

Substituent and steric effects in the oxidation of alkyl aryl sulfides by peroxydisulfate

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The kinetics of oxidation of a number of alkyl aryl sulfides with potassium peroxydisulfate in aqueous ethanol have been investigated. The effect of substituents on the oxidation has been studied by employing a number of *p*- and *m*-substituted phenyl methyl sulfides: the reaction is accelerated by electron-releasing and retarded by electron-withdrawing substituents, indicating a rate-determining electrophilic attack by the peroxydisulfate ion at the reaction site, sulfur. A good correlation is found to exist between the rate constants and the Hammett σ^+/σ^- constants, the ρ^+ value for the reaction being -0.56 with a correlation coefficient of 0.979 . The activation parameters have also been determined.

Studies with different alkyl phenyl sulfides clearly indicate that the reaction is quite sensitive to steric congestion around the reaction site. The results obtained in this study are compared with those found for the oxidation of the same set of sulfides with different oxidants.

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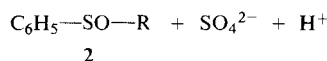
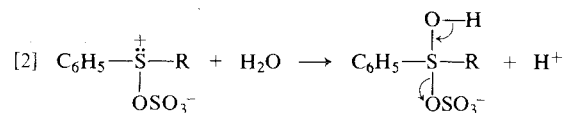
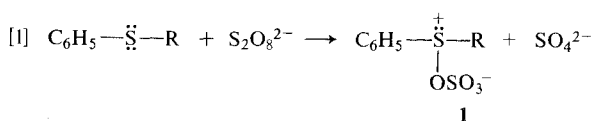
On a examiné la cinétique de l'oxydation de plusieurs sulfures d'alkyle et d'aryle avec le peroxydisulfate de potassium dans l'éthanol aqueux. On a étudié l'influence des substituants sur la réaction d'oxydation à l'aide d'une série de sulfures possédant un groupe alkyle et un groupe phényle substitué aux positions *mé*ta et *para*. Les substituants électro-donneurs accélèrent la réaction, tandis que les substituants électro-attracteurs la ralentissent. Cet effet indique que l'étape déterminante est une attaque électrophile de l'ion peroxydisulfate sur la site de réaction, soit le soufre. On observe une bonne corrélation entre les constantes de vitesse et les constantes σ^+/σ^- de Hammett; on obtient pour cette réaction une valeur de ρ^+ de -0.56 avec un coefficient de corrélation de 0.979 . On a également déterminé les paramètres d'activation.

Des études sur différents sulfures d'alkyle et de phényle montrent clairement que la réaction est grandement influencée par l'encombrement stérique au voisinage du site réactionnel. On compare les résultats recueillis dans le présent travail avec ceux qui ont été rapportés pour l'oxydation de la même série de sulfures avec différents oxydants.

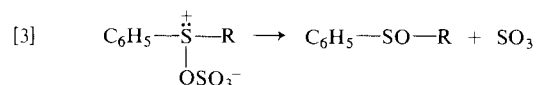
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Introduction

In our earlier paper (1), we have proposed that the oxidation of alkyl aryl sulfides with peroxydisulfate in 50% aqueous ethanol (v/v) proceeds by a rate-determining electrophilic attack of the peroxydisulfate ion [1] at sulfur of the sulfide to form sulfoxide.



The intermediate **1** may decompose to give the sulfoxide **2** by the attack of water as indicated in [2] or according to the step [3] which is very similar to that proposed by Ogata and Akada (2) in the kinetics of peroxydisulfate oxidation of *p*-nitrosophenol.



However, the question regarding the origin of the sulfoxide oxygen, whether from water or from peroxydisulfate ion, has not been solved. The present work describes the substituent and steric effects on the reaction of alkyl aryl sulfides with peroxydisulfate.

The sulfides studied are listed in Tables 1 and 2. Twelve *m*- and *p*-substituted phenyl methyl sulfides are used to study the effect of structure on reactivity by keeping the steric effects constant at the reaction centre (Table 1). Five alkyl phenyl sulfides are chosen to study the steric effects and in these sulfides there is a gradual increase in the size of the alkyl group attached to sulfur (Table 2).

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TABLE 1. Second-order rate constants, enthalpies, and entropies of activation for substituted phenyl methyl sulfides*

Sulfides	$k_2 \times 10^3 \ell \text{ mol}^{-1} \text{ s}^{-1}$			ΔH^\ddagger kcal/ mol	ΔS^\ddagger (eu) at 40°C
	35°C	40°C	45°C		
<i>p</i> -Methoxyphenyl methyl sulfide	12.6	16.8†	22.0	10.3	-34.1
Methyl <i>p</i> -tolyl sulfide	6.44	8.64†	11.5	10.8	-33.5
<i>p</i> -Isopropylphenyl methyl sulfide	5.86	7.74	10.3	10.3	-35.0
<i>p</i> -Fluorophenyl methyl sulfide	5.60	7.39	9.75	10.6	-35.3
Methyl <i>m</i> -tolyl sulfide	5.00	6.84	9.15	11.4	-31.8
Methyl phenyl sulfide	4.54†	6.13†	8.24†	11.1	-33.2
<i>m</i> -Methoxyphenyl methyl sulfide	4.35	6.06	8.13	11.7	-31.3
<i>p</i> -Chlorophenyl methyl sulfide	3.99	5.48	7.24	11.0	-33.8
<i>p</i> -Bromophenyl methyl sulfide	3.83	5.20	7.07	11.4	-32.7
<i>m</i> -Chlorophenyl methyl sulfide	2.24	3.26	4.08	11.4	-33.2
<i>p</i> -Methylthioacetophenone	1.71	2.32†	3.12	11.1	-35.3
Methyl <i>p</i> -nitrophenyl sulfide	1.26	1.91	2.53	13.2	-29.3
<i>p</i> -Methylthiobenzoic acid	1.15	1.64	2.23	12.7	-36.2

*General conditions: [sulfide]:[S₂O₈²⁻] = 10:1 in 50% aqueous ethanol (v/v) at a constant ionic strength of 0.015 M. ΔH^\ddagger values were evaluated graphically.

†Values from ref. 1.

TABLE 2. Second-order rate constants for the oxidation of alkyl phenyl sulfides with peroxydisulfate ion at 40°C and relative rates of oxidation*

Sulfide	$k_2 \times 10^3$ ($\ell \text{ mol}^{-1} \text{ s}^{-1}$)	Relative rates of oxidation by			
		S ₂ O ₈ ²⁻	Br ₂ †	H ₂ O ₂ ‡	Chloramine-T§
Methyl phenyl sulfide	6.13	100	100	100	100
Ethyl phenyl sulfide	2.44	39.1	109	108	123
<i>n</i> -Propyl phenyl sulfide	1.97	32.1	71	88	86
Isopropyl phenyl sulfide	0.938	15.3	3.6	95	179
<i>tert</i> -Butyl phenyl sulfide	0.104	1.70	—	60	241

*General reaction conditions: [sulfide]:[S₂O₈²⁻] = 10:1 in 50% aqueous ethanol (v/v) at a constant ionic strength of 0.015 M.

†Values from ref. 31.

‡Values from ref. 32.

§Values from ref. 33.

||Since the rate is very slow k_2 value has been calculated from the initial rates.

Experimental

Materials

Potassium peroxydisulfate (G.R., E. Merck) was used after recrystallization from double distilled water. Methyl phenyl sulfide, *p*-methoxyphenyl methyl sulfide, methyl *p*-tolyl sulfide, and *p*-methylthioacetophenone were prepared as described earlier (1). *p*-Chlorophenyl methyl sulfide and *p*-bromophenyl methyl sulfide were prepared by the methylation of the corresponding benzenethiols obtained by the reduction of their respective benzenesulfonyl chlorides (3). *p*-Isopropylphenyl methyl sulfide was prepared by the methylation of *p*-isopropylbenzenethiol (4). The procedure adopted by Baliah, Shanmuganathan, and Varadachari (5) was employed for the preparation of *p*-methylthiobenzoic acid. Methyl *p*-nitrophenyl sulfide (6), *p*-fluorophenyl methyl sulfide (7), methyl *m*-tolyl sulfide (8), *m*-chlorophenyl methyl sulfide (9), and *m*-methoxyphenyl methyl sulfide (10) were prepared as described in literature.

Ethyl phenyl sulfide (11) was prepared by using benzenethiol and diethyl sulfate. Phenyl *n*-propyl and phenyl isopropyl sulfides (12) were prepared by the alkylation of benzenethiol with the appropriate alkyl bromides in the presence of sodium ethoxide. *tert*-Butyl phenyl sulfide was obtained by passing

isobutylene (13) into sulfuric acid followed by the addition of benzenethiol (12).

Kinetic Measurements

The procedure employed for the kinetic studies was essentially the same as described in our earlier paper (1). Measurements were carried out under pseudo first-order conditions in 50% aqueous ethanol (v/v) at constant ionic strength (14, 15).² All the reactions were homogeneous. The rate of the reaction was followed by estimating the unreacted peroxydisulfate by the iodometric procedure of Kolthoff and Carr (16). The kinetics were generally followed up to 60–70% of the reaction. The second-order rate constants were calculated from the pseudo first-order rate constants as described in ref. 1. The rate constants were confirmed in each substrate by performing at least a set of duplicate runs in all of them at all the temperatures mentioned here (Table 1).

Product Analysis

TLC analysis showed that alkyl phenyl sulfides are oxidised

²Oxidation of 50% aqueous ethanol (v/v) by peroxydisulfate is found to be negligible in our experimental conditions. See also refs. 14 and 15.

by peroxydisulfate solely to their sulfoxides (see also ref. 1). Product analyses were carried out with the same initial concentration of the reactants employed in the kinetic measurements.

Results and Discussion

Substituent Effects

The results of the kinetic studies with substituted phenyl methyl sulfides show that the reaction is first-order in peroxydisulfate and in sulfide for over 60–70% of the reaction. From the data in Table 1, it is evident that electron-releasing substituents accelerate and electron-withdrawing substituents retard the rate of the reaction.

It is generally known that the linear free-energy relationships apply to a reaction series in which either the entropies of activation for the series are constant or in which the variation in activation entropy is linearly related to changes in enthalpy of activation (17–20). An examination of the activation parameters in Table 1 shows clearly that the reaction under investigation has nearly constant entropies of activation, favouring a linear free-energy relationship.

Hence the reactivity pattern is brought out by two different correlations³ at 40°C; one, $\log k_2$ with σ and the other $\log k_2$ with σ^+/σ^- . Since sulfur can act as an electron-donor or an electron-acceptor depending on the substituent present *para* to the methylthio group (21), we have used both σ^+ and σ^- simultaneously in the latter correlation. It may be pointed out here that in some reactions (22), both σ^+ and σ^- are employed simultaneously. A fair correlation (23) is obtained with Hammett's σ constants ($\rho = -0.87$, $r = 0.930$, $s = 0.11$); but a good correlation is found to exist when σ^+/σ^- values are plotted against the logarithms of rate constants. The ρ^+ value obtained for the latter correlation by the method of least squares is -0.56 ($r = 0.979$ and $s = 0.06$).

The negative ρ^+ value indicates that the nucleophilic sulfur atom of the sulfide is more positively charged in the transition state of the rate-determining step of the oxidation reaction than it is in the reactant. This is consistent with step [1] being the rate-determining. The small ρ^+ value obtained in our case may be attributed to the fact that the dinegative peroxydisulfate ion is not a typical electrophilic

reagent (27). Such small ρ values are commonly observed in most studies of other electrophilic reactions at sulfur centre. For instance, ρ value of -1.13 has been observed in the oxidation of aryl alkyl sulfides by hydrogen peroxide (28). But the higher ρ value observed in the reactions of aryl alkyl sulfides with chloramine-T (29) and bromine (30) may be due to the strong electrophilic character of the attacking species.

Steric Effects in the Oxidation of Alkyl Phenyl Sulfides

The steric effect on the oxidation of sulfides with peroxydisulfate was also studied by changing the alkyl moiety from methyl to *tert*-butyl in a series of alkyl phenyl sulfides. The rate data are given in Table 2. The rate decreases in the order $\text{PhSMe} > \text{PhSEt} > \text{PhSP}^n > \text{PhSP}^i > \text{PhSBu}^t$.

The results show that the reaction is sensitive to steric congestion at the reaction centre. It is evident from Table 2, which exhibits the results obtained by us and those of Modena (31, 32) and Oae and co-workers (33) with other oxidizing agents, that the steric retardation in the oxidation of alkyl phenyl sulfides depends on the nature and size of the oxidizing agent. The rate constants in the present study (Table 2) decreased monotonically with the increasing bulkiness of the alkyl groups. The retardation observed here is larger than those found for the oxidation of the same sulfides by bromine (31), hydrogen peroxide (32), and chloramine-T (33). This is probably due to the larger size of the peroxydisulfate ion. This is also supported by the observation that steric effect is almost absent in the chloramine-T oxidation (33) of these sulfides, which is presumably due to the smaller size of the attacking species Cl^+ .

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³We have used σ_p and σ_m values (24) for the $\log k_2 - \sigma$ correlation. In the $\log k_2 - \sigma^+/\sigma^-$ correlation, σ_p^+ values (24) have been used for *p*-methoxy, *p*-methyl, *p*-isopropyl, *p*-chloro, *p*-bromo, and *p*-fluoro substituents. σ_p^- values (25) are used for *p*-acetyl and *p*-carboxylic groups. σ^- value given by Bordwell and Andersen (26) has been used for *p*-nitro group. σ_m^+ values were used for the *meta* substituents (24).

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