Mechanistic Aspect of Iridium(III) Catalyzed Oxidation of Ethylene Glycol by Chloramine-T in Aqueous Acidic Medium: A Kinetic Model

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Abstract

The kinetic investigation of homogeneously Ir(III) chloride catalyzed oxidation of Ethylene glycol by chloramine-T [CAT] in perchloric acid medium has been carried out in the temperature range of 30 to 45 °C. The reaction is carried out in the presence of mercuric acetate as a scavenger for chloride ion. The reaction exhibitsfirst order kinetics with respect to the oxidant [CAT] and catalyst [Ir(III)] while zero order kineticswith respect to substrate, i.e., Ethylene glycol (EG) was observed. [$Hg(OAc)_2$], [H^+] and ionic strength of the medium have negligible effect on the reaction rate. Chloride ion positively influenced the rate of reaction. The various activation parameters have been calculated from the rate measurements at different temperatures (30 to 45°C). The product of the reaction has been identified as the corresponding monocarboxylic acid. The reaction between chloramine-T and Ethylene glycol in acid medium shows 2:1 stoichiometry. On the basis of kinetic studies, reaction stoichiometry and product analysis, a suitable mechanism has been proposed and rate law has been derived.

Key Words: Kinetics, Ir(III) Catalysis , Ethylene Glycol, Chloramine-T, Acidic Medium

Introduction

The organic sulphonyl haloamines (N-haloamines), a group of mild oxidizing agents, has been extensively used for the oxidation of several organic compounds due to its diverse behavior. The versatile nature of N-haloamines is attributed to the presence of halonium cations and nitrogen anions in their structure, which can act as both a base and a nucleophile[1-5]. As a result, these compounds can react with a wide range of functional groups to cause numerous kinds of molecular changes. Sodium N-chloro-p-toluenesulfonamide or Chloramine-T (CAT; p-$CH_3C_6H_4SO_2NClNa.3H_2O$) is one of the prime members of organic halo-amine family and behaves as an oxidizing agent in both acidic and alkaline media. Depending upon the pH of the medium, it forms various oxidizing species and thus shows a variety of kinetic results[6-9]. Several researchers have studied the oxidizing behavior of CAT[10-13]and numerous studies focus on the mechanistic aspects of the redox reactions in acidic media. In most of the studies one of the species, RNHCl (R = $CH_3C_6H_4SO_2$), HOCl, or H_2OCl^+, has been considered as the reactive species[14]. It can behave as both electrophile and nucleophile depending on the reaction conditions.

A polyhydric alcohol or polyalcohol is a hydrogenated form of carbohydrate, whose carbonyl group (aldehyde or ketone, reducing suger) has been reduced to primary and secondary hydroxyl group. Glycol is widely used as a solvent, as an antifreeze agent and a raw material for synthetic vegetable oil and fats as the glycerol esters of higher acids. Commonly the study oxidation of polyhydric alcohols has great importance in sugar chemistry.Various investigation on oxidation involving polyhydric alcoholsand various oxidants i.e., periodic acid[15], lead acetate[16], permanganate[17], chloramine-B[18], potassium dichromate[19]in the presence / absence of catalyst in acidic medium have been reported by various workers. However, there are only few reports available in the literature for the oxidation of Ethylene glycol[20-21].

Various transition metal catalysts have been used in the N-haloamine oxidation of organic substrates [22]. Recently, the use of transition metal ions, such as osmium, ruthenium and iridium either alone or as binary mixtures, as catalyst in various redox processes has drawn considerable attention[23]. Iridium(III) chloride is an important platinum group metal ion and has been extensively used as homogeneous catalyst in a number of redox reactions[24]. Several studies have reported the use of Ir(III) chloride as a non-toxic and homogeneous catalyst[25-27] Preliminary experimental results indicate that the reaction of Ethylene glycol with CAT in the acidic medium without a catalyst were very sluggish but the reaction becomes facile in the presence of Ir(III) catalyst.

In the present study, we examine the kinetic and mechanistic aspect of the Ir(III) catalyzed oxidation of Ethylene glycol by CAT in acidic medium with the following objectives: (i) to ascertain the reactive species of catalyst and oxidant, (ii) find the catalytic efficiency of Ir(III), (iii) identify the oxidation products, (iv) to elucidate the plausible reaction mechanism, (v) to deduce rate law consistent with kinetic results and (vi) to calculate the activation parameters.

Experimental Work

Materials

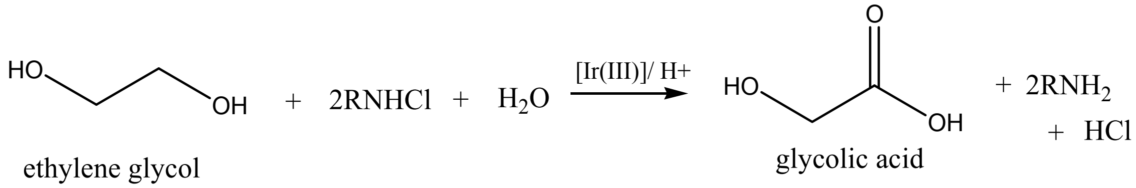
A stock standard solution of chloramine-T (S.D. Fine Chem. Ltd) was prepared by dissolving its known weight in doubly distilled water and its concentration was estimated iodometrically. In order to avoid photochemical deterioration, the solution of chloramine-T was preserved in black coated flask. The standard solution of Ethylene glycol (Thomas Baker) was freshly prepared. Iridium(III) chloride (Johnson Matthey) solution was prepared in HCl of known strength (0.018 N). Other reagents used were, A.R. grade and their solutions were also prepared in doubly distilled water. The reaction vessels were also black coated from outside to avoid photochemical effects.

Kinetic measurements or Procedure

The kinetic runs were carried out at 35±0.1°C. The reaction was initiated by mixing the already thermostated solution of Ethylene glycol to the thermally equilibrated reaction mixture containing required volume of solution of Chloramine-T, H^+, Ir(III) and all other reagents. Aliquots (5ml) of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5ml of 4% KI solution and 5ml of dilute sulphuric acid. The liberated iodine equivalent to unconsumed oxidant was estimated with standard sodium thiosulphate solution using starch as an indicator. The initial rates were obtained from the slope of concentration vs. time graph in the initial stages of the reactions by plane mirror method.

Stoichiometry and product analysis

In order to ascertain the stoichiometry of the reaction, different sets of experiments with varying [RNHCl]:[EG] ratios were performed at 35 °C for 48 h and constant concentrations of all other reactants under the conditions [RNHCl] >>[EG]. Iodometric estimation of unconsumed [RNHCl] in different sets shows that 2 moles of RNHCl were consumed to oxidize 1 mole of Ethylene glycol. Accordingly, the following stoichiometric equations can be formulated:



Glycolic acid (hydroxyacetic acid), the main product in the oxidation of were identified by the help of chromatography (TLC) and conventional (spot test) method. The acidic group (-COOH) was confirmed by adding sodium bicarbonate into the solution. Evolution of carbon dioxide indicates that the product was corresponding acid.

$$\text{R-COOH} + \text{NaHCO}_3 \longrightarrow \text{R-COONa} + \text{H}_2\text{O} + \text{CO}_2$$

The nature of Glycolic acid further confirmed by its IR spectrum (Figure1). The symmetric stretching vibration of υ OHobserves at 3261 cm^{-1}, out of plane bending (OH) observe at 936 cm^{1} in the IR spectrum indicates the presence of CH_2OH group in studied molecule. C-O stretching vibration occurs at 1232 cm^{-1} and C=O stretching at 1729 cm^{-1}.The C-C stretching vibration appears at 1004 cm^{-1}.The C-H stretching vibration of υ (C-H) appears at 2927cm^{-1}.

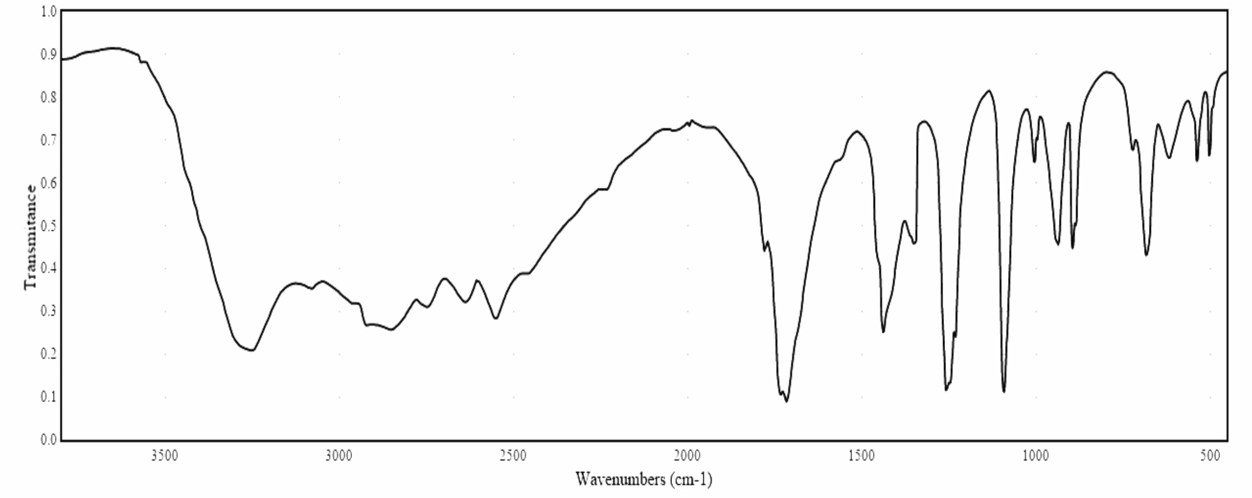


Figure 1. IR-Spectra of the main product Glycolic acid.

Results and Discussion

Kinetics of Ir(III) catalyzed oxidation of Ethylene glycol by chloramine-T in acidic medium was investigated at 35 ^{0}C. The kinetic results were collected at several initial concentrations (Table1). First order kinetics was observed with respect to oxidant chloramine-T (Figure 2). The order of reaction with respect to each reactant was determined by varying the concentration of oxidant, Ethylene glycol, Ir(III) chloride (Table 1), H^+ ions, $[Cl^-]$ and mercuric acetate one by one in different sets keeping concentration of all other reactants constant at constant temperature 35°C. In each kinetic runs, the initial rate (i.e., –dc/dt) of the reaction was determined from the slope of the tangent drawn at a fixed concentration of chloramine-T except for the chloramine-T variation in which the slope of the tangent was drawn at fixed time. The first order reaction rate constant (k_1) for the variation of all the reagents were calculated as

$$k_1 = \frac{-dc/dt}{[RNHCl]^*}$$

where [RNHCl]* denotes the [RNHCl] at which (-dc/dt) was determined.

A plot of (-dc/dt) versus [Chloramine-T] was linear with the slope value (0.98) near unity, which further confirms first order dependence of reaction on chloramine-T (Figure 2). A plot of (-dc/dt) versus [Ir(III)] gives a slope which is close to the average value of first order rate constant at 35^{0}C(Figure 3).

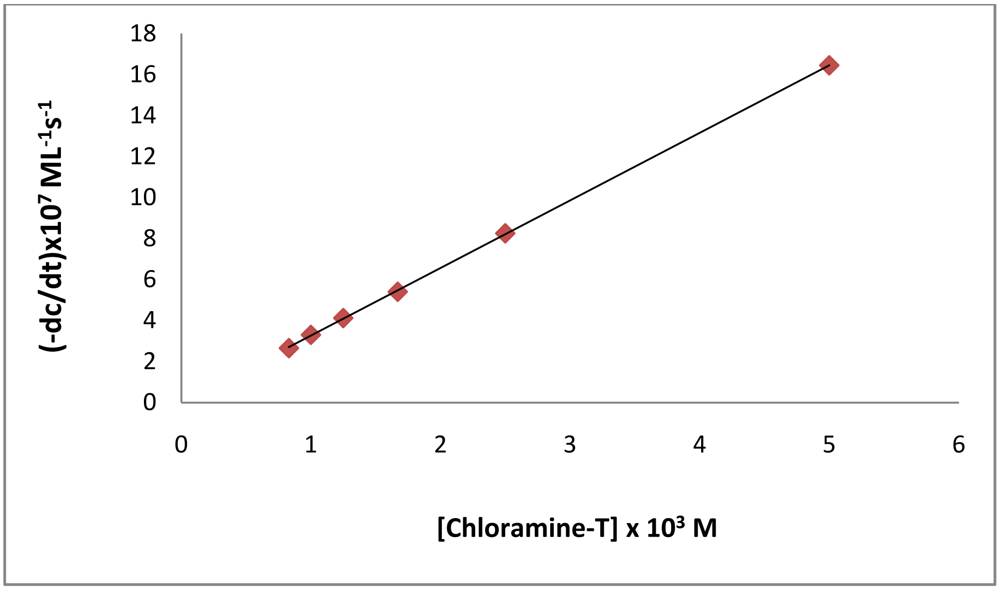


Figure 2. Plot between (-dc/dt)and [Chloramine-T] for the oxidation of Ethylene glycol at 35 °C. [Ir (III)] = 8.02 x 10^{-5} M, [Ethylene glycol] = 2.00 x 10^{-2}, [Hg(OAc)$_2$] = 1.25 x 10^{-3} M,[HClO$_4$] =1.00 x 10^3 M, [KCl] = 1.00 x 10^{-3} M.

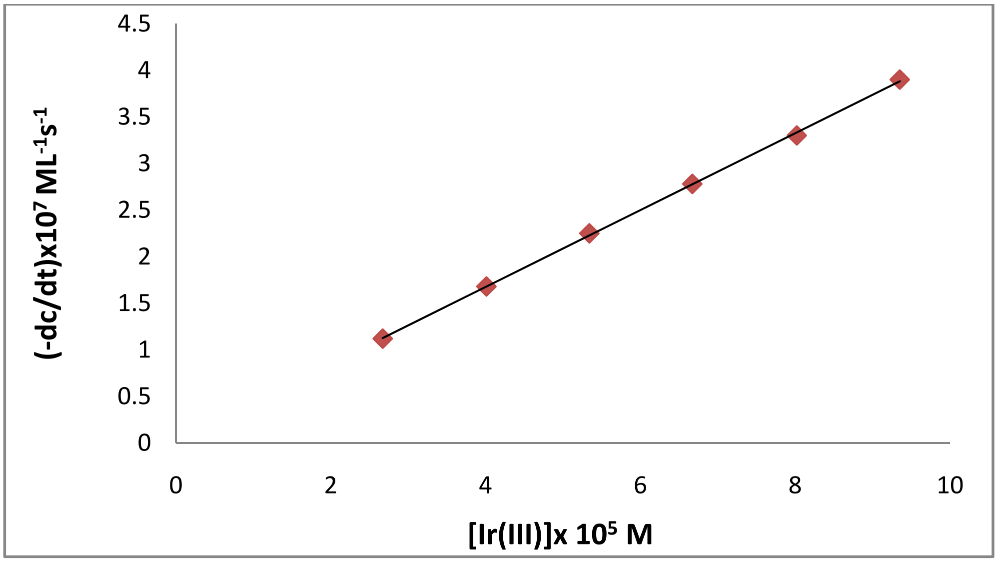


Figure 3. Plot between (-dc/dt)and [Ir(III)] for the oxidation of Ethylene glycol at 35 °C . [Ethylene glycol] = 2.00 x 10^{-2} M, [Chloramine-T] = 1.00 x 10^{-3}, [Hg(OAc)$_2$] = 1.25 x 10^{-3} M, [HClO$_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

Insignificant effect on the rate was observed on increasing the concentration of the substrate, indicating zero order in substrate *i.e.* ethylene glycol (Table 1). Variation of [KCl] concentration shows positive effect on reaction rate (Table 2). Negligible effect of mercuric acetate eliminate the probability of its involvement either as a catalyst or as an oxidant because it does not help the reaction proceed without [CAT]. Hence, the function of mercuric acetate is to act as scavenger for any chloride ion formed in the reaction[28]. It helps to eliminate the parallel oxidation by Cl_2 which would have been formed as a result of interaction between Cl^- and RNHCl ion. Experimental data indicate negligible effect of ionic strength of the medium on the rate (affected by addition of $NaClO_4$). In acidic solution of chloramine-T quick formation of RNHCl has been reported [29]. The reaction is unaffected by H^+ concentration (Table 2).

Table 1. Effect of variation of oxidant, Ethylene glycol, Ir(III) at 35°C

[Oxidant] x 10^3 M (Chloramine-T)	[Substrate]x 10^2 M (Ethylene glycol)	[Ir(III)] x 10^5 M	(-dc/dt)x10^7 $ML^{-1}s^{-1}$
0.83	2.00	8.02	2.65
1.00	2.00	8.02	3.30
1.25	2.00	8.02	4.12
1.67	2.00	8.02	5.40
2.50	2.00	8.02	8.25
5.00	2.00	8.02	16.45
1.00	0.33	8.02	2.75
1.00	0.40	8.02	3.20
1.00	0.50	8.02	3.00
1.00	0.66	8.02	2.90
1.00	1.00	8.02	3.12
1.00	2.00	8.02	3.30
1.00	2.00	2.67	1.12
1.00	2.00	4.01	1.68
1.00	2.00	5.34	2.25
1.00	2.00	6.67	2.78
1.00	2.00	8.02	3.30
1.00	2.00	9.35	3.90

Solution conditions: $[Hg(OAc)_2] = 1.25 \times 10^{-3}$ M, $[HClO_4] = 1.00 \times 10^{-3}$ M, $[KCl] = 1.00 \times 10^{-3}$ M.

Table 2. Effect of variation of $HClO_4$, KCl and $NaClO_4$ at 35 ° C

$[HClO_4]$ x 10^3 M	[KCl] x10^3M	$NaClO_4$x10^3M	(-dc/dt) x $10^7$$ML^{-1}s^{-1}$
0.83	1.00	1.00	3.48
1.00	1.00	1.00	3.30
1.25	1.00	1.00	3.55
1.67	1.00	1.00	3.20
2.50	1.00	1.00	3.15
5.00	1.00	1.00	3.62
1.00	0.83	1.00	2.95
1.00	1.00	1.00	3.30

1.00	1.25	1.00	3.52
1.00	1.67	1.00	3.85
1.00	2.50	1.00	4.15
1.00	5.00	1.00	4.45
1.00	1.00	0.83	3.45
1.00	1.00	1.00	3.30
1.00	1.00	1.25	3.60
1.00	1.00	1.67	3.15
1.00	1.00	2.50	3.08
1.00	1.00	5.00	3.34

Solution conditions: [Ir (III)] =8.02 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3} M, [Ethylene glycol] = 2.00 x 10^{-2}, [Hg(OAc)$_2$] = 1.25 x 10^{-3} M.

The kinetic measurements were also taken in the temperature range of 30-45^{0}C and the specific rate constants were obtained at 30°, 35°, 40° and 45°C. These specific rate constants were used to draw a plot of log k versus 1/T (Figure 4) which was linear. The various activation parameters were calculated from the slope of curves obtained from the figure 4.

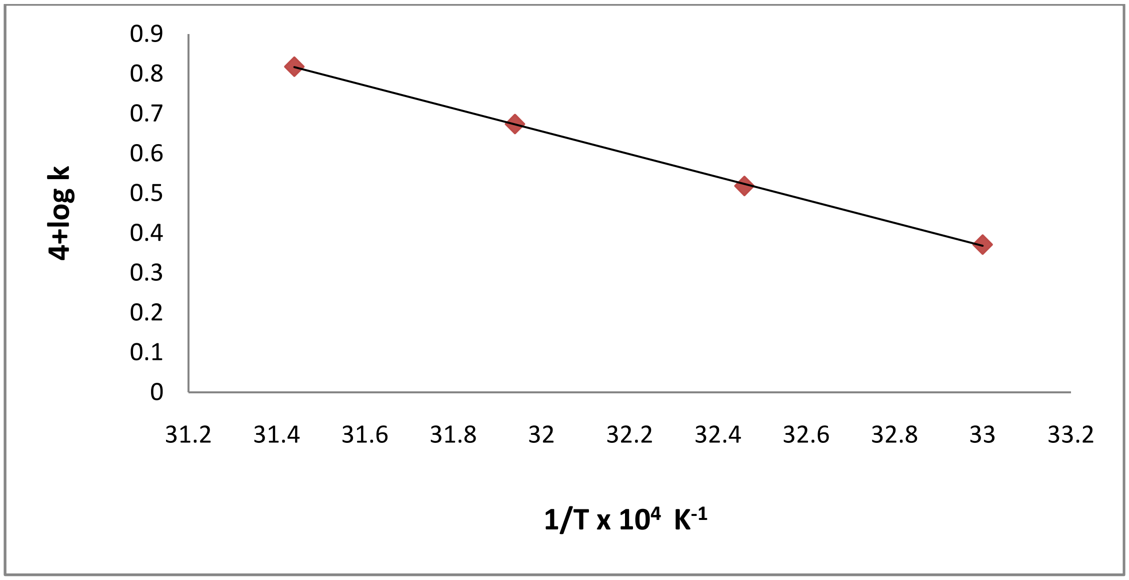


Figure 4. Arrhenius plot for the oxidation of Ethylene glycol. [Ir (III)] = 8.02 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3} M, [Ethylene glycol] = 2.00 x 10^{-2}, [Hg(OAc)$_2$] = 1.25 x 10^{-3} M, [HClO$_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

The value of energy of Activation (ΔE*), Arrhenius factor (A), entropy of activation (ΔS*), free energy of activation (ΔG*) and enthalpy of activation (ΔH*) were calculated from rate measurement and these values have been provided in Table 3. Moderate ΔH* and ΔS* values are favorable for electron transfer reaction. The value of ΔH* was due to energy of solution changes in transition state. The high positive value of ΔG* represents highly solvated transition state. The negative value of ΔS* indicates that the intermediate complex is more ordered than the reactants so the formation of activated complex occurs with reduction in the degree of freedom. The observed modest enthalpy of activation and higher rate constant for the slow step shows that oxidation presumably occurs by means of an inner sphere mechanism. This conclusion is supported by earlier observations. The activation parameters evaluated for the catalyzed reaction explain the catalytic effect on the reaction. Kinetic observations show that the reaction under investigation is complex reaction, which usually takes place in more than one step.

Table 3. Activation parameters for the oxidation of Ethylene glycol

Parameters	**Temperature($^{\circ}$C)**	**Ethylene glycol**
K_1x 10^4 s^{-1}	30	2.35
K_1x 10^4 s^{-1}	35	3.30
K_1x10^4 s^{-1}	40	4.72
K_1x 10^4 s^{-1}	45	6.58
Log A	--	9.82
ΔE* (k J mol^{-1})	35	54.93
ΔG* (k J mol^{-1})	35	71.16
ΔH * (k J mol^{-1})	35	52.40
ΔS* ($JK^{-1}mol^{-1}$)	35	-60.09

Solution conditions: [Ir (III)] = 8.02 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3} M, [Ethylene glycol] = 2.00 x 10^{-2}, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M, [$HClO_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

Mechanism and derivation of rate law

The acidic solution of Iridium chloride exists as $[IrCI_6]^{3-}$. It has also been reported that $[IrCI_6]^{3-}$ is involved in equilibrium as follows[30]:'

$$[IrCI_6]^{3-} + H_2O \rightleftharpoons [IrCI_5(H_2O)]^{2-} + CI^-$$

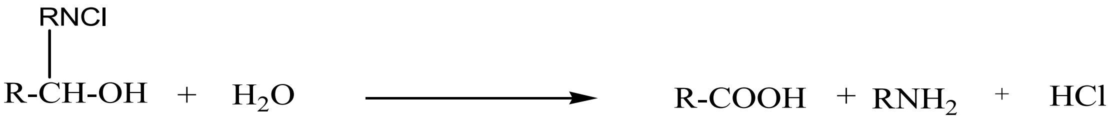
Thus either $[IrCI_6]^{3-}$ or $[IrCI_5H_2O]^{2-}$ may act as catalytic species[31]. If $[IrCI_5H_2O]^{2-}$ is taken as catalytic species the rate law would require negative effect of chloride ion contrary to the positive effect of chloride ion on the oxidation rate observed by us. Hence the only choice is $[IrCI_6]^{3-}$ which when assumed as reactive species of Iridium trichloride in acidic medium, explains the positive effect of chloride ion. The kinetic results reported in table 1, 2, 3 along with the above discussion lead us to suggest the following reaction scheme:

$$\underset{[C_1]}{[IrCI_5(H_2O)]^{2-} + CI^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{[C_2]}{[IrCI_6]^{3-} + H_2O}$$

$$\underset{[C_2]}{[IrCI_6]^{3-}} + RNHCl \xrightarrow[\substack{\text{slow step} \\ \text{r.d.s}}]{k_2} \underset{[C_3]}{[IrCI_6 \text{-----} RNHCl]^{3-}}$$

$$[C_3] + RCH_2OH \longrightarrow [IrCl_5H]^{3-} + R\text{-}\overset{RNCl}{\overset{|}{C}}H\text{-}OH + HCl$$

$$[IrCl_5H]^{3-} + RNHCl \longrightarrow [IrCl_6]^{3-} + RNH_2$$



$$R\text{-}\overset{RNCl}{\overset{|}{C}}H\text{-}OH + H_2O \longrightarrow R\text{-}COOH + RNH_2 + HCl$$

[P]

Where,

R = CH_2OH

[P] = Product i.e. Glycolic acid.

Now considering the above reaction steps and applying the steady-state treatment with reasonable approximation, the rate law may be written as

$$Rate = \frac{-d[RNHCl]}{dt} = k_2[C_2][RNHCl] \qquad (i)$$

$$[Ir(III)]_T = [C_1] + [C_2] \qquad (ii)$$

$$\frac{d[C_1]}{dt} = k_{-1}\,[C_2] - k_1\,[C_1][Cl^-] \qquad (iii)$$

$$[C_1] = \frac{k_{-1}\,[C_2]}{k_1\,[Cl^-]} \qquad (iv)$$

$$[C_1] = \frac{[C_2]}{K_1\,[Cl^-]} \qquad (v)$$

(where $K_1 = k_1/k_{-1}$)

Putting the value of $[C_1]$ in equation (ii), we get

$$[Ir(III)]_T = [C_1] + [C_2]$$

$$[Ir(III)]_T = \frac{[C_2]}{K_1[Cl^-]} + [C_2]$$

$$= \left[\frac{[C_2] + K_1\,[Cl^-][C_2]}{K_1[Cl^-]}\right]$$

$$= [C_2]\left[\frac{1 + K_1\,[Cl^-]}{K_1[Cl^-]}\right].$$

This gives

$$[C_2] = \frac{[Ir(III)]_T \, K_1 \, [Cl^-]}{1 + K_1 \, [Cl^-]}.$$

Putting the value of C_2 in equation (i), we get

$$Rate = \frac{K_1 \, k_2 [Ir(III)]_T [Cl^-][RNHCl]}{1 + K_1 \, [Cl^-]}.$$

Conclusion

The following conclusions can be derived in the present study of Ir(III) catalyzed oxidation of Ethylene glycol by chloramine-T in acidic medium. (a) Among the various species of Ir(III) in acidic medium, $[IrCl_6]^{3-}$is considered as the reactive species while (b) RNHCl is the reactive species of Chloramine-T in acidic medium. (c) In the absence of catalyst oxidation of Ethylene glycol by Chloramine-T is very sluggish, but it becomes facile in the presence of Ir(III) catalyst. (d) The stoichiometry of the reaction was found to be 2:1 and the oxidation products of Ethylene glycol were identified (e) Activation parameters were computed from the Arrhenius plot. (f) The observed results have been explained by a plausible mechanism and the related rate law has been deduced. It can be concluded that Ir(III) chloride act as an efficient catalyst for the oxidation of Ethylene glycol by Chloramine-T in acidicmedium.

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