

Mechanism of Ir(III) Catalysis in Potassium Bromate Oxidation of Amines in Acidic Medium

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ABSTRACT: Kinetic studies of oxidation of methyl amine (MA) and ethyl amine (EA) by potassium bromate in presence of iridium (III) chloride as catalyst in perchloric acid and mercuric acetate as Br⁻ ions scavenger have been carried out. The results indicate zero-order kinetics with respect to potassium bromate and first-order kinetics in both amines. First-order kinetics in [Ir (III)] was also observed. The reaction rate increased on increasing the [HClO₄] but addition of various amounts of KCl decreased the rate. Zero effect of addition of mercuric acetate showed that role of mercuric acetate is limited to Br⁻ ion scavenger only. Negligible effect of variation of ionic strength of the medium was observed. A suitable mechanism consistent with the observed kinetic data is proposed.

INTRODUCTION

Potassium bromate with redox potential¹ 1.44 V is a powerful oxidizing agent and it has been used in the oxidation of many organic substrates^{2,3}. Apart from its action as oxidant, potassium bromate has also been used as a source of bromine in the presence of bromide ions. Bromine thus produced in bromate oxidation sets the parallel oxidation of the substrate. Hence in order to eliminate the parallel Br₂ oxidation and to ensure pure bromate oxidation, the product bromide ion has been scavenged by mercuric acetate⁴⁻⁶. The use of transition metal ions⁷⁻¹³ such as Os(VIII), Ru(III), Ru(VIII), Ir(III), Pd(II) and Rh(III) as homogeneous catalysts in the oxidation of several organic substrates by different oxidants has generated greater interest in the industries. However, the reaction involving iridium(III) as homogeneous catalyst^{14,15} have not been much investigated. In view of importance of potassium bromate as a mild oxidant and role of Ir(III) as catalyst, an attempt has been made to study the kinetics of Ir(III)-catalysed oxidation of methyl amine and ethyl amine by acidic solution of potassium bromate.

EXPERIMENTAL

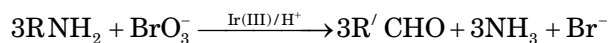
All reagents were of the highest purity available. The reagents employed were KBrO₃, methyl amine, ethyl amine, NaClO₄, HClO₄, KCl (all of E. Merck). Mercuric acetate (E. Merck) and iridium(III) chloride (Johnson and Matthey) and all other reagents of A.R. grade were used. Solution of all the reagents were prepared in doubly distilled water. The solution of catalyst IrCl₃ was prepared by dissolving the sample in 0.01 M HCl solution.

The reactants i.e. KBrO₃, Ir(III), HClO₄, Hg(OAc)₂ and KCl were mixed in a black coated conical flask and thermostated at 308 K for thermal equilibrium. A measured amount of solution of methyl amine or ethyl amine, also equilibrated at the same temperature, was rapidly the reaction was monitored by estimating the unreacted KBrO₃ iodometrically.

Stoichiometry and Product Identification

Various sets of reactions were performed with different sets of [KBrO₃] : [Amine] ratios under the kinetic condition for 72 hours. Estimation of unreacted KBrO₃ revealed that for the oxidation of 3 moles of each amine, one mole of KBrO₃ was required and accordingly stoichiometric equation are as follows :

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Where R stands for $-\text{CH}_3$ and $-\text{C}_2\text{H}_5$ in methyl amine and ethyl amine respectively and R' stands for $-\text{H}$ and $-\text{CH}_3$ in oxidation product of methyl amine and ethyl amine respectively.

Thus corresponding aldehyde, NH_3 and Br^- ions were confirmed as oxidation products of the amines.

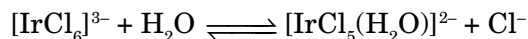
KINETIC RESULTS AND DISCUSSION

In kinetics of Ir(III) catalysed oxidation of methyl amine (MA) and ethyl amine (EA) by acidic solution of potassium bromate was investigated at several initial concentrations of reactants at 30 °C. The rate of the reaction ($-\text{dc}/\text{dt}$) did not significantly change on increasing $[\text{KBrO}_3]$, indicating zero-order with respect to $[\text{KBrO}_3]$. At constant experimental conditions, the initial rate ($-\text{dc}/\text{dt}$) increases in direct proportionality with increase in initial concentrations of both amines i.e. MA and EA, showing first-order kinetics with respect to both $[\text{MA}]$ and $[\text{EA}]$. The first-order in $[\text{Amines}]$. The straight line (Fig. 1) passing through origin confirms first-order dependence on $[\text{Amines}]$. The rate of the reaction ($-\text{dc}/\text{dt}$) also increases linearly with increase in initial $[\text{Ir(III)}]$, indicating first-order in $[\text{Ir(III)}]$ in oxidation of both amines. k_{obs} i.e. first-order rate constant obtained from the slope of the straight line of the plot of ($-\text{dc}/\text{dt}$) vs. $[\text{Ir(III)}]$ (fig. 2) closely resembles with k_{obs} calculated from $(-\text{dc}/\text{dt}) / [\text{Ir(III)}]$ in oxidation of both MA and EA. This further proves and confirms first-order kinetics with respect to $[\text{Ir(III)}]$ (Table 1).

Table 2 contains the effect of variation of $[\text{HClO}_4]$, $[\text{KCl}]$ and temperature. The rate of the reaction increases with increase in $[\text{HClO}_4]$, indicating positive effect of $[\text{H}^+]$ on the rate. Increased in $[\text{KCl}]$ decreases the rate, showing negative effect of variation of $[\text{Cl}^-]$ on the rate of reaction. The value of energy of activation (E_a) was calculated from the rate measurements at 25, 30, 35 and 40 °C. E_a was found to be 16.16 K Cal/mole and 18.32 k Cal/mole for the oxidation of methyl amine and ethyl amine respectively. Variation of ionic strength from 2.05×10^{-2} M to 12.05×10^{-2} in case of MA and from 2.55×10^{-2} M to 10.00×10^{-2} M in case of EA was found to have no change in rate of the reaction significantly, indicating negligible effect of ionic strength (m). Successive addition of

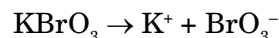
mercuric acetate from 1.00×10^{-3} M to 10.00×10^{-3} M did not bring about any significant change in the rate of oxidation of both amines i.e. MA and EA, which indicates that mercuric acetate does not act here as co-catalyst but its role is limited to Br^- ions scavenger.

In acidic medium Ir(III) chloride is reported^{16,17} to exist as $[\text{IrCl}_6]^{3-}$ and this species is involved in the following equilibrium.



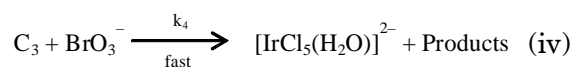
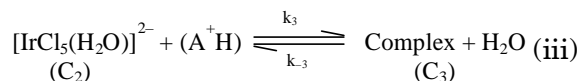
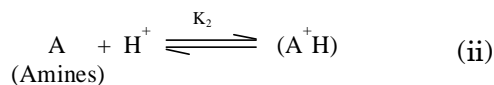
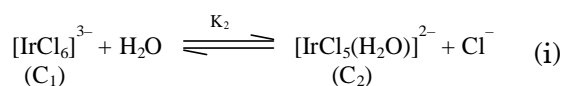
Thus either $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ or $[\text{IrCl}_6]^{3-}$ may act as effective catalytic species in acidic medium. Negative effect $[\text{Cl}^-]$ on reaction rate suggests that $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ is the real catalytic species of Ir(III) in acidic medium, which is also supported by earlier worker¹⁸. Hence in the present studies $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ has been taken as reactive catalytic species.

KBrO_3 has been reported¹⁹ to act as oxidant in acidic solutions. It ionizes in acidic medium as



BrO_3^- ion as such has been reported²⁰ to participate as oxidizing species. Therefore in the present reaction also BrO_3^- has been taken as oxidizing species, although it matter little if other species are also involved as it will participate in fast step after slow and rate determining step because of zero-order observed in $[\text{BrO}_3^-]$.

Considering BrO_3^- ions and $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ as the real oxidizing and catalytic species and other similar kinetic results in case of oxidation of methyl amine and ethyl amine. The following mechanistic steps are suggested for the oxidation of both amines (A) by KBrO_3 .



The rate of the reaction i.e. rate of formation of products (P) i.e. $\frac{d[P]}{dt}$ may be expressed as equation (1)

$$\frac{d[P]}{dt} = k_4 [C_3] [BrO_3^-] \quad (1)$$

but,
$$-\frac{d[BrO_3^-]}{dt} = \frac{d[P]}{dt}$$

hence,
$$-\frac{d[BrO_3^-]}{dt} = k_4 [C_3] [BrO_3^-] \quad (2)$$

By applying chemical equilibrium to steps (i) and (ii), we have C_2 as equation (3) and $[A+H]$ as equation (4) respectively

$$[C_2] = \frac{K_1 [C_1]}{[Cl^-]} \quad (3)$$

$$[A+H] = K_2 [A] [H^+] \quad (4)$$

By Applying steady state treatment to $[C_3]$ and considering equation (3) and (4), we have equation (5) after assuming $k_4 [BrO_3^-] \gg k_3$ as step (iv) is fast

$$[C_3] = \frac{k_3 K_1 K_2 [A][H^+][C_1]}{k_4 [BrO_3^-][Cl^-]} \quad (5)$$

On substituting the value of $[C_3]$ in equation (2), we have

$$-\frac{d[BrO_3^-]}{dt} = \frac{k_3 K_1 K_2 [C_1][A][H^+]}{[Cl^-]} \quad (6)$$

Total concentration of A i.e. $[A]_T$ can be written as

$$[A]_T = [A] + [A+H] \quad (7)$$

Considering equation (4) and (6) and solving for $[A]$, we have

$$[A] = \frac{[A]_T}{1 + K_2 [H^+]} \quad (8)$$

The total concentration of iridium (III) i.e. $[Ir(III)]_T$ can be written as equation (9).

$$[Ir(III)]_T = [C_1] + [C_2] + [C_3] \quad (9)$$

By substituting the values of $[C_2]$ and $[C_3]$ from equations (3) and (5) in equation (9) and further

solving for $[C_1]$, we have equation (10) with assumption of inequality $k_4 [BrO_3^-] (K_1 + [Cl^-]) \gg k_3 K_1 K_2 [A] [H^+]$

$$[C_1] = \frac{[Ir(III)]_T [Cl^-]}{(K_1 + [Cl^-])} \quad (10)$$

By considering equation (6), (8) and (10) together, the final rate law may be

$$-\frac{d[BrO_3^-]}{dt} = \frac{k_3 K_1 K_2 [Ir(III)]_T [A]_T [H^+]}{(K_1 + [Cl^-]) + K_1 K_2 [H^+] + K_2 [H^+] [Cl^-]} \quad (11)$$

On assuming $(K_1 + [Cl^-]) + K_1 K_2 [H^+] \gg K_2 [H^+] [Cl^-]$

Equation (11) can be written as equation (12)

$$-\frac{d[BrO_3^-]}{dt} = \frac{k_3 K_1 K_2 [Ir(III)]_T [Amines]_T [H^+]}{(K_1 + [Cl^-]) + K_1 K_2 [H^+]} \quad (12)$$

The rate law (12) is in complete agreement with all the observed kinetic results.

Table 1
Effect of Variation of [reactants] on the rate of oxidation of methyl amine (MA) and ethyl amine (EA) by $KBrO_3$ using Ir(III) as catalyst at 30 °C

$[Hg(OAc)_2] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[HClO_4] = 0.50 \times 10^{-2} \text{ (MA)}$ and $1.00 \times 10^{-2} \text{ (EA) mol dm}^{-3}$, $[KCl] = 0.25 \times 10^{-2} \text{ mol dm}^{-3}$

$[KBrO_3] \times 10^4$ mol dm ⁻³	$[Ir(III)] \times 10^6$ mol dm ⁻³	$[Amine]$ $\times 10^2$ mol dm ⁻³	$[-dc/dt] \times 10^7$ mol dm ⁻³ s ⁻¹		
	(MA)	(EA)	(MA)	(EA)	
4.00	1.17	1.96	2.00	1.56	1.25
5.00	1.17	1.96	2.00	1.58	1.26
10.00	1.17	1.96	2.00	1.58	1.28
12.50	1.17	1.96	2.00	1.52	1.23
20.00	1.17	1.96	2.00	1.58	1.27
25.00	1.17	1.96	2.00	1.55	1.25
10.00	1.17	1.96	0.50	0.41	0.31
10.00	1.17	1.96	1.00	0.80	0.66
10.00	1.17	1.96	1.50	1.23	1.03
10.00	1.17	1.96	2.00	1.58	1.28
10.00	1.17	1.96	2.50	2.06	1.64
10.00	1.17	1.96	3.00	2.41	1.88
12.50	0.59	0.98	2.00	0.74	0.64
12.50	1.17	1.96	2.00	1.52	1.23
12.50	2.34	3.92	2.00	3.00	2.52
12.50	3.51	5.88	2.00	4.58	3.76
12.50	4.68	7.84	2.00	6.16	5.08
12.50	5.85	9.80	2.00	7.68	6.28

Table 2
Effect of Variation of $[\text{HClO}_4]$, $[\text{KCl}]$ and temperature on the rate of oxidation of amines by KBrO_3 using Ir(III) as catalyst at 30°C (unless otherwise stated)

$[\text{KBrO}_3] = 10.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Ir(III)}] = 1.17 \times 10^{-7}$ (MA) and 1.96×10^{-7} (EA) mol dm^{-3} , $[\text{Amine}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Unless otherwise stated) and $[\text{Hg}(\text{OAc})_2] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}$

[Temperature] $^\circ\text{C}$	$[\text{HClO}_4] \times 10^2$ mol dm^{-3}	$[\text{KCl}] \times 10^2$ mol dm^{-3}	$[-dc/dt] \times 10^7$ $\text{mol dm}^{-3} \text{ s}^{-1}$	
			(MA)	(EA)
30	0.50	0.25	1.58	0.88
30	1.00	0.25	1.98	1.28
30	1.50	0.25	2.46	1.52
30	2.00	0.25	2.92	2.02
30	2.50	0.25	3.22	2.34
30	3.00	0.25	3.72	2.56
30	0.50	0.10 ^a	3.08	2.86 ^b
30	0.50	0.25 ^a	2.41	1.88 ^b
30	0.50	0.50 ^a	2.06	1.62 ^b
30	0.50	0.75 ^a	1.78	1.30 ^b
30	0.50	1.00 ^a	1.54	0.98 ^b
30	0.50	1.25 ^a	1.28	0.70 ^b
30	0.50	1.50 ^a	1.02	0.44 ^b
25	0.50	0.25	1.08	0.76 ^b
35	0.50	0.25	2.28	2.08 ^b
40	0.50	0.25	3.44	2.86 ^b

a \rightarrow $[\text{Methyl amine}] = [\text{Ethyl amine}] = 3.00 \times 10^{-2} \text{ mol dm}^{-3}$

b \rightarrow $[\text{HClO}_4] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Ethyl amine)

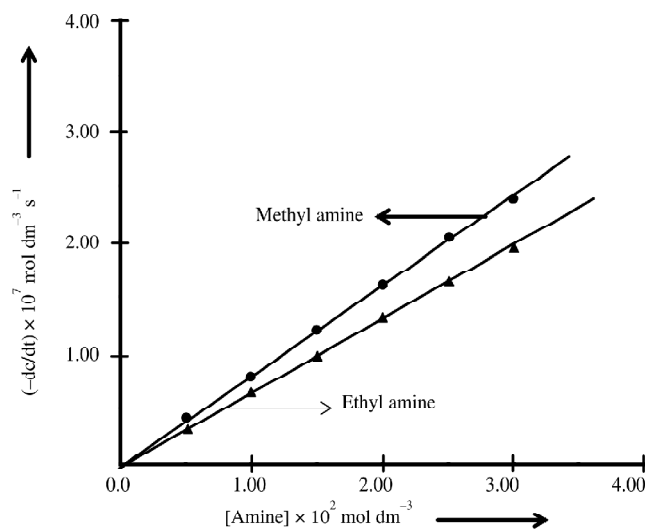


Figure 1: Plot of $(-dc/dt)$ vs. $[\text{Amine}]$ at 30°C under the condition of Table 1

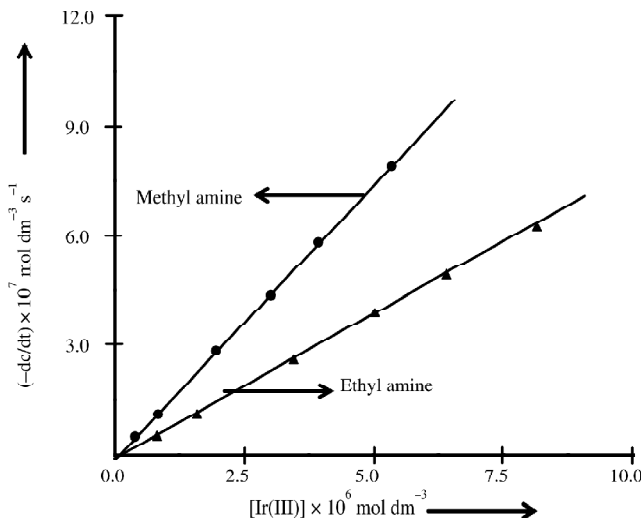


Figure 2: Plot of $(-dc/dt)$ vs. $[\text{Ir(III)}]$ at 30°C under the condition of Table 1

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