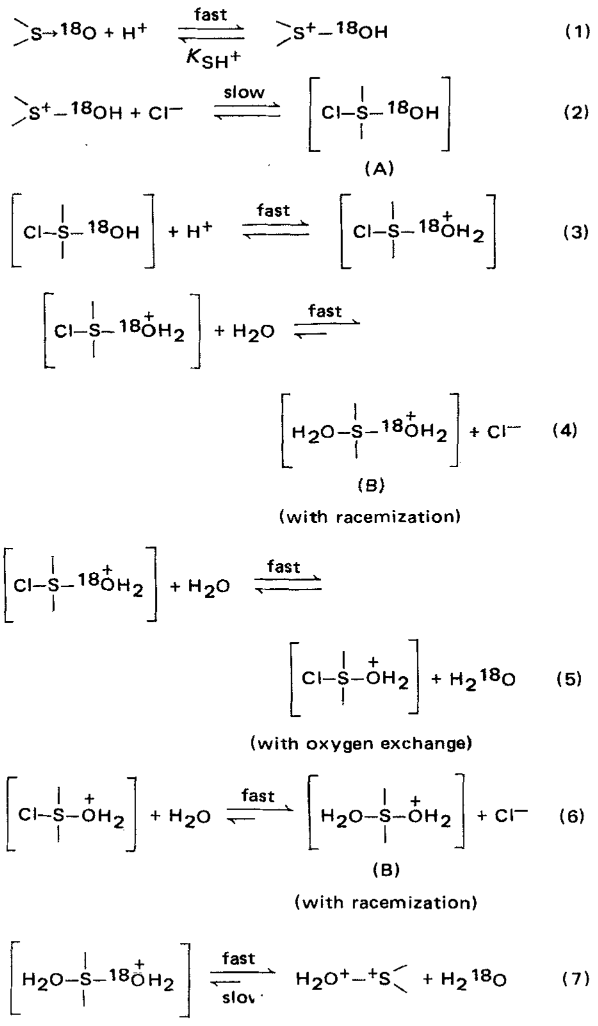
† *The similar water exchange mechanism was also speculated by H. Kwart and H. Omura: J. Am. Chem. Soc.*, **93**, *7250 (1971).*



SCHEME II

concentration of the Cl^- ion in the media, the reaction is not considered to afford the chlorosulfonium ion intermediate. Moreover, the smaller steric effect of substituents (see Table V) seems also to point out that the formation of the chlorosulfonium ion should be excluded. Moreover, the small positive ρ value for the oxygen exchange reaction for *p*-substituted diphenyl sulfoxides (see Table IV) also suggests the S_N2 type reaction.

Experimental Section

Materials

^{18}O-Labeled sulfoxides were prepared by the bromine-oxidation of the corresponding sulfides in the presence of ^{18}O-enriched water (1.62 atom %-^{18}O) and pyridine in acetic acid by the similar procedure described in our previous paper.[1c] The crude sulfoxides obtained were purified by recrystallization. Their mp and atom%-^{18}O are as follows. $C_6H_5SOC_6H_4-R$; (R; mp (lit),[11] atom%-^{18}O), *p*-CH_3; 71.5–72.0°C (71°C), 1.06%, H; 70–71°C (71°C), 1.07%, *p*-Cl; 45–46°C (45–46°C), 1.23% 107°C (106–107°C), 1.37%. (This sulfoxide was prepared using 3.50 atom%-$H_2{}^{18}O$.)

Optically active sulfoxides were prepared by the reaction of the corresponding Grignard's reagent of aryl or alkyl halides with (–) menthyl (–) *p*-toluenesulfinate [mp 107–107.5°C, $[\alpha]_D$-202.0° (c = 0.76, 1 = 1, acetone) (lit[12] mp 106–107°C, $[\alpha]^{25}{}_D$ -199.2° (acetone)] in ethyl ether according to the method developed by Andersen.[13] Their mp or bp and specific rotations follow: *p*-$CH_3C_6H_4-SO-R$; (R; mp or bp, specific rotation (1 = 0.5), (lit)[14]). CH_3; 74°C, $[\alpha]_D^{23}$ + 146° (c = 1.08), acetone), (73–74.5°C, $[\alpha]_D$+ 145.5° (acetone)), C_2H_5; 95–97°C/0.5 mmHg, $[\alpha]_D^{25}$ + 184° (c = 1.3, acetone), (123–126°C/1.5 mmHg, $[\alpha]_D$+ 186° (acetone)), C_6H_5; 92°C, $[\alpha]_D^{19}$ + 21.0° (c = 1.01, acetone), (91–92,5°C, $[\alpha]_D$ + 21.1° (acetone)), *o*-$CH_3C_6H_4$; 78–78.5°C, $[\alpha]_D^{20}$-90.5° (c = 21.1°, acetone), (77.8–78.5°C, $[\alpha]_D$-89.1° (acetone)), Mesityl; 107–107.5°C, $[\alpha]_D^{19}$-285.3° (c = 0.35, acetone), (107.0–107.5°C, $[\alpha]_D$-284° (acetone)).

Potassium Chloride used here is commercial grade (Wako Pure Chem. Ind. Ltd., Osaka).

The concentration, wt%, of sulfuric acid medium was determined by titration with a standard alkali solution. The H_0 and H_A values of sulfuric acid media are from the tables of Johnson *et al.*[6] and Yates *et al.*,[7] respectively.

Kinetic Procedures

Method A (for Racemization Reaction)

The racemization reaction was carried out in the square shape cell (5 ml), the polarimeter (Yanagimoto OR-10 Type polarimeter) was set at a desired temperature with a constant temperature bath connected. In the cell was placed 7 ml of sulfuric acid solution containing an optically active sulfoxide and KCl of set moles. The rate of the racemization was measured directly by checking the rotation, α, of the polarimeter. The pseudo first-order rate constant, k_{rac}, was then evaluated by the following equation; $\log(\alpha_0/\alpha_t) = kt/2.303$, where α_0 and α_t are the rotations at time 0 and *t*, respectively.

Method B (for both Oxygen Exchange and Racemization Reactions)

In order to compare the rate constants between oxygen exchange and racemization, both reactions were carried out under identical conditions. Thus an ^{18}O-labeled or an optically active sulfoxide (0.16 mol/ℓ) was dissolved in sulfuric acid containing KCl of set mole at a preset temperature, and aliquot portion (5 ml) of the solution was pipetted out from time to time and was quenched with 100 ml of ice-water. The sulfoxide precipitated was extracted with carbon tetrachloride. The recovered sulfoxide was dried thoroughly and subjected to measurements of both specific rotation and ^{18}O-analysis (by Hitachi RMU-6E Type mass-spectrometer) by the same procedure as described in our previous paper.[1c] The pseudo first-order rate constants were determined from the equations for racemization; $\log(\alpha'_0/\alpha'_t) = kt/2.303$, where α'_0 and α'_t are the specific rotations at time 0 and *t*, respectively, and for oxygen exchange; $\log[(\beta_0 - \beta)/(\beta_t - \beta)] = kt/2.303$, where β_0 and β_t are atom%-^{18}O at time 0 and *t*, respectively, and β is the atom%-^{18}O of natural CO_2.

Typical Runs of Kinetics

Racemization Run (Method A)

(+) Phenyl *p*-tolyl sulfoxide (0.16 mol/ℓ) in 64.3% H_2SO_4 containing 0.08 mol/ℓ KCl at 40°C.

Time (min.)	0	40	66	83	116	137
α_t	0.196°	0.140°	0.111°	0.095°	0.076°	0.060°

$k_{rac} = 13.8 \pm 0.4 \times 10^{-5}\ sec^{-1}$

Oxygen Exchange Run (Method B)

^{18}O-Labeled phenyl *p*-tolyl sulfoxide (1.06 atom %-^{18}O) (0.16 mol/ℓ) in 64.3% H_2SO_4 containing 0.16 mol/ℓ) in 64.3% H_2SO_4 containing 0.16 mol/ℓ KCl at 30°C.

Time (min.)	0	30	66	90	180
$\beta_t - \beta$	0.856	0.760	0.633	0.590	0.394 (atom%-excess ^{18}O)

$k_{ex} = 7.08 \pm 0.30 \times 10^{-5}\ sec^{-1}$
($\beta = 0.206$ atom%-^{18}O)

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