

Mechanistic Study of Ir(III) Catalyzed Oxidation of Amines by Acidic Solution of Potassium Bromate

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Kinetics and mechanism of Ir(III) catalyzed oxidation of methyl amine (MA) and ethyl amine (EA) by KBrO_3 in acidic medium have been investigated. Zero-order dependence in $[\text{KBrO}_3]$ was observed, while first-order with respect to both methyl amine and ethyl amine and Ir(III) was observed. Variation of ionic strength (μ) of the medium and addition of $\text{Hg}(\text{OAc})_2$ (used as Br^- scavenger) had an insignificant effect on the rate of the reaction. Positive effect of addition of $[\text{Cl}^-]$ on the rate of reaction were observed. A suitable mechanism consistent with the observed kinetic data has been suggested and related rate law deduced.

Key Words: Kinetics and Mechanism, Methylamine, Ethyl amine, Potassium bromate, Ir(III) chloride.

INTRODUCTION

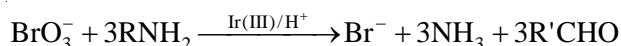
Potassium bromate is known to be a powerful oxidising agent with redox potential 1.44 volts and it has been used as oxidizing agent for a variety of compounds in acidic medium¹⁻⁸ and alkaline medium^{9,10}. Although catalytic role of Ir(III) has been studied in N-bromosuccinimide¹¹ and N-bromoacetamide oxidation of sugars, but to date catalytic activity of Ir(III) towards potassium bromate has not been studied. The prompted us to study Ir(III) catalyzed oxidation of methyl amine and ethyl amine by an acidic solution of potassium bromate.

EXPERIMENTAL

An aqueous solution of potassium bromate (E-Merck) was prepared by dissolving a weighed sample in double distilled water and standardized iodometrically. A solution of iridium(III) chloride (Johnson & Matthey) was prepared by dissolving its 1 g sample in 0.01 M solution of HCl. Standard solutions of methyl amine and ethyl amine were prepared by dissolving their weighed samples (E-Merck) in double distilled water. All other chemicals used were of AnalaR grade.

All reactants except solution of amines were mixed and thermostated at 30 ± 0.1 °C for thermal equilibrium. The reaction was initiated by adding the requisite volume of pre-equilibrated amine solution to the reaction mixture and the progress of the reaction was monitored by estimating the amount of unreacted potassium bromate at regular time intervals iodometrically.

Stoichiometry and product analysis: Various experiments were performed with different [KBrO₃]: [Reducing amine] ratios. Estimation of unreacted potassium bromate indicated that 3 moles of each of methyl amine and ethyl amine consumed one mole of potassium bromate and accordingly stoichiometric equation can be written as:



The end products identified were NH₃ and corresponding aldehydes which were identified by spot test¹³. Here R stands for -CH₃ and -C₂H₅ group and R' stands for -H and -CH₃ group in methyl and ethyl amine, respectively.

RESULTS AND DISCUSSION

The kinetics of oxidation of methyl amine (MA) and ethyl amine (EA) was investigated at several initial concentrations of the reactants. The reactions were carried out by varying the concentration of KBrO₃, methyl amine and ethyl amine, Ir(III) and H⁺ (perchloric acid was used as source of H⁺) ions in turn while keeping the concentration of rest of reactants and other conditions constant (Table-1).

TABLE-1
EFFECT OF VARIATION OF [REACTANTS] ON THE REACTION RATE AT 30 °C

[KBrO ₃] × 10 ⁴ (mol dm ⁻³)	[Amine] × 10 ² (mol dm ⁻³)	[Ir(III)] × 10 ⁶ (mol dm ⁻³)	[HClO ₄] × 10 ² (mol dm ⁻³)	[(-dc/dt)] × 10 ⁷ (mol dm ⁻³ s ⁻¹)	
				MA	EA
4.00	2.00	1.17	0.50	1.56	1.25 ^a
5.00	2.00	1.17	0.50	1.58	1.26 ^a
10.00	2.00	1.17	0.50	1.58	1.28 ^a
12.50	2.00	1.17	0.50	1.52	1.23 ^a
20.00	2.00	1.17	0.50	1.58	1.27 ^a
25.00	2.00	1.17	0.50	1.55	1.25 ^a
10.00	0.50	1.17	0.50	0.41	0.31 ^a
10.00	1.00	1.17	0.50	0.80	0.66 ^a
10.00	1.50	1.17	0.50	1.23	1.03 ^a
10.00	2.50	1.17	0.50	2.06	1.64 ^a
10.00	3.00	1.17	0.50	2.41	1.88 ^a
12.50	2.00	0.59	0.50	0.74	0.64 ^{b,g}
12.50	2.00	2.34	0.50	3.00	2.52 ^{c,g}
12.50	2.00	3.51	0.50	4.58	3.76 ^{d,g}
12.50	2.00	4.68	0.50	6.16	5.08 ^{e,g}
12.50	2.00	5.85	0.50	7.68	6.28 ^{f,g}
10.00	2.00	1.17	0.50	1.58	0.88 ^h
10.00	2.00	1.17	1.00	1.98	1.28 ^h
10.00	2.00	1.17	1.50	2.46	1.52 ^h
10.00	2.00	1.17	2.00	2.92	2.02 ^h
10.00	2.00	1.17	2.50	3.22	2.34 ^h
10.00	2.00	1.17	3.00	3.72	2.56 ^h

[Hg(OAc)₂] = 4.00 × 10⁻³ mol dm⁻³, [KCl] = 0.25 × 10⁻² mol dm⁻³,

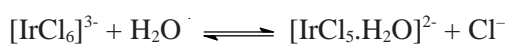
a = [Ir(III)] = 1.96 × 10⁻⁶ mol dm⁻³ and [HClO₄] = 1.00 × 10⁻² mol dm⁻³,

[Ir(III)] = 0.98 (b), 3.92 (c), 5.88 (d), 7.84 (e) and 9.80 (f) × 10⁻⁶ mol dm⁻³,

g = [HClO₄] = 1.00 × 10⁻² mol dm⁻³, h = [Ir(III)] = 1.96 × 10⁻⁶ mol dm⁻³

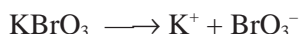
Initial rates were measured while varying the [KBrO₃] insignificant changes in reaction rate (-dc/dt) at various [KBrO₃] indicates zero order dependence on [KBrO₃]. The rate of reaction increases linearly with the increase in the concentration of methyl amine and ethyl amine, showing first-order kinetics with respect to each amines. The increase in [Ir(III)] increased the rate of the reaction linearly, indicating first-order dependence on [Ir(III)]. The rate of the reaction increases non-linearly, showing the positive effect of [H⁺] on the reaction rate. Successive addition of KCl decreases the reaction, showing negative effect of [Cl⁻] on the rate of reaction. Addition of NaClO₄ and variation of [Hg(OAc)₂] did not bring about any significant change in the rate of reaction, indicating zero-effect of ionic strength of the medium and negligible effect of mercuric acetate. This indicates that mercuric acetate functions here only as Br⁻ ions scavenger. The reactions were carried out at 30, 35, 40 and 45 °C and the rate measurement at these temperatures led to computation of energy of activation (E_a). The value of E_a are 16.16 kcal/mol (methyl amine) and 18.32 kcal/mol (ethyl amine).

The results of Ir(III) catalyzed oxidation of methyl amine and ethyl amine, recorded here have revealed that the reactions have identical kinetics and thus appear to have common mechanism. Negative effect of chloride is favoured to right side¹⁴ in acidic solution of iridium(III) chloride.



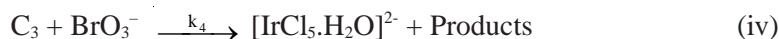
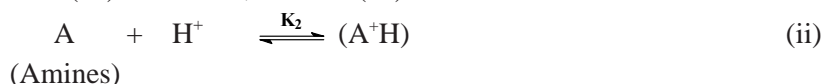
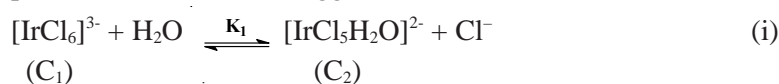
It may, therefore, be assumed that [IrCl₅.H₂O]²⁻ is the active species of iridium(III) chloride.

In acidic and alkaline medium, potassium bromate is ionized as:



The BrO₃⁻ species has been reported to act as an oxidant in acid⁴ as well as in alkaline⁹ medium. The parallel oxidation of amines by Br₂ formed due to interaction of Br⁻ (reduction product of BrO₃⁻) with BrO₃⁻ is eliminated by using Hg(OAc)₂ as Br⁻ ions scavenger¹⁵. The role of Hg(OAc)₂¹² as catalyst or oxidant in the present investigation is absent *i.e.* neither here it is involved as catalyst or co-catalyst or oxidant.

Considering reactive species of Ir(III) and KBrO₃ in acidic medium and other kinetic result of probable mechanism is suggested below:



The rate of reaction may be written in terms of rate of loss of [BrO₃⁻] as eqn. 1

$$-\frac{d[\text{BrO}_3^-]}{dt} = k_4[\text{C}_3][\text{BrO}_3^-] \quad (1)$$

On applying steady state approximation of $[\text{C}_3]$, we have

$$\frac{d[\text{C}_3]}{dt} = 0 = k_3[\text{C}_2][\text{A}^+\text{H}] - k_{-3}[\text{C}_3] - k_4[\text{C}_3][\text{BrO}_3^-]$$

$$\text{or} \quad [\text{C}_3] = \frac{k_3[\text{C}_2][\text{AH}^+]}{k_{-3} + k_4[\text{BrO}_3^-]} \quad (2)$$

On applying law of chemical equilibrium to steps (i) and (ii), we have

$$[\text{C}_2] = K_1 [\text{C}_1] \neq [\text{Cl}^-] \quad (3)$$

$$[\text{AH}^+] = K_2 [\text{A}] [\text{H}^+] \quad (4)$$

Considering eqns. 2, 3 and 4, we have

$$[\text{C}_3] = \frac{k_3 K_1 K_2 [\text{C}_1][\text{A}][\text{H}^+]}{(k_{-3} + k_4[\text{BrO}_3^-])[\text{Cl}^-]} \quad (5)$$

The total concentration of Ir(III) *i.e.* $[\text{Ir(III)}]_{\text{T}}$ can be written as

$$[\text{Ir(III)}]_{\text{T}} = [\text{C}_1] + [\text{C}_2] + [\text{C}_3] \quad (6)$$

By eqns. 3, 5 and 6, we have

$$[\text{Ir(III)}]_{\text{T}} = [\text{C}_1] + \frac{K_1[\text{C}_1]}{[\text{Cl}^-]} + \frac{k_3 K_1 K_2 [\text{C}_1][\text{A}][\text{H}^+]}{(k_{-3} + k_4[\text{BrO}_3^-])[\text{Cl}^-]}$$

$$\text{or} \quad [\text{C}_1] = \frac{[\text{Ir(III)}]_{\text{T}}(k_3 + k_4[\text{BrO}_3^-])[\text{Cl}^-]}{(k_{-3} + k_4[\text{BrO}_3^-])(K_1 + [\text{Cl}^-]) + k_3 K_1 K_2 [\text{A}][\text{H}^+]} \quad (7)$$

Considering eqns. 1, 5 and 7 and on solving with assumption $k_4 [\text{BrO}_3^-] \gg k_3$ and $(k_4 [\text{BrO}_3^-] + k_3)$

$(K_1 + [\text{Cl}^-]) \gg k_3 K_1 K_2 [\text{A}] [\text{H}^+]$, we have

$$-\frac{d[\text{BrO}_3^-]}{dt} = \frac{k_3 K_1 K_2 [\text{Ir(III)}]_{\text{T}} [\text{A}][\text{H}^+]}{K_1 + [\text{Cl}^-]} \quad (8)$$

Further, total concentration of A *i.e.* $[\text{A}]_{\text{T}}$ can be written as

$$[\text{A}]_{\text{T}} = [\text{A}] + [\text{A}^+\text{H}] \quad (9)$$

By eqn. 4 and 9, we have

$$[\text{A}] = \frac{[\text{A}]_{\text{T}}}{1 + K_2[\text{H}^+]} \quad (10)$$

By considering eqns. 8 and 10, we have

$$-\frac{d[\text{BrO}_3^-]}{dt} = \frac{k_3 K_1 K_2 [\text{Ir(III)}]_{\text{T}} [\text{A}]_{\text{T}} [\text{H}^+]}{(K_1 + [\text{Cl}^-])(1 + K_2[\text{H}^+])} \quad (11)$$

TABLE-2
EFFECT OF VARIATION OF IONIC STRENGTH (μ), [Hg(OAc)₂] AND [KCl] ON REACTION RATE AT 30 °C

[KCl] × 10 ² (mol dm ⁻³)	[Hg(OAc) ₂] × 10 ³ (mol dm ⁻³)	[μ] × 10 ² (mol dm ⁻³)	[(-dc/dt)] × 10 ⁷ (mol dm ⁻³ s ⁻¹)	
			MA	EA
0.10	4.00	3.55	3.08	2.86
0.25	4.00	3.55	2.41	1.88
0.50	4.00	3.55	2.06	1.62
1.00	4.00	3.55	1.54	0.98
1.50	4.00	3.55	1.02	0.44
0.25	1.00	4.30	0.82 ^a	1.88
0.25	3.00	4.30	0.81 ^a	1.84
0.25	6.00	4.30	0.80 ^a	1.81
0.25	8.00	4.30	0.79 ^a	1.87
0.25	10.00	4.30	0.81 ^a	1.83
0.25 ^b	4.00	2.55	2.10	1.64
0.25 ^b	4.00	5.05	2.01	1.61
0.25 ^b	4.00	9.05	2.05	1.64
0.25 ^b	4.00	12.05	2.04	1.62
0.25 ^c	4.00	3.55	1.08	0.76
0.25 ^c	4.00	3.55	1.52	1.28
0.25 ^c	4.00	3.55	2.28	2.08
0.25 ^c	4.00	3.55	3.44	2.86

[KBrO₃] = 10.00 × 10⁻⁴ mol dm⁻³, [MA] = [EA] = 3.00 × 10⁻² mol dm⁻³,

[Ir(III)] = 1.17 × 10⁻⁶ mol dm⁻³ [MA] and 1.96 × 10⁻⁶ mol dm⁻³ [EA],

[HClO₄] = 0.50 × 10⁻² mol dm⁻³ [MA] and 1.00 × 10⁻² mol dm⁻³ [EA],

a = [MA] = 1.00 × 10⁻² mol dm⁻³; b = [MA] = [EA] = 2.50 × 10⁻² mol dm⁻³

c = [MA] = [EA] = 2.00 × 10⁻² mol dm⁻³

The rate law (11) explains all the kinetic results. Hence proposed mechanism is valid.

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