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KINETICS AND ORIENTATION IN THE PEROXYDISULFATE OXIDATION OF PHENOL[1]

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Abstract—Oxidation of phenol by aqueous alkaline peroxydisulfate to form *o*- and *p*-dihydroxybenzenes has been studied. The rate is expressed as: $v = k[S_2O_8^=][PhOH]$, where the *k* value tends to increase with an increase of the concentration of alkali and a plot of log *k vs* pH at pH 9·5–10 is a straight line with a slope of *ca* unity. The effects of ionic strength, concentration of alkali and temperature on the *o*/*p* ratio has been determined. In view of these facts a probable mechanism involving a nucleophilic attack of a C atom of phenoxide ion on the peroxide oxygen of the peroxydisulfate ion has been postulated and discussed.

OXIDATION of phenol by aqueous alkaline peroxydisulfate to form dihydroxybenzenes has been called Elbs oxidation, since Elbs discovered the reaction of *o*-nitrophenol with ammonium peroxydisulfate to form 2,5-dihydroxynitrobenzene.[2]

The initial product formed in this type of reaction is hydroxyaryl sulfate,[3] which on acid-catalysed hydrolysis gives dihydroxybenzene. The reaction has been extended to a number of phenols.[4] The *para*-dihydroxyarenes are preferred to the *ortho* isomer,[5,6] and no *meta* isomer has been observed. In some cases, the *ortho* substitution is favourable, especially when the *para* position is substituted.

Both homolytic[7] and heterolytic[8] mechanisms have been postulated for the reaction. The kinetics of the reaction have been studied.[8] But the effect of conditions on *o*/*p* orientation has not yet been reported. The present paper describes the kinetics studied by the iodometric measurement of consumption of peroxydisulfate and the effects of ionic strength, concentration of alkali and temperature on the *o*/*p* ratio. On the basis of these facts, a probable mechanism is discussed.

RESULTS

Kinetics

(a) *Effect of initial concentration of phenol.* The rate of consumption of peroxydisulfate ion was measured by iodometry in a 1·7M KOH at 30° at a constant ratio 10 of initial concentrations of phenol *vs* peroxydisulfate ion, $[PhOH]_0/[S_2O_8^=]_0$. The kinetic data are listed in Table 1. From the Table it is apparent that the reaction is first-order with respect to both phenol and peroxydisulfate ion, and the constancy of the calculated second-order rate constants (*k*) is satisfactory.

$$-\frac{d[S_2O_8^=]}{dt} = k'[S_2O_8^=] = k[S_2O_8^=][PhOH] \quad (1)$$

(b) *Effect of alkali concentration on the second-order rate constant.* Both NaOH and KOH were used as alkali at 30°. The pH value was calculated from the amounts of alkali and phenol. The results are shown in Fig 1. As evident from the Fig, the second-order rate constant tends to increase with an increase in the concentration of alkali.

TABLE 1. EFFECT OF INITIAL CONCENTRATION OF PHENOL ON THE RATE CONSTANTS FOR THE PEROXYDISULFATE OXIDATION AT 30°

$[PhOH]_0$ (M)	$[K_2S_2O_8]_0$ (M)	First-order rate constant $10^3\ k'$ (sec^{-1})	Second-order rate constant $10^2\ k$ ($M^{-1}\ sec^{-1}$)
0·20	0·020	2·92	1·46
0·15	0·015	2·24	1·49
0·10	0·010	1·53	1·53
0·05	0·005	0·70	1·40

Initial concentration: KOH, 1·7 M aq.

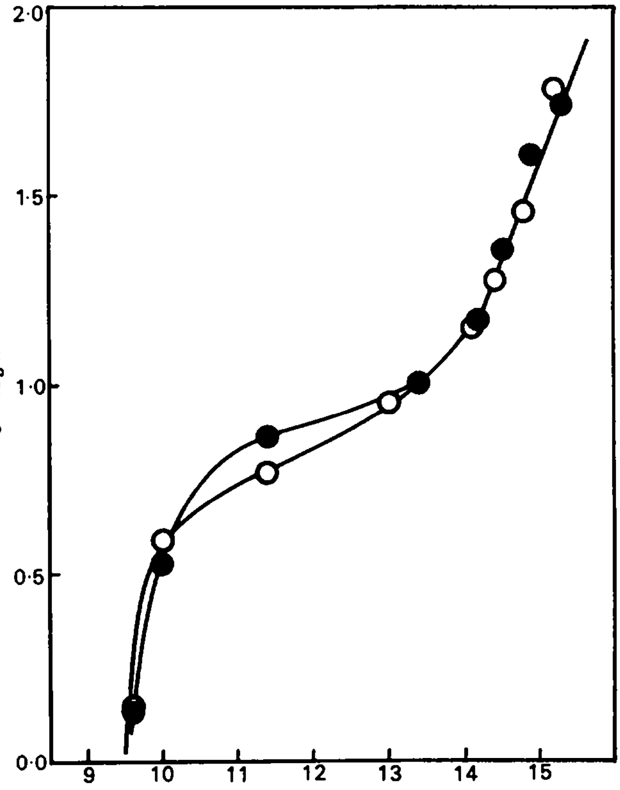


FIG 1. Plot of log k vs pH at 30°
Initial concentration: PhOH, 0·15 M; $K_2S_2O_8$, 0·015M
NaOH, ○; KOH, ●

The slope of line at pH 9·5–10 is *ca* unity. Generally, the change of alkali from NaOH to KOH has virtually no effect except at pH of 10–14, while the change of alkali metal at pH 10–14 caused a small increase in the second-order rate constant.

(c) *Effect of ionic strength.* The effect of ionic strength (μ) was studied by changing the amount of added NaCl using 0·5M NaOH. The results are shown in Table 2, which shows that an increase in ionic strength results in an increase of k and a plot of log k vs $\sqrt{\mu}$ gives a straight line.

TABLE 2. EFFECT OF IONIC STRENGTH ON THE SECOND-ORDER RATE CONSTANT FOR PEROXYDISULFATE OXIDATION OF PHENOL AT 30°

NaCl	$10^2 k$ (M^{-1} sec^{-1})	μ
None	0·895	0·5
0·5	1·222	1·0
1·0	1·280	1·5
3	2·76	3·5

Initial concentration: NaOH, 0·5N; PhOH, 0·15M; $K_2S_2O_8$, 0·015M.

Yields of dihydroxybenzenes and o/p ratio

(a) *Effect of alkali concentration.* The yields of dihydroxybenzenes and their *o/p* ratios were determined by changing the alkali concentration with the $[PhOH]_0/[S_2O_8^{=}]_0$ ratio of 1 and 3 at 30° using NaOH. The yields were calculated on the basis of used $K_2S_2O_8$. The results are shown in Tables 3a and b. With increasing concentration of alkali the *o/p* ratio decreased at first, but then increased gradually with a minimum at the ratio $[NaOH]_0/[PhOH]_0$ of 1·25.

TABLE 3. EFFECT OF ALKALINE CONCENTRATION ON *o/p* RATIO OF DIHYDROXYBENZENES AT 30°

a

NaOH (mol)	$[NaOH]_0/[PhOH]_0$	Yield		*o/p*
		$o\text{-}C_6H_4(OH)_2$ (%)	$p\text{-}C_6H_4(OH)_2$ (%)	
0·5	25·0	7·4	24·6	0·30
0·3	15·0	9·3	35·1	0·26
0·1	5·0	8·3	40·4	0·21
0·05	2·5	8·1	42·1	0·19
0·025	1·25	4·0	23·3	0·17
0·0157	0·79	2·9	13·3	0·22
0·0058	0·03	2·6	4·3	0·59

Initial concentration: PhOH, 0·02 mol; $K_2S_2O_8$, 0·02 mol.

b

NaOH (mol)	$[NaOH]_0/[PhOH]_0$	Yield		*o/p*
		$o\text{-}C_6H_4(OH)_2$ (%)	$p\text{-}C_6H_4(OH)_2$ (%)	
0·2	10·0	6·8	17·3	0·40
0·05	2·5	8·5	28·7	0·29
0·025	1·25	9·7	34·6	0·28
0·0125	0·625	7·5	17·3	0·43

Initial concentration: PhOH, 0·02 mol; $K_2S_2O_8$, 0·007 mol.

(b) *Effect of salts.* The effect of NaCl and KCl addition on the *o/p* ratio is shown in Table 4. The *o/p* ratio increases with increasing concentration of these salts. This salt effect seems to be analogous to the observed effect of alkali at the higher concentration (Table 3). There was little difference in the salt effect on the *o/p* ratio between KCl and NaCl.

TABLE 4. EFFECT OF SALT ON o/p RATIO OF DIHYDROXYBENZENES AT 30°

Salt	mol	Total cation conc (mol)	Yield		o/p
			o-$C_6H_4(OH)_2$ (%)	p-$C_6H_4(OH)_2$ (%)	
	None	0·05	8·1	42·1	0·19
NaCl	0·05	0·10	7·8	36·0	0·22
	0·25	0·30	7·5	27·5	0·27
KCl	0·05	0·10	7·8	35·5	0·22
	0·25	0·30	7·9	26·3	0·30

Initial concentration: NaOH, 0·05 mol; PhOH, 0·02 mol; $K_2S_2O_8$, 0·02 mol.

(c) *Effect of temperature.* The dependence of the o/p ratio on the temperature was determined at 10°, 30°, 50° and 70° which is shown in Table 5. Increasing temperature results in an increase in the yield of *ortho* but a decrease in the yield of *para* compounds.

TABLE 5. EFFECT OF TEMPERATURE ON o/p RATIO OF DIHYDROXYBENZENES

Temp (°C)	Yield		o/p
	o-$C_6H_4(OH)_2$ (%)	p-$C_6H_4(OH)_2$ (%)	
10	7·5	41·7	0·18
30	8·3	40·4	0·21
50	8·7	37·1	0·23
70	9·5	36·7	0·25

Initial concentration: NaOH, 0·1 mol; PhOH, 0·02 mol; $K_2S_2O_8$, 0·02 mol.

DISCUSSION

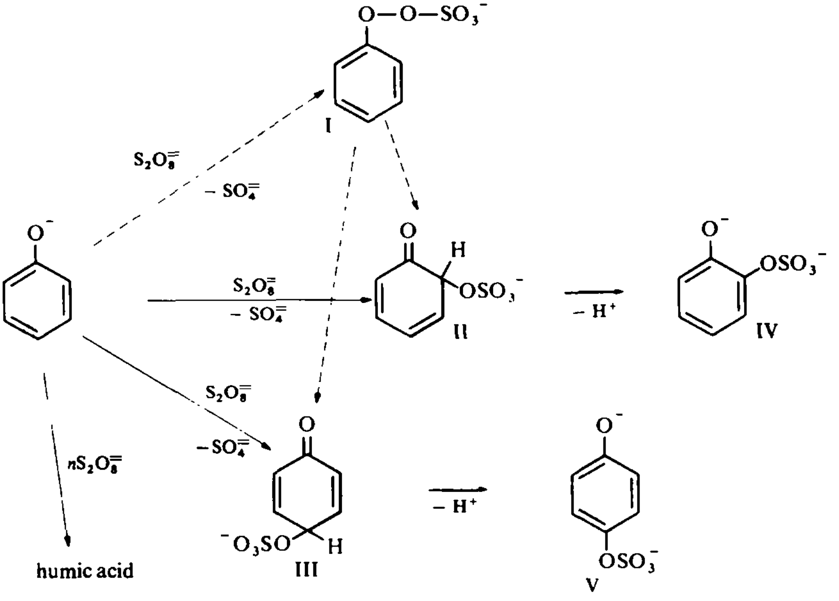
A generally accepted mechanism for the reaction is a bimolecular nucleophilic attack of phenoxide ion on the peroxide bond of peroxydisulfate ion.[8] This type of attack is often observed in the oxidation of phenols with ordinary peroxides. A similar mechanism has been postulated in the reaction of aniline with peroxydisulfate.[9, 10]

We observed that the rate of consumption of peroxydisulfate ion is expressed as: $v = k[S_2O_8^{=}][PhOH]$, which is consistent with the previous report.[8] The slope of a line for the plot of log k *vs* pH is *ca* unity at pH 9·5–10, hence k is proportional to $[OH^-]$. Therefore, the reaction species should not be free phenol but the phenoxide ion, PhO^-, which is formed by a preliminary equilibrium: $PhOH + OH^- \rightleftarrows PhO^- + H_2O$. The rate was too small to measure at pH 9, probably because the concentration of PhO^- at this pH range is small.

These data suggest a mechanism shown in Scheme 1 which involves the simultaneous formation of hydroquinone, catechol and humic acid[11] (polyoxidative compound).

The effect of ionic strength indicates the presence of a positive salt effect, which supports the above reaction between ionic species of same sign, i.e., peroxydisulfate

Scheme 1



and phenoxide ions. The slope of a plot of log *k* *vs* pH is larger with KOHaq than with NaOHaq at pH 10–14. This difference is probably caused by the difference in the dissociation extent of phenoxide ions, PhO^-K^+ and PhO^-Na^+, since potassium salts of weak acids are generally more dissociated.[12] A sharp increase of log *k* at pH above 11 may be caused by an increase of ionic strength, because a plot of log *k* *vs* $\sqrt{\mu}$ gives a straight line. The slopes of the plots of log *k* *vs* $\sqrt{\mu}$ for NaOH and KOH were 0·41 and 0·44, respectively. These values are similar to the value of slope (0·42) for the plot of log *k* *vs* $\sqrt{\mu}$ using NaCl.

The effect of changing reactants on the *o*/*p* ratio has been reported,[4] but the effect of changing conditions is still unknown and will be discussed below.

Forrest[4] reported that the peroxydisulfate oxidation of phenol at pH 14 and the ratio $[NaOH]_0/[PhOH]_0$ of 5 at 20° gave hydroquinone and catechol in yields of 23% and 2·1%, respectively, i.e., *o*/*p* ratio ≃ 0·1 by estimating the yields. The yields of hydroquinone and catechol in the present reaction were 42% and 7·5%, respectively, (*o*/*p* ratio ≃ 0·2) at 10° at the same pH and the ratio $[NaOH]_0/[PhOH]_0$ of 5. The difference in yields and *o*/*p* ratio may be due to the different method of analysis. Our GLC analysis is more suitable for these reaction products. No resorcinol was detectable in the product.

Our results show that the *para* position of the phenoxide ion is ten times as reactive as the *ortho* position. The higher reactivity of the *para* position may be due to the more favourable negative charge delocalisation in the transition state for the *para* substitution.[13] The *o*/*p* ratio tends to increase with increasing temperature because of the decrease in selectivity. A similar thermal effect on *o*/*p* ratio was reported in the nitration of phenol,[14] where the attacking species is NO_2^+.

By raising the concentration of alkali (the ratio $[NaOH]_0/[PhOH]_0$ from 0·03 to 1·25), the *o*/*p* ratio decreases from 0·59 to 0·17. A similar phenomenon has been observed in a reaction of phenol with formaldehyde,[15] which involves a nucleophilic attack of a C atom of the phenoxide ion on a carbonyl C atom. This phenomenon may be explained as follows. At lower concentration of alkali, metallic ions may associate around a phenoxide O atom forming an ionic atmosphere consisting of ionic pairs e.g., Na^+OH^-. This ionic cloud may spread over the whole molecule of phenoxide ion at higher concentration of alkali. Hence, an attack of peroxydisulfate ion on the *para* position of phenol may be sterically hindered at high concentration of ions.

An increase in *o*/*p* ratio by increasing the concentration of phenol was observed as shown in Tables 3a and b, a similar tendency has been reported for the reaction of phenol with formaldehyde.[16]

The *o*/*p* ratio for the reaction of phenol with benzoyl peroxide,[17] which presumably goes by way of an intermedate similar to I in Scheme 1, has been reported to be 4;[18] the difference between the values for benzoyl peroxide and peroxydisulfate may be ascribed to the H-bonding ability of free phenol with peroxide oxygen of benzoyl peroxide and the inability of the phenoxide ion to H-bond with peroxydisulfate ion. Hence, the former reaction may proceed via an initial attack of a peroxide O atom on an O atom of phenol. Similarly, the reaction of aniline with peroxydisulfate[10] proceeds via an initial attack of peroxydisulfate ion on a N atom of aniline followed by the rearrangement of the sulfate ion and no *p*-substitution is observed.[9] In view of these facts, an initial attack of phenoxide oxygen is not conceivable for the present Elbs oxidation of phenol, probably because a reaction between anions, i.e., an attack of $S_2O_8^=$ on O atom of PhO^- is difficult.

EXPERIMENTAL

Materials. Phenol was distilled *in vacuo* (b.p. 99°/37 mm). Commercial G. R. grade potassium peroxydisulfate was used without further purification.

Kinetic procedure. The reaction of phenol with aqueous peroxydisulfate was carried out as described by Behrman.[8] The reaction was followed by iodometric determination of the disappearance of peroxydisulfate.

A typical reaction and analysis of products for determination of o/p *ratio*. Phenol (0·02 mol) was dissolved in a 10% NaOH aq (0·1 mol) and oxidised by the slow addition of saturated $K_2S_2O_8$ aq (0·02 mol) with stirring for 3 hr. After standing overnight, the soln was neutralised with conc H_2SO_4, the ppt (polymer) was removed by filtration. An aliquot (5 ml) of the mixture was pipetted out and poured into 5N H_2SO_4 (10 ml). Hydrolysis of the sulfate obtained was carried out by heating the soln with stirring at 100° for 1 hr. The resulting soln was added with NaOH aq and dimethyl sulfate (8 ml), the pH being 15. The soln was heated with stirring. After the dimethyl sulfate had dissolved, the reaction mixture was cooled and extracted with benzene (7 ml),[19] and the extract was injected directly into the gas chromatograph. A Yanagimoto Model GCG 550-F gas chromatograph employing a flame ion detector and a 2-meter stainless steel column packed with 15% Apiezone grease L on Celite 545 was used at 184° to separate the dimethoxybenzenes. The retention times of catechol dimethyl ether and hydroquinone dimethyl ether were 11·8 and 13·6 min, respectively

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