MECHANISM OF Ir(III) CATALYSED OXIDATION OF GLYCOLIC ACID BY CERIC SULPHATE

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Oxidation of Glycolic acid by ceric sulphate was carried out in acidic medium in presence of Ir(III) chloride as catalyst. From kinetic result, it was found to be of 1st order with respect to glycolic acid and also in ceric sulphate.

KEY WORDS : Glycolic acid, Ceric sulphate, Ir(III) chloride.

INTRODUCTION

Kinetics of oxidation of Glycolic acid by acidic solution of Ce(IV) using Ir(III) chloride as a homogeneous catalyst in perchloric acid medium. The reaction shows fractional order in both glycolic acid and Ir(III) chloride and first order to zero order at high concentration of Ce(IV) solution. An inverse first order in H^+ is observed. A suitable mechanism in agreement with observed kinetics is proposed.

In the present communication an attempt has been made to study the kinetics and mechanism of oxidation of glycolic acid using Ir(III) chloride as a catalyst.

EXPERIMENTAL

Aqueous solution of glycolic acid was prepared by dissolving its desired quantity in distilled water.

The reaction was initiated by quickly adding desired volume of glycolic acid solution in the reaction vessel containing requisite volumes of perchloric acid Ir(III) chloride and other reagents, maintained at a desired temperature in a thermostatic water bath ($\pm 0.1^0$C). The progress of the reaction was monitored by estimating unconsumed $Ce(SO_4)_2$ iodometrically at the regular intervals of time till 60 to 70% of the reaction.

RESULTS & DISCUSSION

Table-1 records the reaction rate constants at different concentration of various reactants. First order dependence in Ce(IV) solution at its low concentration tends to zero order in high concentration range. Fractional order of glycolic acid is obvious from log $K_{(obs)}$ vrs log [GA] with slope 0.304 (Fig. 1).
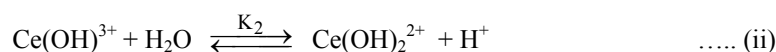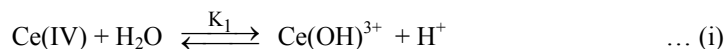
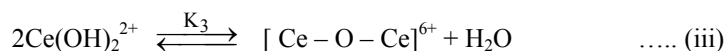**Table – 1. Effect of variation of reactants on reaction rate at 30°C.**

$Ce(SO_4)_2 \times 10$ ml^{-1} -	0.50	0.80	1.00	1.25	1.67	2.00
$(-dc/dt) \times 10^7$ ml^{-1} s^{-1}-	6.14	6.08	6.06	6.04	5.98	6.10
[GA] = 2.00×10^{-2} M, [HClO$_4$] = 10.00×10^{-1} M, Ir(III) = 7.65×10^{-6}, [KCl] = 2.00×10^{-3} M, Ce(IV) = 2.00×10^{-3} M						
$[GA] \times 10^2$ ml^{-1} -	0.25	0.50	0.75	1.00	1.50	2.00
$(-dc/dt) \times 10^7$ ml^{-1} s^{-1}-	0.74	1.52	2.24	3.06	4.62	6.10
Ce(IV) = 2.00×10^{-3} M [HClO$_4$] = 10.00×10^{-1} M Ir(III) = 7.65×10^{-6}, [KCl] = 1.00×10^{-3} M						
$Ir(III) \times 10^5$ ml^{-1} -	1.91	3.82	5.73	7.65	8.60	9.55
$(-dc/dt) \times 10^7$ ml^{-1} s^{-1}-	1.50	2.98	4.54	6.10	6.80	7.54
Ce(IV) = 2.00×10^{-3} M [GA] = 2.00×10^{-2} M [HClO$_4$] = 10.00×10^{-1} M, [KCl] = 1.00×10^{-3} M						
$[HClO_4] \times 10^2$ M -	7.50	10.00	12.50	20.00	25.00	30.00
$(-dc/dt) \times 10^7$ ml^{-1} s^{-1}-	3.76	3.93	4.46	4.96	6.14	8.12
Ce(IV) = 2.00×10^{-3} M [G.A] = 1.67×10^{-2} M Ir(III) = 7.65×10^{-6} M, [KCl] = 1.00×10^{-3} M						
$[KCl] \times 10^3$ M -	0.50	1.00	1.50	2.00	3.00	4.00
$(-dc/dt) \times 10^7$ ml^{-1} s^{-1}-	6.04	6.01	5.98	5.96	6.08	6.04
Ce(IV) = 2.00×10^{-3}M [GA] = 2.00×10^{-2} M Ir(III) = 7.65×10^{-6} M, [HClO$_4$] = 10.00×10^{-1} M						
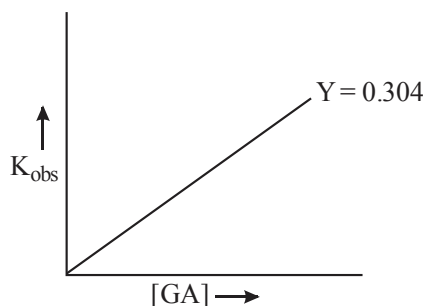
Fig. 1

The rate constant decreases linearly with [H$^+$] showing the inverse first order kinetics in [H$^+$]. Insignificant effect for successive addition of Cl$^-$ suggest that neutral molecule IrCl$_3$(H$_2$O)$_3$ is involved in reaction as catalyst species.
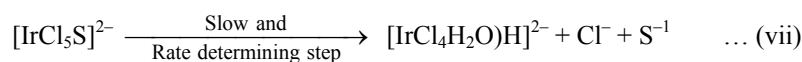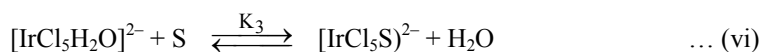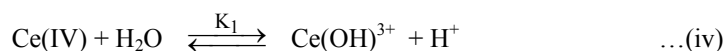
The following equilibrium are reported to exist in acidic solution of Ce(IV) :-

$$Ce(IV) + H_2O \underset{}{\overset{K_1}{\rightleftarrows}} Ce(OH)^{3+} + H^+ \qquad \dots \text{(i)}$$

$$Ce(OH)^{3+} + H_2O \underset{}{\overset{K_2}{\rightleftarrows}} Ce(OH)_2^{2+} + H^+ \qquad \dots\dots \text{(ii)}$$

$$2Ce(OH)_2{}^{2+} \xrightleftharpoons{K_3} [Ce-O-Ce]^{6+} + H_2O \qquad \ldots\ldots \text{(iii)}$$

Considering the kinetic features with respect to [H$^+$] and Ce(IV) the rate law expression obtained on the basis of H$_2$O as oxidizing species confirmed well to all observed kinetic data.

The following reaction scheme is suggested on the basis of reactive species of Ir(III) chloride, Ce(SO$_4$)$_2$ and other kinetic features in the present investigation, where *S* is written for glycolic acid and Ir(III) stands for IrCl$_3$(H$_2$O)$_3$ –

$$Ce(IV) + H_2O \xrightleftharpoons{K_1} Ce(OH)^{3+} + H^+ \qquad \ldots\text{(iv)}$$

$$Ir(III) + H_2O \xrightleftharpoons{K_2} [IrCl_5H_2O]^{2-} + Cl^- \qquad \ldots\text{(v)}$$

$$[IrCl_5H_2O]^{2-} + S \xrightleftharpoons{K_3} [IrCl_5S]^{2-} + H_2O \qquad \ldots \text{(vi)}$$

$$[IrCl_5S]^{2-} \xrightarrow[\text{Rate determining step}]{\text{Slow and}} [IrCl_4H_2O)H]^{2-} + Cl^- + S^{-1} \qquad \ldots \text{(vii)}$$

$$[IrCl_4(H_2O)H]^{2-} + Cl^- \xrightarrow{\text{Fast}} [IrCl_5(H_2O)] \qquad \ldots\text{(viii)}$$

$$S^+ + H_2O \longrightarrow \text{Product} \qquad \ldots\text{(ix)}$$
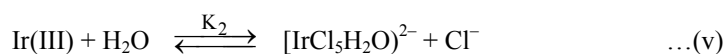
Considering the above reaction steps (iv) to (vi) of the oxidation of glycolic acid in terms of rate of loss of Ce(So$_4$)$_2$ may be written as equation (x)

$$\frac{-d[Ce(SO_4)_2]}{dt} = \frac{K'[Ce(SO_4)_2]\,Ir(III)\,[GA]}{K_3[H^+]\times K_3[GA]\times K_1[Ce(SO_4)_2] + K_2\,Ir(III) + K_1.K_2[Ce(SO_4)_2]} \qquad \ldots\text{(x)}$$

where $\qquad$ K$'$ = K$_1$, K$_2$, K$_3$

$\qquad\qquad\qquad$ K$_1$ = K$_1$/K$_{-1}$, $\quad$ K$_3$ = K$_3$/K$_{-3}$

The rate law (x) agrees fully with all kinetics observations.

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