Kinetic Studies of Oxidation of D-Mannose by Potassium Bromate in Aqueous Perchloric Acid Medium Catalyzed by Ir(III)

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The kinetics of iridium(III) catalyzed oxidation of D-mannose by potassium bromate in aqueous perchloric acid medium has been studied. The reaction rate shows first-order dependence on $KBrO_3$ and Ir(III). Zero-order kinetics with respect to D-mannose, negative effect to the medium *i.e.* [H+]. There is insignificant effect of ionic strength (μ), (P.T.S.) and KCl, $Hg(OAc)_2$ on the reaction rate. Elevation of temperature increases the rate of reaction in oxidation of reducing sugar. The activation parameters have been calculated. Mechanism consistent with the above kinetic results has been suggested.

$$\text{Rate} = \frac{a[BrO_3^-][Ir(III)]_T}{b[H^+] + k_d(K_1 + [Cl^-])}$$

Key Words: Oxidation, D-Mannose, Potassium bromate, Ir(III) catalyst, Kinetics and mechanism, Acidic medium.

INTRODUCTION

Most of the works in connection with the kinetics of oxidation of reducing sugars have been done by halogens[1,2] in alkaline and acidic media as oxidizing agents. Ingels and Israel[3] have studied the kinetics of oxidation of simple monosaccharides as well as disaccharides by alkaline hypo iodide. Isbell and co-workers[4], while studying the kinetics of oxidation of different anomeric pairs of aldoses with aqueous bromine, found in general that β-forms react faster. The systematic studies of the kinetics of oxidation of D-glucose, D-galactose, D-fructose, L-arabinose and D-xylose by cupric tartrate and cupric citrate in presence of NaOH were made by Singh *et al.*[5].

Earlier, potassium bromate has been used as an oxidant for a variety of compounds in acidic medium[6,7] and sometimes in the presence of catalyst[8,9]. Although kinetic studies involving potassium bromate as oxidant has been made for iridium(III) catalyzed reaction. To our best of knowledge there is no report on Ir(III) catalysis in oxidation involving

potassium bromate is known. In present studies, the kinetics and mechanism of Ir(III) catalysis of potassium bromate oxidation of D-mannose in perchloric acid media have been carried out.

EXPERIMENTAL

All chemicals were of AR grade and doubly distilled water was used throughout. The stock solution of potassium bromate (E. Merk) was prepared by dissolving its weighed amount in doubly distilled water and its strength was checked by estimating it iodometrically using starch as an indicator. Iridium(III) chloride (Johnson-Matthey) solution was prepared by dissolving the sample in hydrochloric acid of known strength[10]. The reagents employed was D-mannose (E. Merck) and perchloric acid (E. Merck) was prepared by dissolving its weighed amount in double distilled water.

All the kinetic measurements were carried out at constant temperature (± 0.1ºC). The reaction was initiated by rapid addition of potassium bromate to the reaction mixture, containing appropriate quantities of D-mannose, perchloric acid, iridium(III) chloride, water and mixing them by vigorous shaking. The progress of the reaction was monitored by estimating the amount of unconsumed potassium bromate at regular time intervals iodometrically.

Stoichiometry and product analysis: Various set of reactions were carried out with different [KBrO$_3$]:[Sugar] ratios under [KBrO$_3$] >> [Sugar] conditions for 72 h. Estimation of unreacted KBrO$_3$ revealed that for the oxidation of each mole of sugar one mole of KBrO$_3$ was required. The stoichiometric equation is as follows :

$$C_6H_{12}O_6 + BrO_3^- \rightarrow BrO_2^- + C_5H_{11}COOH$$
$$\quad (S) \qquad\qquad\qquad\qquad (S'COOH)$$
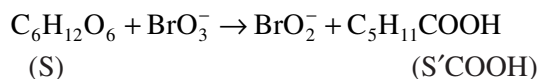
where S is mannose and S'COOH stands for the corresponding acids *i.e.* mannonic acid respectively. The product mannonic acid was detected and estimated gravimetrically[11].

RESULTS AND DISCUSSION

The kinetic investigation were carried out at several initial concentrations of reactants. The reaction followed first-order kinetic with respect to potassium bromate (Fig. 1) and iridium(III) chloride (Fig. 2). The reaction shows zero-order kinetics with respect to D-mannose (Table-1). The reaction shows negative effect with respect to perchloric acid medium. The results of variation of ionic strength (μ) of the medium affected by the ammounts of (NaClO$_4$), addition of KCl and Hg(OAc)$_2$ indicate that there is almost negligible effect of (μ), (Cl$^-$) and Hg(OAc)$_2$ on k$_{obs}$ (Table-2).
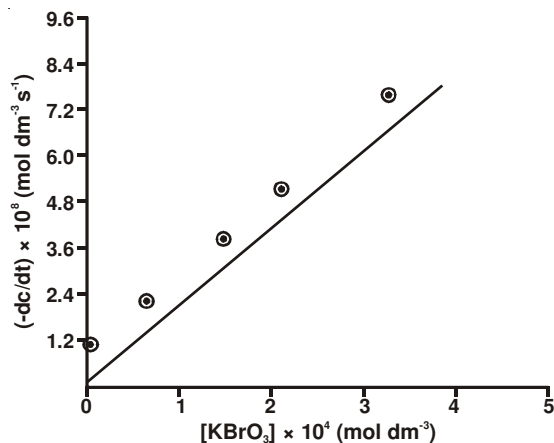
Fig. 1. Variation of oxidant $KBrO_3$ at 35ºC; [D-mannose] = 1.50×10^{-3} mol dm^{-3}
[$HClO_4$] = 1.00×10^{-3} mol dm^{-3} [Ir(III)] = 1.00×10^{-7} mol dm^{-3}
[KCl] = 0.50×10^{-3} mol dm^{-3} [$Hg(OAc)_2$] = 2.00×10^{-4} mol dm^{-3}
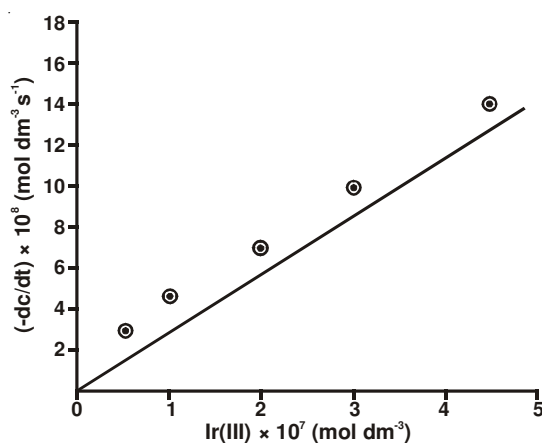
Fig. 2. Variation of catalyst Ir(III) at 35ºC; [D-mannose] = 1.50×10^{-3} mol dm^{-3}
[$KBrO_3$] = 2.50×10^{-4} mol dm^{-3} [$HClO_4$] = 1.00×10^{-3} mol dm^{-3}
[KCl] = 0.50×10^{-3} mol dm^{-3} [$Hg(OAc)_2$] = 2.00×10^{-4} mol dm^{-3}

It is also seen that on variation of ionic strength (μ), KCl and $Hg(OAc)_2$, the rate of reaction does not change (Table-2) showing negligible effect of these reagents.

The reaction were carried out at 30, 35, 40 and 45ºC and results at these temperatures led to compute energy of activation ($E_a^\#$), entropy of activation ($\Delta S^\#$) and free energy of activation ($\Delta G^\#$) for the title reactions (Table-3).

TABLE-1
EFFECT OF VARIATION OF [H$^+$], [KBrO$_3$], [D-MANNOSE] AND
CATALYST ON REACTION RATE CONSTANT AT T = 35ºC
[KCl] = 0.50 × 10^{-3} mol dm^{-3} [Hg(OAc)$_2$] = 2.00 × 10^{-4} mol dm^{-3}

[D-Mannose] × 10^3 (mol dm^{-3})	[KBrO$_3$] × 10^4 (mol dm^{-3})	[HClO$_4$] × 10^3 (mol dm^{-3})	[Ir(III)] × 10^7 (mol dm^{-3})	(-dc/dt) × 10^8 (mol dm^{-3} s^{-1})	k$_1$ × 10^4 (s^{-1})
1.50	0.50	1.00	1.00	0.56	1.40
1.50	1.50	1.00	1.00	1.70	1.41
1.50	2.50	1.00	1.00	2.80	1.40
1.50	3.50	1.00	1.00	3.98	1.42
1.50	5.00	1.00	1.00	5.60	1.40
0.50	2.50	1.00	1.00	2.80	1.40
1.50	2.50	1.00	1.00	2.82	1.41
2.50	2.50	1.00	1.00	2.83	1.41
3.50	2.50	1.00	1.00	2.86	1.43
5.00	2.50	1.00	1.00	2.84	1.42
1.50	2.50	1.00	1.00	2.80	1.40
1.50	2.50	1.50	1.00	2.45	1.22
1.50	2.50	2.50	1.00	2.20	1.10
1.50	2.50	3.50	1.00	2.00	1.00
1.50	2.50	5.00	1.00	1.90	0.95
1.50	2.50	1.00	1.50	4.18	2.78
1.50	2.50	1.00	2.50	6.98	2.79
1.50	2.50	1.00	3.50	9.84	2.81
1.50	2.50	1.00	5.00	14.00	2.80

TABLE-2
EFFECT OF IONIC STRENGTH, Cl$^-$, Hg(OAc)$_2$ AND TEMPERATURE
[KBrO$_3$] = 2.50 × 10^{-4} mol dm^{-3} [D-mannose] = 1.50 × 10^{-3} mol dm^{-3}
[HClO$_4$] = 1.00 × 10^{-3} mol dm^{-3} [Ir(III)] = 1.00 × 10^{-7} mol dm^{-3}

Temp. (ºC)	Ionic strength (μ) × 10^2 (mol dm^{-3})	[KCl] × 10^3 (mol dm^{-3})	[Hg(OAc)$_2$] × 10^4 (mol dm^{-3})	(-dc/dt) × 10^8 (mol dm^{-3} s^{-1})
	0.26	0.50	2.00	2.80
	0.76	0.50	2.00	2.79
35	1.26	0.50	2.00	2.81
	1.76	0.50	2.00	2.83
	2.26	0.50	2.00	2.85
	0.26	1.00	2.00	2.78
	0.26	2.00	2.00	2.82
35	0.26	3.00	2.00	2.76
	0.26	4.00	2.00	2.84
	0.26	5.00	2.00	2.72

Temp. (°C)	Ionic strength (μ) $\times 10^2$ (mol dm^{-3})	[KCl] $\times 10^3$ (mol dm^{-3})	[Hg(OAc)$_2$] $\times 10^4$ (mol dm^{-3})	(-dc/dt) $\times 10^8$ (mol dm^{-3} s^{-1})
	0.26	0.50	0.50	2.78
	0.26	0.50	1.00	2.76
35	0.26	0.50	1.50	2.79
	0.26	0.50	2.00	2.80
	0.26	0.50	2.50	2.84
30	0.26	0.50	2.00	2.02
40	0.26	0.50	2.00	4.36
45	0.26	0.50	2.00	5.82

TABLE-3
THERMODYNAMIC PARAMETERS

$E_a^{\#}$ (kJ mol^{-1})	log A	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
54.04	5.32	51.48	-35.04	62.07

Considering reactive species of potassium bromate and Ir(III) chloride as BrO_3^- ions and $[IrCl_5(H_2O)]_2^-$, respectively along with all other kinetic effects, the following reaction mechanism is suggested where S stands for sugar undertaken here.

$$[IrCl_6]^{3-} + H_2O \xrightleftharpoons{K_1} [IrCl_5(H_2O)]_2^- + Cl^- \qquad (i)$$
$$(C_1) \qquad\qquad (C_2)$$

$$[IrCl_5(H_2O)]^{2-} + BrO_3^- \xrightleftharpoons[k_{-2}]{k_2} \left[\begin{array}{c} O\diagdown \\ Br\diagdown O \\ IrCl_5 \diagdown \\ O-H \end{array} \right] + H^+ \qquad (ii)$$
$$(C_2) \qquad\qquad\qquad\qquad (C_3)$$

$$[Ir(Cl_5)(OH)(BrO_3)]^{4-} + H_2O \xrightarrow{k_d slow} [IrCl_5(H_2O)(BrO_3)]^{3-} + OH^- \qquad (iii)$$
$$(C_3) \qquad\qquad\qquad\qquad (C_4)$$

$$C_1 + S \xrightarrow{k_3 fast} [IrCl_5(H_2O)^{2-} + BrO^{2-} + Product \qquad (iv)$$
$$(X)$$

$$H^+ + OH^- \rightarrow H_2O \qquad (v)$$
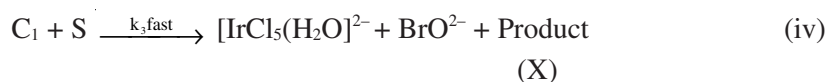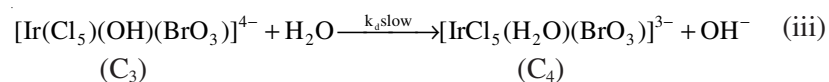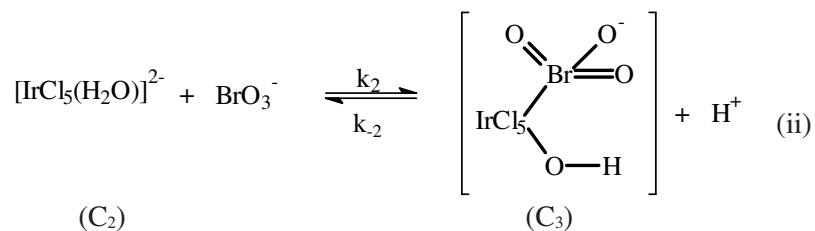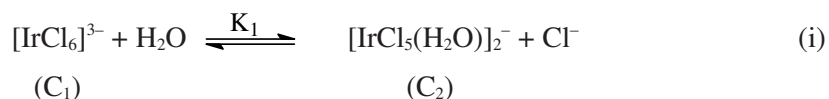
where X is corresponding acid as product.

Considering the above reaction steps, the rate of the reaction can be written in terms of loss of concentration of bromate ion with time *i.e.*

$$\left(\frac{-d[BrO_3^-]}{dt}\right) \text{ as eqn. 1}$$

$$\frac{-d[BrO_3^-]}{dt} = k_d[C_3] \tag{1}$$

Considering steady state approximation for $[C_3]$ we have

$$\frac{d[C_3]}{dt} = 0 = k_2[C_2][BrO_3^-] - k_{-2}[C_3][H^+] - k_d[C_3]$$

or, $k_{-2}[C_3][H^+] + k_d[C_3] = k_2[C_2][BrO_3^-]$

or, $[C_3](k_{-2}[H^+] + k_d) = k_2[C_2][BrO_3^-]$

or, $[C_3] = \dfrac{k_2[BrO_3^-][C_2]}{(k_{-2}[H^+] + k_d)} \tag{2}$

Considering step (i), we have

or, $K_1 = \dfrac{[C_2][Cl^-]}{[C_1]}$

or, $[C_2] = \dfrac{K_1[C_1]}{[Cl^-]} \tag{3}$

Considering eqns. 2 and 3 we have eqn. 4

$$[C_3] = \frac{K_1 k_2[BrO_3^-][C_1]}{(k_{-2}[H^+] + k_d)[Cl^-]} \tag{4}$$

On substituting the value of $[C_3]$ from eqn. 4 in eqn. 1 we have

$$\frac{-d[BrO_3^-]}{dt} = \frac{k_d k_2 K_1[BrO_3^-][C_1]}{[Cl^-](k_{-2}[H^+] + k_d)} \tag{5}$$

Total concentration of Ir(III) chloride *i.e.* $[Ir(III)]_T$ can be written as eqn. 6

$$[Ir(III)]_T = [C_1] + [C_2] \tag{6}$$

By eqns. 3 and 6 we have

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

$$= [C_1]\left(1 + \frac{K_1}{[Cl^-]}\right)$$

$$= [C_1]\left(\frac{[Cl^-] + K_1}{[Cl^-]}\right)$$

or, $[C_1] = \dfrac{[Ir(III)]_T[Cl^-]}{K_1 + [Cl^-]} \tag{7}$

On substituting the value of $[C_1]$ from eqn. 7 in eqn. 5 we have

$$\frac{-d[BrO_3^-]}{dt} = \frac{k_d k_2 K_1 [BrO_3^-][Ir(III)]_T [Cl^-]}{[Cl^-](k_{-2}[H^+] + k_d)(K_1 + [Cl^-])}$$

or, $\quad \dfrac{-d[BrO_3^-]}{dt} = \dfrac{k_d k_2 K_1 [BrO_3^-][Ir(III)]_T}{(k_{-2}[H^+] + k_d)(K_1 + [Cl^-])}$

or, $\quad \dfrac{-d[BrO_3^-]}{dt} = \dfrac{k_d k_2 K_1 [BrO_3^-][Ir(III)]_T}{(k_{-2}K_1[H^+] + k_{-2}[H^+][Cl^-] + k_d K_1 + k_d[Cl^-])}$

or, $\quad \dfrac{-d[BrO_3^-]}{dt} = \dfrac{k_d k_2 K_1 [BrO_3^-][Ir(III)]_T}{(k_{-2}K_1[H^+] + k_d K_1 k_d[Cl^-] + k_{-2}[H^+][Cl^-])}$ (8)

On assuming $\{k_{-2}K_1[H^+] + k_d(K_1 + [Cl^-])\} \gg k_{-2}[H^+][Cl^-]$ eqn. 8 can written as eqn. 9

or $\quad \dfrac{-d[BrO_3^-]}{dt} = \dfrac{a[BrO_3^-][Ir(III)]_T}{b[H^+] + k_d(K_1 + [Cl^-])}$ (9)

where $a = k_d k_2 K_1$ and $b = k_{-2} K_1$

The rate eqn. 9 fully explains the first-order with respect to $[BrO_3^-]$ and $[Ir(III)]$, zero-order dependence on (D-mannose) and negative effect of $[H^+]$ and $[Cl^-]$ as well as insignificant effect of mercuric acetate and ionic strength (μ) of the medium, hence suggested mechanism is valid.

ACKNOWLEDGEMENT

REFERENCES

1. J.W. Green, *Adv. Carbohyd. Chem.*, **3**, 129 (1948).
2. F. Shafizadeh, *Adv. Carbohyd. Chem.*, **13**, 9 (1958).
3. O.G. Ingels and F.C. Israel, *J. Chem. Soc.*, 810 (1948).
4. H.S. Isbell and W.W. Pigman, *J. Res. Natl. Bur. Std.*, **18**, 141 (1937).
5. M.P. Singh, B. Krishna and S. Ghosh, *Z. Physik. Chem.*, **204**, 1 (1955); **205**, 285 (1956); **208**, 265 (1958).
6. V. Awasthi and A.C. Chatterji, *Z. Phys. Chem. (Leipzig)*, **245**, 154 (1990).
7. C.S. Reddy and E.V. Sundaram, *J. Indian Chem. Soc.*, **62**, 209 (1985).
8. B. Singh and R. Srivastava, *Oxid. Comm.*, **12**, 140 (1989).
9. B. Singh and S. Srivastava, *React. Kinet. Catal. Lett.*, **39**, 243 (1989).
10. J.P. Sharma, R.N.P. Singh, A.K. Singh and B. Singh, *Tetrahedron*, **42**, 2739 (1986).
11. A.I. Vogel, In Quantitative Organic Analysis, Part 3, E.L.B.S. Longman, London, p. 739 (1958).