

Substituent Effect in the Oxidation of Phenols by Peroxydisulphate Ion in Aqueous Ethanol, *t*-Butanol, Acetonitrile & Acetone

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Kinetics of Elb's peroxydisulphate oxidation of phenols in aquo-organic solvent mixtures such as aq. ethanol (20%), aq. acetonitrile (20%), aq. acetone (20%) and aq. *t*-butanol (20%) have been investigated. The reaction is first order in oxidant and first order in substrate. The order with respect to alkali has been found to be ~ 0.5 . A mechanism consistent with the electrophilic attack of peroxydisulphate ion at oxygen atom of phenoxide ion and the neutral phenol rather than at carbon atom has been suggested.

BEHRMAN^{1,2} studied the kinetics of oxidation of phenols in aqueous medium and postulated that the rate determining step involved either attack on oxygen or carbon, though no conclusive evidence was provided for this assumption. In a recent work³ it has been indicated that solvent polarity affects the chemical reactions. It was, therefore, decided to undertake the title study in various binary aquo-organic solvent mixtures to throw light on the mechanism of the reaction.

Materials and Methods

Analytical reagent grade phenol and substituted phenols were freshly distilled or recrystallized before use. Solvents were purified by standard procedures. The reaction was followed by estimating peroxydisulphate in the reaction mixture at various intervals. Aliquots of peroxydisulphate were pipetted out into 10% KH_2PO_4 solution and 10 ml of 10% KI solution and left for 30 min in the dark. The liberated iodine was titrated against standard hypo. The results are reproducible to within $\pm 5\%$. Self decomposition of peroxydisulphate is negligible under the experimental conditions.

Results and Discussion

Phenols in alkaline media have been oxidized by $\text{S}_2\text{O}_8^{2-}$ in aq. EtOH (20%) and aq. acetonitrile (20%) at constant ionic strength. The rates were measured at 35°.

Dependence on [substrate] and $[\text{S}_2\text{O}_8^{2-}]$ —The results obtained at different [substrate] are presented in Table 1. The reactions were first order with respect to $\text{S}_2\text{O}_8^{2-}$ as revealed by the constancy of first order constants at least up to 50% of the reaction in any single run. Further the first order rate constants varied linearly with [substrate] and $k_1/[\text{S}]$ values were constant (Table 1). This proves that the order with respect to the substrate is also one.

Dependence on [alkali]—The rate of oxidation increases with the increase in [alkali]. A plot of $\log k_1$ vs $\log [\text{OH}^-]$ was linear with a slope

of ~ 0.5 suggesting the order of dependence on hydroxide is ~ 0.5 . Further a plot of k_{obs} vs $[\text{OH}^-]$ is also linear with a positive intercept and positive slope, pointing to the existence of two reaction paths, one independent and the other dependent on $[\text{OH}^-]$ and obeying the following rate law

$$-\frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = (k' + k''[\text{OH}^-]) C_{\text{ox}} = k_{\text{obs}} C_{\text{ox}}$$

where C_{ox} represents the total [oxidant] and the specific rate constants k' and k'' are those corres-

TABLE 1 — RATE CONSTANTS FOR THE OXIDATION OF PHENOLS AT 35° IN Aq. ETHANOL (20%) AND Aq. ACETONITRILE (20%)

[Substrate] (M)	Aq. ethanol*	
	$k_1 \times 10^3$ (min ⁻¹)	$k_2 \times 10^2$ (litre mole ⁻¹ min ⁻¹)
SUBSTRATE: PHENOL		
0.01035	3.8 (2.02)	37.0 (20.1)
0.0255	8.86 (4.83)	35.0 (19.0)
0.035	12.3 (6.95)	35.2 (19.4)
0.05085	17.7	35.0
SUBSTRATE: <i>p</i> -CRESOL		
0.0101	14.4	142.4
0.0160	21.1	133.0
0.0252	34.0	134.6
0.0350	44.0	125.5
SUBSTRATE: <i>p</i> -CHLOROPHENOL		
0.0100	3.62	36.2
0.0156	4.80	31.0
0.0253	7.30	29.0

*Values in parentheses are in aq. acetonitrile (20%, v/v) as solvent.

ponding to the uncatalysed and the base-catalysed paths respectively.

Thus k' and k'' represent the intercept and the slope of the plots of k_{obs} vs $[\text{OH}^-]$ respectively. The values of k' ($\times 10^3$) and k'' ($\times 10^3$) for the oxidation of phenol, *p*-cresol and *p*-chlorophenol are 4.02, 15.00; 9.00, 50.00; and 2.5, 10.75 min^{-1} respectively.

No definite order with respect to alkali was established in the earlier work. Thus the present work brings out a clear relationship between the rates of oxidation and [alkali] in the medium.

Influence of structure on reactivity: Substituent effect—Table 2 lists the second order rate constants for the oxidation of a number of monosubstituted phenols by peroxydisulphate. It is clear that electron releasing substituents increase the rate of the reaction while electron withdrawing substituents retard it. The correlation of these data in aq. ethanol and aq. acetonitrile with Hammett σ values yields linear plots with slopes of ~ -2.3 (reaction constant) (Fig. 1). The plots assume a rate limiting attack at oxygen. However, a rate limiting attack at carbon would require a linear plot between $\log k_2$ of *meta* compounds versus *para* substituent constants. Similarly $\log k_2$ of *para* substituted compounds against *meta* substituent constants would be linear if a rate limiting attack on carbon is expected. Further, for the *ortho* substituted compounds, oxygen attack should show a correlation between the $\log k_2$ and σ_o , while for carbon attack the same rate constants should be correlated with σ_m for the same substituents. All these factors have been taken into consideration and the data obtained clearly bring out a rate limiting attack on oxygen rather than on carbon.

Effect of allyl alcohol—The rates are unaffected in the presence of allyl alcohol, and this is in agreement with earlier finding.

Dependence on pK_a and ionic strength of the medium—Various phenols were found to react broadly in accordance with their pK_a values in

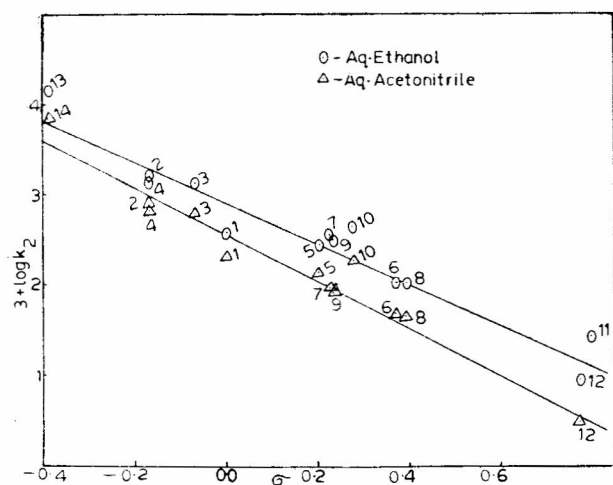


Fig. 1 — Hammett plots in aq. ethanol and aq. acetonitrile (20%, v/v) [1, H; 2, *o*-CH₃; 3, *m*-CH₃; 4, *p*-CH₃; 5, *o*-Cl; 6, *m*-Cl; 7, *p*-Cl; 8, *m*-Br; 9, *p*-Br; 10, *p*-I; 11, *o*-nitro; 12, *p*-nitro; and 13, *o*-OCH₃]

TABLE 2 — SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF SUBSTITUTED PHENOLS AT 35° IN DIFFERENT AQUO-ORGANIC SOLVENT MIXTURES (20%, v/v)

{[KCl] = 0.01M; [NaOH] = 0.1M}

Substituent	pK_a	$k_2 \times 10^2$ (litre mole ⁻¹ min ⁻¹)		
		Aq. ethanol	Aq. acetonitrile	Aq. acetone*
H	10.0	37.05	20.0	25.1
<i>p</i> -CH ₃	10.26	142.4	68.0	44.6
<i>m</i> -CH ₃	10.09	132.0	62.2	52.7
<i>o</i> -CH ₃	10.29	152.1	83.0	75.4
<i>p</i> -Cl	9.42	36.5	9.5	9.7
<i>m</i> -Cl	—	10.4	4.8	6.6
<i>o</i> -Cl	8.53	28.1	12.5	16.7
<i>p</i> -Br	9.36	32.2	8.05	8.1
<i>m</i> -Br	—	10.2	4.5	5.5
<i>p</i> -I	9.3	44.0	18.6	18.0
<i>p</i> -NO ₂	7.15	0.9	0.3	—
<i>o</i> -NO ₂	—	2.71	—	—
<i>o</i> -OMe	—	1452.0	695.0	508.0

*Reactions were carried out in the presence of 0.01M NaOH.

TABLE 3 — SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF PHENOL IN DIFFERENT SOLVENT MIXTURES

{[KCl] = 0.01M; [NaOH] = 0.1M; temp.: 35°}

Solvent	$k_2 \times 10^2$ (litre mole ⁻¹ min ⁻¹)	Solvent	$k_2 \times 10^2$ (litre mole ⁻¹ min ⁻¹)
ETHANOL-WATER		ACETONE-WATER	
0: 100	87.0	10: 90	27.0*
10: 90	52.0	20: 80	25.0*
20: 80	37.1	30: 70	20.0*
30: 70	31.0		
ACETONITRILE-WATER		<i>tert</i> -BUTANOL-WATER	
0: 100	87.0		
10: 90	38.0		
20: 80	20.0	0: 100	87.0
30: 70	14.0	20: 80	41.0

all the three solvent mixtures as seen from the data in Table 3. A plot of $\log k_2$ vs pK_a of phenols⁶ is fairly linear with a Bronsted slope of 0.66. A Bronsted slope greater than 0.5 means a higher degree of bond formation in the transition state⁷.

Data on variation of ionic strength suggest that the reacting species are ionic in nature.

Reactivity in aqueous acetonitrile (20%) and aqueous acetone (20%)—It is seen that the reactions are uniformly slower in aq. acetonitrile than in aq. ethanol (20%) (Table 2). Further, the order of reactivity among the substituted phenols broadly remains the same in all the three solvent mixtures. A plot of $\log k_2$ (aq. ethanol) vs $\log k_2$ (aq. acetonitrile or aq. acetone) is linear. This points to a similarity in mechanism in all the three solvent mixtures.

The reaction is dependent on the dielectric constant of the medium in a given binary solvent mixture. A plot of $\log k_2$ vs $1/D$ is linear with a

negative slope, which, according to Amis⁹, means that the inorganic reactant is a negative ion. However, the dependence on dielectric constant is not observed, when the organic component in the solvent mixtures is different. This can be traced to specific solvent influence.

The order of reactivity in different binary solvent mixtures, as seen from Tables 2 and 3 is: ethanol-water \sim *t*-butanol-water \sim acetone-water $>$ acetonitrile-water.

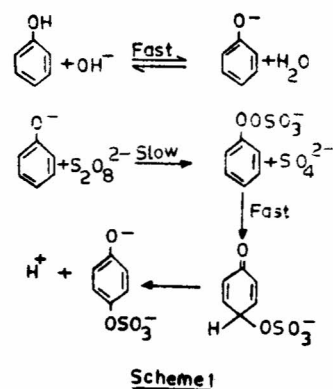
Rate law and mechanism of the reaction—The reaction is first order in oxidant and first order in substrate and nearly half order in hydroxide. Hence the rate law can be written as

$$\begin{aligned} -\frac{d(S_2O_8^{2-})}{dt} &= k_{\text{obs}}[S][\text{Ox}][\text{OH}^-]^{\frac{1}{2}} \\ &= k'_{\text{obs}}[S][\text{Ox}] + k''_{\text{obs}}[S][\text{Ox}][\text{OH}^-] \end{aligned}$$

which is in conformity with the fact that the reaction involves a hydroxide-catalysed path and a path independent of hydroxide ions. The fact that (i) the products of oxidation of phenols by $S_2O_8^{2-}$ in binary solvent mixtures are the corresponding *p*-hydroxyaryl sulphates, and (ii) the reactants are ionic in nature suggests that the rate determining step involves a nucleophilic attack of phenoxide ion on the $S_2O_8^{2-}$ species.

The order with respect to alkali clearly proves that there are two reactive species and they are neutral phenol and phenoxide ion. Because both the reactive species are operating in the reaction the fractional dependence on alkali is observed. It might appear that there is no possibility of neutral phenol molecules being present at the concentrations of alkali used, but a close analogy is found in the earlier work^{10,11} on halogenation of aniline where even at high H_2SO_4 concentrations, free molecules of base have been postulated to be the reactive species. Hence the neutral molecule as well as phenoxide ions are the reactive species.

The reaction mechanism involving preferably an attack on the oxygen consistent with the results is shown in Scheme 1.



The neutral molecule may also participate in a similar fashion yielding the product.

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