KINETICS AND MECHANISM OF Ir (III) CHLORIDE CATALYSED OXIDATION OF ETHYL AMINE BY SODIUM META PERIODATE IN ACIDIC MEDIA

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ABSTRACT

Kinetics and mechanism of oxidation of ethyl amine catalysed by Ir(III) chloride has been investigated in perchloric acid medium in the temperature range 30-45ºC using, solution meta periode as an oxidizing agent. The individual order of oxidation for each of sodium meta periode, ethyl amine and Ir(III) chloride has been found zero, fractional and unity respectively. There is no effect on reaction rate on varying ionic strength and adding mercuric acetate. The reaction shows positive effect of hydrogen ion concentration. The activation energy and other thermodynamic parameters are determined. A probable reaction mechanism is proposed.

KEY WORDS: Ionic strength, scavenger, reactive species

In the present project an attempt will be made to investigate transition metal ion catalysed (Bajpai et al., 1991) reaction with a view and aim to suggest the mechanism of catalysed reactions which are faster route for the reactions as compared to uncatalysed reactions which are industrially not economic and thus hampered the growth of industries. A survey of literature shows that there is much scope for the study of kinetic and mechanism of transition metal catalysed oxidation of amines by sodium meta periode in the presence of acidic medium.

MATERIALS AND METHODS

The standard solutions of all the reagents of A.R. grade will be prepared. Solution of sodium meta periode, ethyl amine, potassium chloride, sodium perchlorate will be prepared by weighing the desired amount and then dissolving in doubly distilled water. Solution of Ir(III) chloride will be prepared by dissolving its 1gm sample in 0.01M solution of HCl and thereafter making its volume 1 litre in which concentration of Ir(III) chloride as well as HCl acid are $3.34 \times 10^{-7}M$ and $10^{-3}M$ respectively(Sanjeev and Kumar, 1989).

Kinetic studies will be made titrimetrically. The equivalent liberated iodine will be estimated against standard solution of sodium thiosulphate using starch as indicator. The titre value will be unused sodium metaperiodate at different time intervals. The kinetic result observed will be used to propose the reaction mechanism and hence the rate law.

RESULTS AND DISCUSSION

The results obtained from various experiments are consolidated as follows:

1. Determination of order with respect to Sodium Meta Periodate

A number of experiments have been performed at different initial concentration of sodium meta periode and at fixed concentration of all other reactants.The consolidated table for various experiments is given in Table-1.

An examination of Table-1 shows that on varying the initial concentration of solution meta periode the value of (-dc/dt) i.e. the rate of reaction is almost constant indicating that the oxidation of methyl amine follows zero order kinetics with respect to sodium meta periode.

2. Determination of order with respect to Ethyl Amine

A series of experiments have been carried out at different initial concentration of methyl amine and keeping concentration of all other reactants constant. The result obtained is consolidated in Table-2.

It is quite evident from the result of summarized Table-2 that (-dc/dt) value increases non-linearly with increasing the concentration of Ethyl amine. This show that the reaction is of fractional order with respect to ethyl amine.

3. Determination of Order with respect to Ir(III) Chloride

A number of experiments have been performed at

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different initial concentration of Ir(III) chloride and at fixed concentration of all other reactions. The consolidated table for different experiments is given in Table-3.

A close examination of kinetic data of Table-3 clearly shows that (-dc/dt) value increases at direct proportion with increase in [Ir(III)] in oxidation of ethyl amine. This suggest that the reaction follows first order kinetics with respect to Ir(III) chloride.

4. Determination of Effect of H$^+$ Concentration on Reaction Rate

Varying the concentration of perchloric acid, keeping all other reactants unchanged, a number of experiments has been carried out and obtained result is summarized in Table-4.

It seems from the result summarized in Table-4 that (-dc/dt) value increases non-linearly with increase in H$^+$ concentration, showing positive effect of H$^+$ concentration.

5. Effect of Ionic Strength of Medium on Reaction Rate

On performing various experiments with changing concentration of sodium perchlorate it is observed that there is no significant change in (-dc/dt) value, showing zero effect of ionic strength.

6. Effect of Addition of Mercuric Acetate on Reaction Rate

The experimental study shows that successive addition of mercuric acetate does not bring about any appreciable change in value of (-dc/dt). This indicates that mercuric acetate is not involved in the reaction either as co-catalyst or catalyst, conforming its role, only as I$^-$ ions scavenger.

7. Effect of Addition of KCl

Addition of KCl in the reaction mixture to study the effect of chloride ions helps to decide the reactive species of Iridium (III) chloride in acidic medium. There is negligible effect of addition of KCl on rate.

## 8. Effect of Temperature on Reaction Rate

In order to determine the effect of temperature the reaction has been carried out on range of temperature from 30 to 45ºC. The experimental results are given in Table-5.

It is clear from above consolidated result that increase in temperature increases the value of (-dc/dt) i.e. increase in reaction rate. Thus, increase in temperature has

significant effect on the rate of reaction.

The calculated value of energy of activation is 56.13 kJ/mol. The entropy of activation is negative.

It has been reported that in acidic solution Ir(III), chloride exists as $[IrCl_6]^{3-}$ and $[IrCl_5(H_2O)]^{2-}$ takes only a few seconds according to the following equilibrium.

$$[IrCl_6]^{3-} + H_2O \rightleftharpoons [IrCl_5(H_2O)]^{2-} + Cl^-$$
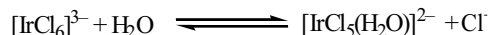
Thus $[IrCl_5(H_2O)]^{2-}$ might be assumed to be reactive species of Iridium (III) chloride (Singh and Singh, 2003).

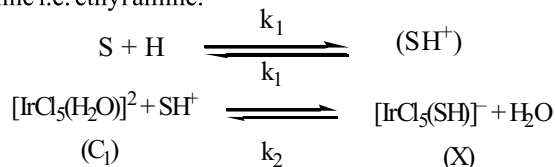Sodium meta periodate is a strong electrolyte, which gives iodate ions as given below in aqueous solution.
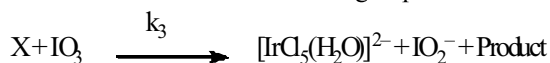
$$NaIO_4 \rightleftharpoons Na^+ + HIO^{4-}$$

$$IO_4^- \longrightarrow IO_3^- + O$$

$$IO_3^- \longrightarrow IO_2^- + O$$
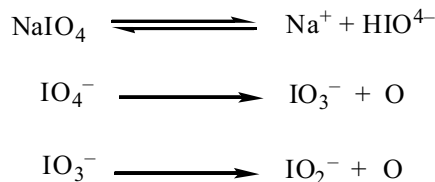
Iodate ions thus present in the aqueous solution takes up a proton to form HIO$_3$ as follows:

$$IO_3^- + H^+ \rightleftharpoons HIO_3$$

Thus in acidic medium, sodium meta periodate participates in the reaction in the form of HIO$_3$(Swarnallakshmi et al., 1987). Estimation of unconsumed [NaIO$_4$] revealed that one mole of NaIO$_4$ were consumed for one mol of ethyl amine. Considering the reactive species, the following reaction mechanism is suggested where S is written for reducing amine i.e. ethyl amine.

$$S + H \underset{k_1}{\overset{k_1}{\rightleftharpoons}} (SH^+)$$

$$[IrCl_5(H_2O)]^{2} + SH^+ \underset{k_2}{\rightleftharpoons} [IrCl_5(SH)]^- + H_2O$$
$$(C_1) \qquad\qquad\qquad (X)$$

Forward reaction is rate determining step and slow.

$$X + IO_3 \overset{k_3}{\longrightarrow} [IrCl_5(H_2O)]^{2-} + IO_2^- + Product$$

Taking into consideration above mechanism the rate law calculated as –

$$\frac{d[NaIO_4]}{dt} = \frac{k_1\,k_2\,S_T\,H\,C_{1\,T}}{1\;\; k_1\,H \;\; k_1\,k_2\,S_T\,H}$$

The derived rate law fully explains the observed kinetics i.e.

zero order with respect to oxidant i.e. $NaIO_4$, first order with respect to Ir(III) chloride, positive effect of $[H^+]$ and fractional order with respect to substrate i.e. ethyl amine. Hence the proposed mechanism is valid(Chaturvedi, 2007).

Table 1: Determination of order with respect to Sodium Meta Periodate

$[C_2H_5NH_2] = 8.00 \times 10^{-2}$ mol dm^{-3}	$[HClO_4] = 1.50 \times 10^{-2}$ mol dm^{-3}
$[KCl] = 1.00 \times 10^{-2}$ mol dm^{-3}	$[Hg(OAc)_2] = 1.00 \times 10^{-3}$ mol dm^{-3}
$[Ir(III)] = 1.00 \times 10^{-6}$ mol dm^{-3}	$[NaClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}

$T = 35ºC$

$[NaClO_4] \times 10^4$ mol dm^{-3}	$[NaClO_4]^* \times 10^4$ mol dm^{-3}	$(-dc/dt) \times 10^7$ mol dm^{-3}sec^{-1}
0.27	0.19	9.28
0.35	0.22	8.86
0.45	0.30	9.10
0.57	0.43	8.84
0.95	0.82	8.96
1.00	0.94	8.86

$[NaIO_4] \rightarrow$ Concentration of $[NaIO_4]$ after 10 minute at which (-dc/dt) has been calculated

Table 2: Determination of order with respect to Ethyl Amine

$[HIO_4] = 4.00 \times 10^{-2}$ mol dm^{-3}	$[NaIO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}
$[KCl] = 1.00 \times 10^{-2}$ mol dm^{-3}	$[Hg(OAc)_2] = 1.00 \times 10^{-3}$ mol dm^{-3}
$[Ir(III)] = 1.00 \times 10^{-6}$ mol dm^{-3}	$[NaClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}

T = 35ºC

$[C_2H_5NH_2] \times 10^2$ mol dm^{-3}	$(-dc/dt) \times 10^7$ mol dm^{-3} sec^{-1}
3.00	0.80
4.50	0.94
6.00	1.28
7.50	1.44
8.50	1.81

[NaIO$_4$] $\rightarrow$ Concentration of [NaIO$_4$] after 10 minute at which (-dc/dt) has been calculated

Table 3: Determination of order with respect to Ir(III) Chloride

$[C_2H_5NH_2] = 6.00 \times 10^{-2}$ mol dm^{-3}	$[NaIO_4] = 1.00 \times 10^{-4}$ mol dm^{-3}
$[KCl] = 1.00 \times 10^{-2}$ mol dm^{-3}	$[HClO_4] = 2.00 \times 10^{-2}$ mol dm^{-3}
$[Hg(OAc)_2] = 1.00 \times 10^{-3}$ mol dm^{-3}	$[NaClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}

T = 35ºC

$[Ir(III)] \times 10^7$ mol dm^{-3}	$(-dc/dt) \times 10^7$ mol dm^{-3}sec^{-1}	$k_1 \times 10^2$ = (-dc/dt)/[Ir(III)] sec^{-1}
3.20	0.67	2.09
4.00	0.80	2.00
4.80	0.98	2.04
6.00	1.21	2.02
7.40	1.50	2.02

[NaIO$_4$]*$\rightarrow$ Concentration of [NaIO$_4$] after 10 minute at which (-dc/dt) has been calculated

Table 4: Determination of effect of H$^+$ concentration on reaction rate

$[C_2H_5NH_2] = 6.00 \times 10^{-2}$ mol dm^{-3}	$[NaIO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}
$[Ir(III)] = 1.00 \times 10^{-6}$ mol dm^{-3}	$[Hg(OAc)_2] = 1.00 \times 10^{-3}$ mol dm^{-3}
$[KCl] = 1.00 \times 10^{-2}$ mol dm^{-3}	$[NaClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}

T = 35ºC

$[HClO_4] \times 10^2$ mol dm^{-3}	$(-dc/dt) \times 10^7$ mol dm^{-3} sec^{-1}
1.00	0.45
1.50	0.62
2.00	0.75
2.50	0.97
3.00	1.17

$[NaIO_4]^* \rightarrow 0.75 \times 10^{-4}$ mol dm^{-3} after 10 minute at which (-dc/dt) has been calculated

Table-5: Effect of temperature on reaction rate

$[NaIO_4] = 1.00 \times 10^{-4}$ mol dm^{-3}	$[C_2H_5NH_2] = 6.00 \times 10^{-2}$ mol dm^{-3}
$[HClO_4] = 4.00 \times 10^{-2}$ mol dm^{-3}	$[Ir(III)] = 1.00 \times 10^{-6}$ mol dm^{-3}
$[KCl] = 1.00 \times 10^{-2}$ mol dm^{-3}	$[Hg(OAc)_2] = 1.00 \times 10^{-3}$ mol dm^{-3}
$[NaClO_4] = 1.00 \times 10^{-2}$ mol dm^{-3}	

T = 35ºC

Temperature (ºC)	$(-dc/dt) \times 10^7$ mol dm^{-3} sec^{-1}	$k_1 \times 10^4$ sec^{-1}
30	0.90	13.64
35	1.28	19.39
40	1.83	27.73
45	2.64	40.00

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