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NOTE

Mechanism of Ru (III) Catalysed Oxidation of *o*-Hydroxybenzoic Acid by Acidic Solution of Bromamine-B

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The kinetics of Ru(III) catalysed oxidation of *o*-hydroxy benzoic acid (*o*-HBA) by acidic solition of bromamine-B has been studied. The results indicate that order of the reaction with respect to each of bromamine-B, *o*-HBA, Ru(III) and H^+ ion is one. Negligible effect of addition of potassium chloride and benzene sulphonamide was observed. A suitable mechanism in conformity with kinetic data has been proposed.

Recently bromamine-B[1] (which is also known as sodium *N*-bromobenzene sulphonamide) has been used as an oxidant in oxidation of methyl phenyl sulphide in the presence of alkaline solution of osmium tetroxide used as catalyst and literature on its oxidative potential is scanty. This prompted us to report on the kinetics of Ru(III) catalysed oxidation of *o*-hydroxy benzoic acid by acidic solution of bromamine-B (BAB).

Bromamine-B was prepared by passing bromine in the solution of benzene sulphonamide by reported method.[2] Its strength was determined iodometrically. All other reagents were of AnalaR grade. Perchloric acid (E. Merck) was used as source of H^+ ions. The solution of *o*-hydroxy benzoic acid was prepared by dissolving its desired amount in 30% AR (BDH) methanol. The reaction was studied under pseudo first order conditions by keeping [*o*-HBA] much more larger than that of BAB. The progress of the reaction was monitored by iodometric estimation of remaining [BAB] at regular time intervals. The course of the reaction was up to 60 to 70%.

The reaction was investigated at several initial concentrations of reactants (Table-1). The results show first-order with respect to each of BAB, *o*-HBA, Ru(III) and H^+ ions. The kinetic data showing zero effect of variation of ionic strength of the medium (adjusted by $NaClO_4$) and negligible effect of addition of benzene sulphonamide (BSA) and potassium chloride are included in Table-2. The value of energy of activation (E_a) was calculated from the rate measurements at 30, 35, 40 and 45°C and it was found to be 15.34 kcal/mole.

TABLE-1
EFFECT OF VARIATION OF [REACTANT] ON THE REACTION RATE AT 35°C

$[BAB] \times 10^3$ M	$[o\text{-HBA}] \times 10^2$ M	$[Ru(III)] \times 10^6$ M	$[HClO_4] \times 10^2$ M	$K_1 \times 10^4$ s^{-1}
0.80	5.00	2.64	1.25	3.64
1.00	5.00	2.64	1.25	3.70
1.32	5.00	2.64	1.25	3.67
2.00	5.00	2.64	1.25	3.64
2.80	5.00	2.64	1.25	3.67
4.00	5.00	2.64	1.25	3.62
1.00	0.50	2.64	1.25	0.41
1.00	1.00	2.64	1.25	0.77
1.00	1.50	2.64	1.25	1.12
1.00	2.00	2.64	1.25	1.60
1.00	3.30	2.64	1.25	2.56
1.00	5.00	0.66	1.25	0.92
1.00	5.00	1.32	1.25	1.78
1.00	5.00	1.98	1.25	2.67
1.00	5.00	3.30	1.25	4.56
1.00	5.00	3.96	1.25	5.42
1.00	5.00	2.64	1.00	2.95
1.00	5.00	2.64	2.00	5.91
1.00	5.00	2.64	3.00	8.82
1.00	5.00	2.64	4.50	13.26

TABLE- 2
EFFECT OF VARIATION OF IONIC STRENGTH (μ) OF THE MEDIUM, ADDITION OF BENZENESULPHONAMIDE (BSA) AND KCl ON RATE AT 35°C

Ionic strength ($\mu \times 10^2$ M)	[BSA] × 10 M	[KCl] × 10^2 M	$K_1 \times 10^4$ s^{-1}
12.00	0.00	1.00[a]	3.62
12.00	0.00	2.00[a]	3.60
12.00	0.00	5.00[a]	3.67
12.00	0.00	7.50[a]	3.68
6.25	0.00	5.00[a]	3.70
8.50	0.00	5.00[a]	3.71
11.50	0.00	5.00[a]	3.70
18.75	0.00	5.00[a]	3.68
6.25	1.00	5.00[b]	2.53
6.25	2.00	5.00[b]	2.59
6.25	4.00	5.00[b]	2.54
6.25	6.00	5.00[b]	2.56

$[BAB] = 1.00 \times 10^{-3}$ M, $[HClO_4] = 1.25 \times 10^{-2}$ M, $[Ru(III)] = 2.64 \times 10^{-6}$ M, $[o\text{-HBA}] = 5.00$ (a) and 3.30×10^{-2} M (b)

The following mechanistic paths are suggested on the basis of kinetic data[3] which indicate that BAB as such is oxidant[4] and $[RuCl_6]^{3-}$ is real catalytic species of ruthenium(III) chloride in acidic medium[5] (where S stands for *o*-hydroxybenzoic acid).

$$S + H^+ \overset{K_1}{\rightleftharpoons} SH^+ \quad (1)$$

$$[RuCl_6]^{3-} + SH^+ \overset{K_2}{\rightleftharpoons} C_1 \text{ (complex)} \quad (2)$$

$$BAB + C_1 \overset{K_3}{\rightleftharpoons} [RuCl_6H]^{4-} + \text{products} \quad (3)$$

Slow and rate determining step:

$$[RuCl_6H]^{4-} + BAB \xrightarrow{\text{fast}} [RuCl_6]^{3-} + BSA + NaBr \quad (4)$$

Considering the above mechanistic steps (1–3) and other kinetic parameters, the rate of the reaction proposed in terms of rate of consumption of BAB may be written as Eq. (5).

$$\frac{-d[BAB]}{dt} = K_1K_2K_3\,[BAB]\,[Ru\ (III)]\,[o\text{-}HAB]\,[H^+] \quad (5)$$

The rate law (5) fully explains all the kinetic observations.

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