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Mechanism of Ir(III)-Catalysis in Oxidation of Mandelic Acid by N-Bromobenzamide in Acidic Media

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The kinetic data obtained in Ir(III) catalysed N-bromobenzamide (NBB) oxidation of mandelic acid in perchloric acid have been reported. Mercuric acetate has been used as bromide ions scavenger. Zero-order kinetics with respect to mandelic acid and first order dependence in Ir(III) have been observed. First-order dependence of the reaction on NBB at its low concentration tends to zero-order in the higher concentration range. Positive effect of $[H^+]$ and $[Cl^-]$ has been observed. A negative effect of acetamide and ionic strength of the medium is observed while mercuric acetate shows zero effect on the reaction velocity. (H_2OBr^+) has been postulated as the oxidising species. The mechanistic steps are suggested for Ir(III) catalysed oxidation of mandelic acid by NBB.

INTRODUCTION

Recently considerable attention has been focussed on the chemistry of N-halogeno compounds[1]. NBB (N-bromobenzamide) is a compound of synthetic value and is one of the members of N-halogeno compounds[2]. Relatively little work has been reported on iridium(III) chloride[3] catalysed oxidation. The potential applications of NBB remain almost unrealised as is evident from the scant information available in the literature. This prompted us to investigate the kinetics and mechanism of Ir(III)- catalysed NBB oxidation of mandelic acid in perchloric acid in the presence of mercuric acetate.

EXPERIMENTAL

All the reagents used were of highest purity available. N-bromobenzamide solution was always prepared afresh from its sample prepared by bromination of benzamide by the usual method. Its strength was checked by estimating its active bromine iodometrically. Perchloric acid (E. Merck) was used as source of H^+ ions and sodium perchlorate (E. Merck) was used for varying the ionic strength of the medium. E. Merck sample of mercuric acetate and fluka grade of mandelic acid were used as such. The kinetic procedure employed was the same as reported by Singh *et al.*[3] The reaction course was studied for two half lives, stoichiometry

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and product analysis. The estimation of unreacted NBB from different sets of experiments with various [NBB] to [mandelic acid] ratios showed consumption of one mole of NBB per mole of mandelic acid and accordingly. The following stoichiometric equation could be formulated:

$$C_6H_5CONHBr + C_6H_5CHOHCOOH \xrightarrow[H^+]{[IrCl_6]^{3-}} C_6H_5CONH_2 + C_6H_5COCOOH + HBr \quad (1)$$

The end product benzoyl formic acid was detected by the conventional method.[4]

RESULTS AND DISCUSSION

The kinetics of oxidation of mandelic acid by NBB in the presence of perchloric acid and Ir(III) was investigated at several initial concentrations of reactants (Table-1). First order dependence in NBB decreases at its higher concentrations. The shifting of order in NBB from first to zero is also obvious from the plot (Fig. 1) of (-dc/dt) values against [NBB]* [where * indicates [NBB] at which (–dc/dt) value was determined]. The reaction was observed to be independent of [mandelic acid], indicating zero order kinetics with respect to mandelic acid. At constant ionic strength plot of lg (–dc/dt) *vs.* lg (Ir(III)] gave slope 1.04 (Fig. 2A) which indicates first order kinetics in Ir(III). The plot of lg (–dc/dt) *vs.* lg [H*] (Fig. 2B) gives a curve with slope equal to 0.46 [B] in HClO$_4$ medium, showing fractional dependence of the reaction on H$^+$ ions.

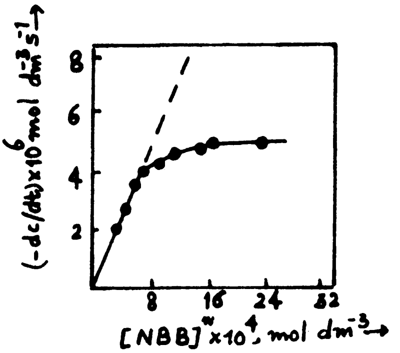


Fig. 1. Plot of –dc/dt) *vs.* [NBB]* under the condition of Table-1

The effects of addition of benzamide and mercuric acetate and variation of (Cl$^-$) and ionic strength (μ) of the medium were studied. The rate increases on increasing [Cl$^-$], thus indicating positive effect of [Cl$^-$] on the reaction velocity. Successive addition of benzamine (NBH) decreases the rate, showing negative effect of [NBH] on reaction rate. The negative effect of ionic strength is also obvious from the kinetic data. The kinetic data indicate that addition of mercuric acetate does not interfere with the reaction.

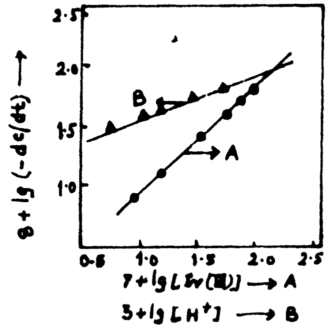


Fig. 2. Plot of (–dc/dt) *vs.* lg [Ir(III)] and lg [H^+] [NBB] = 1.00×10^{-3} mol dm^{-3}, [KCl] = 2.00×10^{-3} mol dm^{-3}, [Mandelic acid] = 2.50×10^{-2} mol dm^{-3}, [Hg(OAc)] = 3.34×10^{-3} mol dm^{-3}, $\mu = 8.00$ (A) and 10.00×10^{-2} mol dm^{-3} (B), [$HClO_4$] = 1.00×10^{-3} (A) mol dm^{-3} and [Ir(III)] = 4.80×10^{-6} mol dm^{-3} (B).

Measurements at different temperatures allowed to determine the energy of activation (E_a), the frequency factor (A) and the entropy of activation (ΔS^*) as 68.94 kJ mol^{-1}, 0.34×10^{11} dm^3 mol^{-2} S^{-2} and –8.20 J mol^{-1} K^{-1} respectively.

Insignificant effect of mercuric acetate on the reaction rate suggests that it acts as bromide ions scavenger only and it is not involved as catalyst in NBB oxidation. Positive effect of [Cl^-] on the reaction velocity suggests that the equilibrium (2) shifts to the right side and thus involvement of $[Ir\ Cl_6]^{3-}$ species[6] in the reaction is ensured.

$$[IrCl_5H_2O]^{2-} + Cl^- \rightleftharpoons [IrCl_6]^{3-} + H_2O \tag{2}$$

NBB exists in the following equilibria like NBA[7,8].

$$\underset{}{C_6H_5CONHBr} + H_2O \rightleftharpoons C_6H_5CONH_2 + \underset{(NBH)}{HOBr} \tag{3}$$

$$HOBr + H_3O^+ \rightleftharpoons (H_2OBr^+) + H_2O \tag{4}$$

$$C_6H_5\ CONHBr + H_3O^+ \rightleftharpoons \underset{(NBBH)^+}{(C_6H_5CONH_2Br)^+} + H_2O \tag{5}$$

$$(C_6H_5CONH_2Br)^+ + H_2O \rightleftharpoons C_6H_5CONH_2 + (H_2OBr^+) \tag{6}$$

Thus NBB as such or HOBr, or $(NBBH)^+$, or (H_2OBr^+) may be involved in the oxidation as active species. The negative effect of benzamide and ionic strength of the medium are not explained on assuming either NBB or protonated $NBBH^+$ as active species, thus ruling out their possibility to act as reactive species. If HOBr is assumed as actual species then reaction should proceed even in the absence of mineral acid contrary to our observation. Hence its involvement is also ruled out. When $(H_2OBr)^+$ is taken as reactive species, it gives the rate law which explains all the observed kinetic data. Thus under the experimental conditions (H_2OBr^+) is propose as active species of NBB.

TABLE-1
EFFECT OF THE CONCENTRATION OF REACTANTS ON THE RATE AT 35°C
$[HClO_4] = 10.00 \times 10^{-3}$ mol dm^{-3}, $[Hg(OAc)_2] = 3.34 \times 10^{-3}$ mol dm^{-3},
$[Ir(III)] = 4.80 \times 10^{-6}$ mol dm^{-3}, $[Cl^-] = 2.00 \times 10^{-3}$ mol dm^{-3} and
μ (ionic strength) $= 2.10 \times 10^{-2}$ mol dm^{-3}

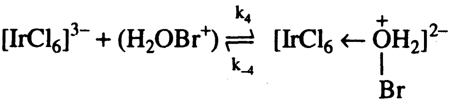
$[NBB] \times 10^3$ mol dm^{-3}	[Mandelic acid] $\times 10^2$ mol dm^{-3}	$k_{obs} \times 10^4$ S^{-1}	
		35°C	40°C
0.40	2.50	8.10	16.32
0.50	2.50	7.86	16.18
0.67	2.50	7.48	16.22
0.80	2.50	5.92	12.38
1.00	2.50	4.96	10.08
1.25	2.50	4.42	9.06
1.67	2.50	3.58	7.16
2.50	2.50	2.24	4.52
1.25	1.00	4.44	9.02
1.25	1.50	4.40	9.12
1.25	2.00	4.39	9.08
1.25	3.34	4.46	8.98
1.25	5.00	4.41	9.16
1.25	7.50	4.28	9.08

On the basis of above discussions and kinetic data the following reaction scheme is suggested.

$$NBB + H_2O \overset{K_1}{\rightleftharpoons} NBH + HOBr \qquad (i)$$

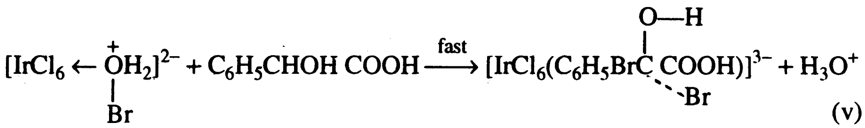
$$HOBr + H_3O^+ \overset{K_2}{\rightleftharpoons} (H_2OBr^+) \qquad (ii)$$

$$[IrCl_5H_2O]^{2-} + Cl^- \overset{K_3}{\rightleftharpoons} [IrCl_6]^{3-} + H_2O \qquad (iii)$$

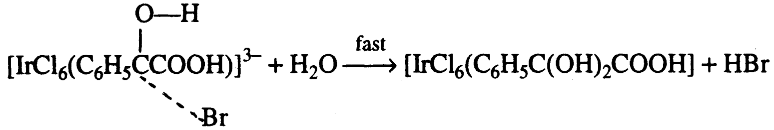


$$[IrCl_6]^{3-} + (H_2OBr^+) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [IrCl_6 \leftarrow \overset{+}{\underset{\underset{Br}{|}}{O}}H_2]^{2-} \qquad (iv)$$

This reaction is the slowest and rate determining step.



$$[IrCl_6 \leftarrow \overset{+}{\underset{\underset{Br}{|}}{O}}H_2]^{2-} + C_6H_5CHOH\,COOH \xrightarrow{\text{fast}} [IrCl_6(C_6H_5Br\overset{\overset{O-H}{|}}{C}COOH)]^{3-} + H_3O^+ \qquad (v)$$



$$[IrCl_6(C_6H_5\overset{O-H}{C}(Br)COOH)]^{3-} + H_2O \xrightarrow{fast} [IrCl_6(C_6H_5C(OH)_2COOH] + HBr \quad (vi)$$

$$[IrCl_6(C_6H_5C(OH)_2COOH)]^{3-} \xrightarrow{fast} IrCl_6 + C_6H_5COCOOH + H_2O \quad (vii)$$

Application of steady state treatment with reasonable approximation yields rate law (7) in terms of consumption of [NBB].

$$\frac{-d[NBB]}{dt} = \frac{k\,[NBB][H^+][Ir(III)]_T[Cl^-]}{k_{-1}[NBH] + k_3[Cl^-][H^+](k_2 + k_1K_2K_4[NBB])} \quad (7)$$

where $k = k_1k_4K_2K_3$, $K_2 = k_2/k_{-2}$ $K_4 = k_4/k_{-4}$. The rate and rate law (7) explains all the experimental observations. The proposed mechanism also suggests the formation of activated complex with reduction in the degree of freedom of molecules.

TABLE-2

EFFECT OF THE ADDITION OF BENZAMIDE AND MERCURIC ACETATE AS WELL AS THE VARIATION OF $[Cl^-]$ AND IONIC STRENGTH (μ) OF THE MEDIUM ON THE REACTION RATE AT 35°C

$[NBB] = 1.00 \times 10^{-3}$ mol dm^{-3}, [mandelic acid] $= 2.50 \times 10^{-2}$ mole dm^{-3}, $[Ir(III)] = 4.80 \times 10^{-6}$ mol dm^{-3}, $[HClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3} and $[Hg(OAc)_2] = 1.50 \times 10^{-3}$ mol dm^{-3} (unless otherwise stated)

[Benzamide] × 10^{-3} mol dm^{-3}	[KCl] × 10^{3} mol dm^{-3}	$\mu \times 10^2$ mol dm^{-3}	$k_{obs} \times 10^4$ s^{-1}
0.00	2.00	1.65	6.12
1.00	2.00	1.65	3.52
2.00	2.00	1.65	2.46
3.00	2.00	1.65	2.08
4.50	2.00	1.65	1.62
6.00	2.00	1.65	1.02
—	1.00	2.00	5.06
—	1.50	2.00	5.72
—	2.50	2.00	6.93
—	4.00	2.00	7.68
—	5.00	2.00	8.96
—	2.00	1.65	6.08
—	2.00	2.00	5.42
—	2.00	3.00	4.82
—	2.00	4.00	4.38
—	2.00	6.00	3.72
—	2.00	7.50	2.28
—	2.00[a]	6.00	3.75
—	2.00[b]	6.00	3.74
—	2.00[c]	6.00	3.78
—	2.00[b]	6.00	3.62

$[Hg(OAc)_2] = {}^a2.00, {}^b4.00, {}^c7.50, {}^d10.00 \times 10^{-3}$ mol dm^{-3}.

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