Kinetics of Oxidation of Phenols by Acid Bromate

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The oxidation of phenols by acid bromate has been studied in acetic acid-water mixture in the presence of sulphuric acid. The reaction is first order each in the substrate and the oxidant. The rate of the reaction increases with the increase in [H₂SO₄]. The solvent effect has been studied at 30° by varying acetic acid content of the medium and keeping the [H₂SO₄] constant at 30°C. The reaction was found to be of an ion-dipole and the value of r (distance of closest approach between the ion and the dipole) has been calculated to be 1·3 Å from the Amis plot. The Hammett's reaction constant ($\rho = -1·74$) has been evaluated. The reaction is accelerated by electron-donating substituent and retarded by electron-withdrawing groups. The order of reactivity in substituted phenols is m-CH₃>p-CH₃>o-CH₃>H>o-Cl>p-Cl>m-Cl>m-NO₂>o-NO₂>p-NO₂.

THE kinetics of oxidation of primary aliphatic and secondary alcohols by acid bromate has been studied[1-5], but similar oxidation studies on phenols are lacking. In the present paper the kinetics of oxidation of phenols by acid bromate has been reported.

Materials and Methods

All the compounds used were of AR grade and further purified either by recrystallization or by distillation. The stock solutions of phenols were prepared by dissolving the known amounts of the substance in a distilled water or in acetic acid-water mixture and standardized titrimetrically.

The reaction was followed by withdrawing aliquots of the reaction mixture at known intervals of time and quenching the reaction by adding excess of potassium iodide solution. The unreacted bromate reacts with potassium iodide in acid solution in accordance with the equation

$$BrO_3^- + 6I^- + 6H^+ = Br^- + 3I_2 + 3H_2O$$
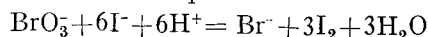
The liberated iodine was estimated by titrating against standard thiosulphate solution using starch as an indicator. First order rate constants were obtained from the plot of log $(a-x)$ versus time and the second order rate constants calculated by dividing the first order rate constants with the [substrate].

Results and Discussion

During the oxidation of phenol by BrO₃⁻, molecular Br₂ will be produced from the Br⁻ ion. Hence there may be a possibility of oxidation of substrates by both bromate and bromine. However, plot of log $(a-x)$ versus time (Fig. 1, curve-A) is linear even up to 60% completion of the reaction indicating
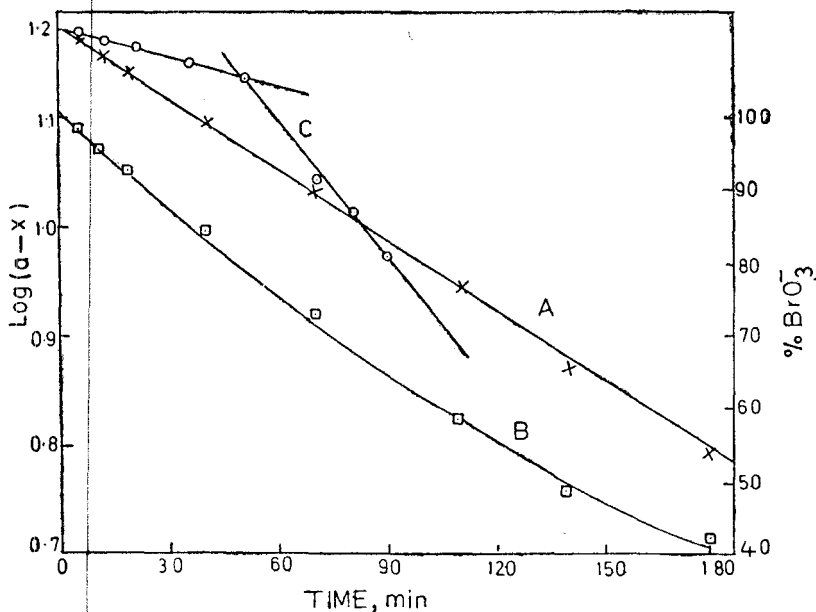

Fig. 1 — Plot of log $(a-x)$ versus time for the oxidation of phenol (curve-A); plot of BrO₃⁻ per cent versus time for the oxidation of phenol (curve-B); and plot of log $(a-x)$ versus time for the oxidation of tribromophenol (curve-C) at [tribromophenol] = $2·5 \times 10^{-2}M$; [phenol] = $5 \times 10^{-2}M$; [H₂SO₄] = $0·05M$; HOAc = 40%; temp. = 50°

no oxidation of phenol by bromine which is in contrast to the observation made by Venkatasubramanian[2] on the oxidation of alcohol by BrO_3^-. The plot of BrO_3^- per cent as a function of time also shows no deviation from linearity (Fig. 1, curve-B). Phenols react with Br_2 in acid medium to give tribromophenol instantaneously. At a later stage of the reaction, there will be oxidation of phenol by BrO_3^- as well as of tribromophenol by BrO_3^-, the later reaction being of much less importance. In the oxidation of tribromophenol by BrO_3^- under indentical conditions, it has been observed that there is a break in the plot of log $(a—x)$ versus time (Fig. 1, curve-C) indicating that after about 15% of the reaction is over, a faster oxidation reaction by Br_2 takes place. It is found that the second order rate constants for the oxidation of phenol and tribromophenol by BrO_3^- under identical conditions (HOAc=40%, $[H_2SO_4] = \cdot05M$, temp. = 50°) are nearly same, e.g. $k_{phenol} = 1\cdot502 \times 10^{-3}$ litre mole⁻¹ sec⁻¹ and $k_{tribromophenol} = 1\cdot380 \times 10^{-3}$ litre mole⁻¹ sec⁻¹. It is also observed that Br⁻ ions cannot be fixed by $Hg(CH_3COO)_2$ as in the case of alcohols, because Hg^{2+} ions oxidize phenol and catalyse the reaction. The following data are given in support of this contention. The values of reaction rate (k) have been found to be 1·50, 1·82, 2·60 and $6\cdot98 \times 10^{-3}$ litre mole⁻¹ sec⁻¹ at $[Hg^{2+}] = 0$, 0·25, 0·5 and $1\cdot0 \times 10^{-2}M$ respectively.

The reaction rate is found to be of second order with respect to [H⁺] (Table 1) showing that the reactive species should be $H_2^+BrO_3$.

The rate constants at constant percentage of acetic acid and sulphuric acid shows first order dependence in bromate ion as well as in phenol. A plot of 1/k versus 1/[phenol] is linear with an intercept, indicating the formation of a complex between phenol and di-protonated bromate ion. The intercept also indicates that the rate expression[6] is of the type $k_2k_3[phenol]/1+k_2[phenol]$.

The effect of dielectric constant on the reaction rate was studied by varying the percentage of acetic acid. It can be seen from Table 2 that the rate increases with an increase in acetic acid content. The dielectric constant (D) of different acetic acid-water mixtures at 30° has been calculated using an approximate validity method[7]. The plot of log k versus 1/D is linear with a positive slope.

The rate constant for an ion-dipole reaction vary with the dielectric constant according to Amis equation :

$$\ln k_d = \ln k + \frac{Ze\mu_0}{kTr^2D} \qquad \ldots(1)$$

If Ze is positive, a plot of log k versus 1/D should be linear with a positive slope. From this slope the value of r (the distance of closest approach for $H_2^+BrO_3$ and phenol molecule) is calculated to be 1·3 Å.

The oxidation of several substituted phenols has been studied and the rate constants are given in Table 3. A plot of log k versus σ or σ^+ is linear with a negative slope. The value σ_R was used for m-nitrophenol[8]. For o-nitrophenol $\sigma = 0\cdot4$ was used[9]. Hammett's reaction constant has been found

TABLE 1 — EFFECT OF VARYING [H₂SO₄] ON THE REACTION RATES OF SUBSTITUTED PHENOLS

{Solvent: HOAc (40%); [substrate] $= 5 \times 10^{-2}M$; $[BrO_3^-] = 5 \times 10^{-3}M$; temp. $= 30°$}

Phenol	$k \times 10^3$ (litre mole⁻¹ sec⁻¹) at [H₂SO₄]				
	0·2	0·4	0·6	0·8	1·0
H	1·09	4·26	9·59	20·80	30·80
o-NO₂	0·32	0·83	1·22	1·90	2·51
p-NO₂	0·31	0·72	1·16	1·62	2·14
m-NO₂	0·56	1·83	2·84	5·01	6·92
o-Cl	1·15	4·04	5·30	11·00	20·50
p-Cl	0·83	2·02	3·97	7·15	11·81
m-Cl	0·63	1·54	3·34	5·69	10·24
o-CH₃	2·65	12·79	20·75	42·63	76·80
p-CH₃	3·82	15·36	36·53	69·77	118·10
m-CH₃	7·68	24·00	49·86	95·93	146·20

TABLE 2 — EFFECT OF VARYING DIELECTRIC CONSTANT OF THE MEDIUM ON THE REACTION RATES OF SUBSTITUTED PHENOLS

{[Substrate] $= 5 \times 10^{-2}M$; $[BrO_3^-] = 5 \times 10^{-3}M$; $[H_2SO_4] = 0\cdot4M$; temp. $= 30°$}

| Phenol	$k \times 10^3$ (litre mole⁻¹ sec⁻¹) at HOAc (%)					
	10	20	30	40	50	60
H*	8·02	10·96	18·28	31·98	90·64	—
o-NO₂	—	0·42	0·56	0·82	1·35	2·80
p-NO₂	0·29	0·35	0·42	0·72	1·28	—
m-NO₂	0·33	0·54	1·01	1·82	3·49	—
o-Cl	0·68	1·00	1·71	4·04	5·40	—
p-Cl	0·52	0·80	1·32	2·02	3·80	—
m-Cl	0·41	0·56	1·03	1·54	2·85	—
o-CH₃	3·48	5·48	10·23	12·79	35·70	—
p-CH₃	3·84	5·91	9·60	15·36	25·59	—
m-CH₃	5·12	8·87	14·40	23·99	48·00	—

*At $[H_2SO_4] = 1\cdot0M$.

TABLE 3 — THERMODYNAMIC PARAMETERS IN THE OXIDATION OF PHENOLS BY BROMATE

{[Substrate] $= 5 \times 10^{-2}M$; $[BrO_3^-] = 5 \times 10^{-3}M$; $[H_2SO_4] = 5 \times 10^{-2}M$; solvent: acetic acid (40%); temp. $= 40°$}

Phenol	$k \times 10^4$ litre mole⁻¹ sec⁻¹	$\Delta E\ddagger$ k cal mole⁻¹	$\Delta H\ddagger$ k cal mole⁻¹	$\Delta S\ddagger$ k cal mole⁻¹
—	6·36	14·08	14·70	−26·74
o-NO₂	3·92	11·94	12·56	−30·00
p-NO₂	2·91	17·72	18·34	−21·76
m-NO₂	5·44	16·15	16·77	−15·46
o-Cl	5·96	17·72	18·34	−15·29
p-Cl	4·93	15·25	15·07	−24·24
m-Cl	3·51	17·72	18·34	−15·66
o-CH₃	21·36	13·56	14·18	−26·03
p-CH₃	23·34	14·08	14·76	−23·41
m-CH₃	34·17	14·60	15·22	−22·55

to be −1·74 at $0\cdot4M$ H_2SO_4 and 30°. The reaction is accelerated by electron-donating substituent and retarded by electron-withdrawing groups. The order of reactivity has been found to be m-CH₃> p-CH₃ > o-CH₃ > H > o-Cl > p-Cl > m-Cl > m-NO₂ > o-NO₂ > p-NO₂.

The rate measurements have been made at five different temperatures (35-55°) from which thermo-

Scheme 1
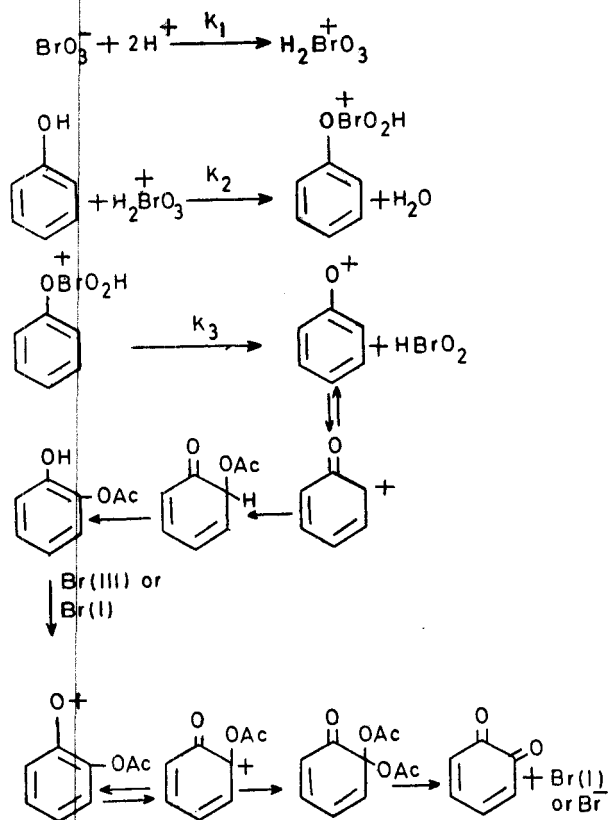
dynamic parameters, viz. $\Delta E^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are calculated at 40° (Table 3). The negative $\Delta S^{\ddagger}$ values indicate the more rigid activated complex formation.

Besides a large amount of polymeric material, two other products could be spotted on TLC, one of which has been identified as o-quinoline[10].

Based on the above data a possible mechanism as shown in Scheme 1 has been proposed for the oxidation of phenol by BrO_3^-.

The subsequent stages of reduction of Br(III) to Br⁻ can proceed by one of the several path ways. It may participate in the second step of oxidation or in oxidizing another phenol molecule. The rate expression is therefore given by

$$\frac{-d[BrO_3^-]}{dt} = \frac{k_1 k_2 k_3 [H^+]^2 [BrO_3^-][phenol]}{1 + k_2[phenol]}$$

Acknowledgement

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