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Selective Oxidation of Ethylenediamine by Chloramine-T in the Presence of Ir(III) Chloride

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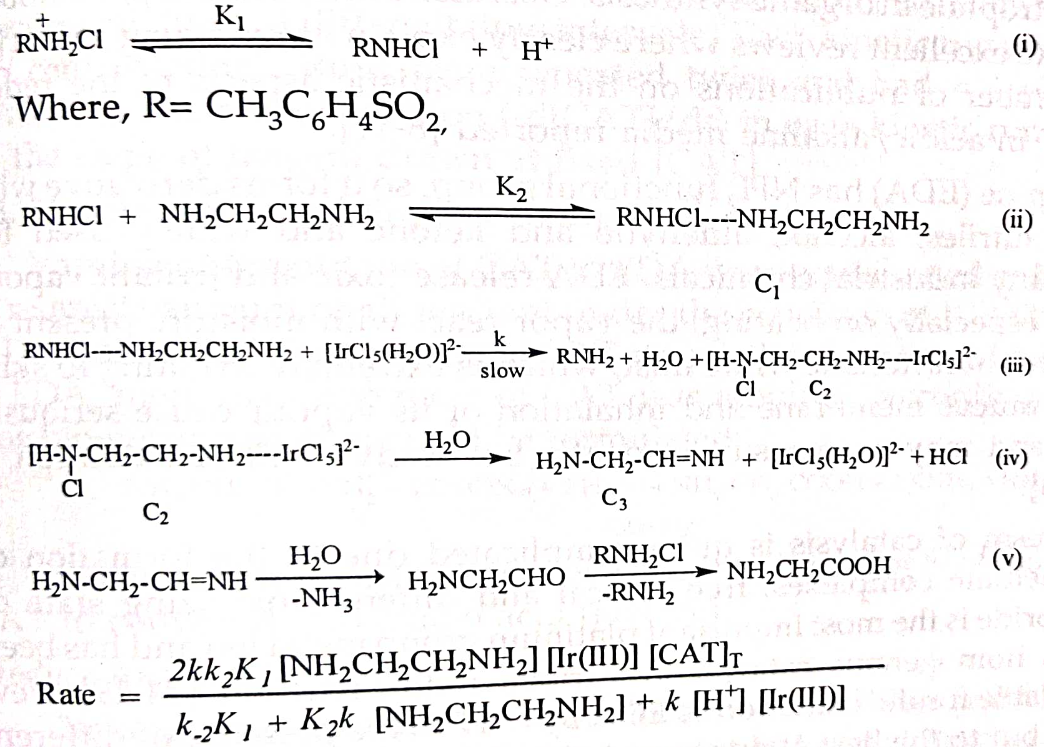
Novelty & Highlights

1. Catalytic activity of Ir(III) chloride.
2. Oxidation of ethylenediamine to glycine.
3. Multiple regression analysis and comparative study.

Graphical Abstract



$$\overset{+}{RNH_2Cl} \underset{}{\overset{K_1}{\rightleftharpoons}} RNHCl + H^+ \quad (i)$$

Where, R= $CH_3C_6H_4SO_2$,

$$RNHCl + NH_2CH_2CH_2NH_2 \overset{K_2}{\rightleftharpoons} \underset{C_1}{RNHCl\text{---}NH_2CH_2CH_2NH_2} \quad (ii)$$

$$RNHCl\text{---}NH_2CH_2CH_2NH_2 + [IrCl_5(H_2O)]^{2-} \xrightarrow[slow]{k} RNH_2 + H_2O + \underset{C_2}{[H\text{-}\underset{Cl}{\underset{|}{N}}\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{---}IrCl_5]^{2-}} \quad (iii)$$

$$\underset{C_2}{[H\text{-}\underset{Cl}{\underset{|}{N}}\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{----}IrCl_5]^{2-}} \xrightarrow{H_2O} \underset{C_3}{H_2N\text{-}CH_2\text{-}CH{=}NH} + [IrCl_5(H_2O)]^{2-} + HCl \quad (iv)$$

$$H_2N\text{-}CH_2\text{-}CH{=}NH \xrightarrow[-NH_3]{H_2O} H_2NCH_2CHO \xrightarrow[-RNH_2]{RNH_2Cl} NH_2CH_2COOH \quad (v)$$

$$Rate = \frac{2kk_2K_1\,[NH_2CH_2CH_2NH_2]\,[Ir(III)]\,[CAT]_T}{k_{-2}K_1 + K_2k\,[NH_2CH_2CH_2NH_2] + k\,[H^+]\,[Ir(III)]}$$

Abstract

The influence of iridium(III) chloride {Ir(III)} for the oxidation of ethylenediamine (EDA) by chloramine-*T* (CAT) in acidic medium at 308K by the kinetic study is reported here. The results showed a first-order with respect to CAT. The Ir(III) chloride and EDA followed first-order kinetics at lower concentration range, but tends to zero order at higher concentration. The rates decreased with increase in the proton concentration. Chloride ion, ionic strength

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(I) and dielectric constant of the medium (D) had no significant effect on the rates. Activation parameters of the reactions were determined by studying the reaction at different temperatures (298-313K). A plausible reaction scheme of the oxidation of EDA by CAT in presence of Ir(III) chloride was proposed, which was found to be in agreement with the rate law and the reaction stoichiometry. The determined stoichiometry ratio was 1:2 and oxidation product was glycine.

Keywords: Kinetics, Oxidation, Ethylenediamine, Ir(III) chloride, Chloramine-T.

1. Introduction

The chemistry of aromatic sulfonyl haloamines (N-haloamines) is of interest due to their diverse behaviour and versatile nature and their abilities to exist as halonium cations and nitrogen anions, which act both as base and nucleophile [1-5]. As a result, these compounds react with wide range of functional groups and affect variety of molecular changes. The prominent members of this class of compounds are Sodium-N-chloro-4-methyl benzensulfonamide, p-$CH_3C_6H_4SO_2NClNa{\cdot}3H_2O$, generally known as chloramine-T (CAT), which has long been used as an analytical reagent. It contains active chlorine so it is used as a source of electrophile in organic synthesis. Ozerassi, Filler, Mukherji, Campbell and Johnson wrote excellent reviews where clearly explain its oxidizing action [6-7]. There are number of publications on the mechanistic aspects of the redox reactions of CAT in acidic/alkaline media reported [8-11].

Ethylenediamine (EDA) has NH_2 functional group, so it forms derivative with carboxylic acid, nitriles, alcohol, aldehyde and ketone and widely used for production of many industrial chemicals. EDA release toxic and irritant vapour to surroundings especially on heating, the vapor react with moisture present in humid air to form characteristic white mist, which is extremely irritating to skin, eyes, lungs and mucus membrane and inhalation of its vapour cause seriously damage health and may even result in death. So, study of EDA oxidation is necessary [12-13].

The mechanism of catalysis is quite complicated due to the formation of different intermediate complexes, free radical and different oxidizing state of Ir(III). Ir(III) chloride is the most important platinum group metal ion and has been widely used as homogenous catalyst in various redox reaction [14-19]. Few reports are available for the oxidation of EDA by CAT in the presence of different metal ions [20], but to the best of our knowledge there is no report available for the oxidation of EDA by CAT in the presence of Ir(III). This has encouraged us to investigate mechanistic aspect of EDA by CAT. Preliminary result indicate that in the absence of the Ir(III) chloride catalyst in acidic medium was very sluggish but reaction become facile in the presence of small amount of iridium. Objectives of the present study are : (i) to ascertain the reactive species of Ir(III) chloride as catalyst and CAT as an oxidant in acidic medium, (ii) to identify the oxidation products, (iii) to elucidate a plausible mechanism, (iv) to deduce an appropriate rate law.

2. Experimental

2.1 Material

AR grade chemicals and double distilled water used throughout the investigation. Stock solution of CAT (Loba) was prepared in doubly distilled water and standardized iodometrically. Solution of Ir(III) chloride was prepared by dissolving a known weight of $IrCl_3$ (S. D. fine) in HCL of known strength. Stock solution of EDA (Fluka) was prepared by dissolving appropriate amount of sample in double distilled water. Standard solution of KCl, $NaClO_4$ and phthalimide were prepared with double distilled water and perchloric acid (GR) was used as a source of H^+ ions and acetonitrile as solvent.

2.2 Kinetic Procedure

All the kinetic measurement were carried out in a black-coated vessel at constant temperature (308 K) and performed under pseudo first-order condition with [EDA] >> [CAT]. The reaction was initiated by the rapid addition of known amounts of oxidant to the reaction mixture containing the required amounts of EDA, perchloric acid, Ir(III) chloride and water in glass stoppered pyrex boiling tubes; thermosttated at the same temperature. Progress of reaction was monitored by iodometric determination of unconsumed [CAT] in known aliquots of the reaction mixtures at different time intervals. Each kinetic run was studied for ~75 per cent reaction. Runs were repeated twice and had < 4 per cent standard deviation. The rate of reaction (-d[CAT]/dt) in each kinetic run was determined by the slope of tangent drawn at fixed [CAT].

2.3. Stoichiometry and Product Analysis

Varying different ratio of CAT to EDA were equilibrated at 308 K in presence of requisite amount of all reactant under the condition of [CAT]>> [EDA], for 48 h. Determination of unconsumed CAT revealed that for the oxidation of each mole of EDA, more than two mole of CAT was required. Accordingly, the following stoichiometric equation could be formulated:

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2 + 2RNClNa + 2\,H_2O \rightarrow NH_2\text{-}CH_2\text{-}COOH + 2\,RNH_2 + NH_3 + 2NaCl$$

Glycine

Stoichiometric investigations revealed that 1 mole of EDA utilized 2 moles of CAT to convert it into amino acid (glycine).

Product Analysis Method

The reaction products were neutralized with NaOH and extracted with ether. The organic products were subjected to spot test and chromatographic analysis which revealed the formation of glycine [21].

3. Kinetic measurements & Results

3.1 Kinetics Study

Initially, the kinetics of the oxidation of EDA by CAT in the presence of Ir(III) chloride in acidic conditions were studied at several initial concentrations of all the reactants at 308 K. For the variation of [CAT], the reaction rate was calculated by the slope of tangent drawn at fixed time. In the variation of concentration of other reactants, tangents were drawn at constant [CAT] ([CAT]*) (**Fig. 1**).

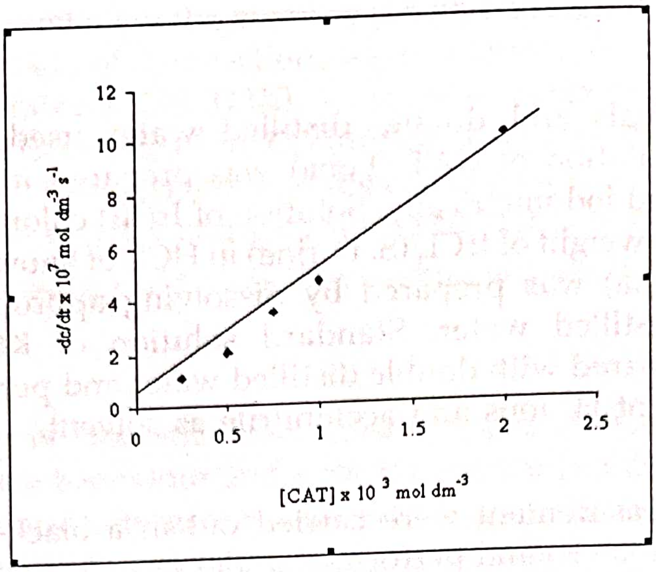


Fig. 1: Plot of Rate versus [CAT] at T = 308K.

[EDA] = 2.00 x 10^{-2} mol dm^{-3}, [$HClO_4$] = 0.50 mol dm^{-3} and [Ir(III)]= 3.34 x 10^{-6} mol dm^{-3}.

The pseudo-first-order rate constant k_1 was calculated as

$$k_1 = \frac{-\,(dc/dt)}{[CAT]^*}$$

The order of reaction in each reactant was determined using log-log plot of (-dc/dt) versus concentration of reactant. Considering CAT, EDA, perchloric acid and Ir(III) chloride as the main reactants, the general form of the rate equation for the oxidation of EDA by CAT can be written as

$$\text{rate} = k_1\,[CAT]^{\alpha}\ [EDA]^{\beta}\ [Ir(III)]^{\gamma}\ [H^+]^{\delta}$$

Uniform pseudo-first-order rate constant (k_1) values for the variation of [CAT] clearly indicate that the order with respect to [CAT] is unity. This is also obvious from the plot of (-dc/dt) versus [CAT] (Fig. 1; **Table 1**). The reactions have been studied for EDA from 0.5 x 10^{-2} to 3.5 x 10^{-2} mol dm^{-3} at constant concentration of all reactants at constant temperature. The rate of reaction calculated at different [EDA], this was showing fractional order kinetics with respect to [EDA] (Fig. 2; **Table 1**).

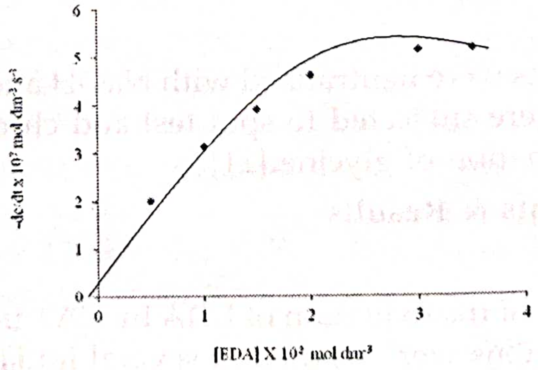


Fig. 2: Plot of Rate versus [EDA] at T = 308K.

[CAT] = 1.00 x 10^{-3} mol dm^{-3}, [$HClO_4$] = 0.50 mol dm^{-3} and [Ir(III)]= 3.34 x 10^{-6} mol dm^{-3}.

The reaction follows first-order kinetics with respect to [Ir(III)] chloride at a low range of concentration and tends to zero-order at high concentration range. This result was further confirmed by the plot of -dc/dt versus [Ir(III)] (Fig. 3; Table 1).

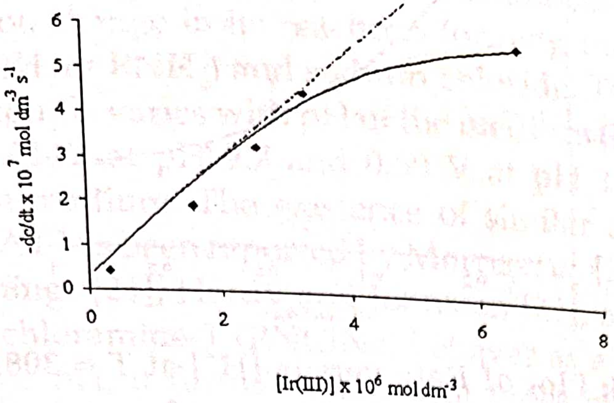


Fig. 3 Plot of rate versus [Ir(III)] at T = 308K.
[CAT] = 1.00 x 10^{-3} mol dm^{-3}, [EDA] = 2.00 x 10^{-2} mol dm^{-3}, [$HClO_4$] = 0.50 mol dm^{-3}.

Table 1: Effect of [CAT], [EDA], [Ir(III)] and [H^+] on the Rate of Oxidation of EDA at 308 K.

[CAT] x 10^3 mol dm^{-3}	[EDA] x 10^2 mol dm^{-3}	[Ir(III)] x10^6 mol dm^{-3}	[H^+] mol dm^{-3}	k_1 x 10^4 s^{-1}(Cal)	k_1 x 10^4s^{-1} (exp)
0.25	2.00	3.34	0.50	5.36	-
0.50	2.00	3.34	0.50	5.78	-
0.75	2.00	3.34	0.50	5.20	-
1.00	2.00	3.34	0.50	5.00	-
2.00	2.00	3.34	0.50	5.47	-
1.00	0.50	3.34	0.50	2.50	2.60
1.00	1.00	3.34	0.50	3.90	3.68
1.00	1.50	3.34	0.50	4.87	4.46
1.00	2.00	3.34	0.50	5.75	5.12
1.00	3.00	3.34	0.50	6.37	6.21
1.00	3.50	3.34	0.50	6.40	6.68
1.00	2.00	0.33	0.50	0.50	0.54
1.00	2.00	1.60	0.50	2.40	2.51
1.00	2.00	2.60	0.50	4.01	4.02
1.00	2.00	3.34	0.50	5.57	5.12
1.00	2.00	6.68	0.50	7.06	10.01
1.00	2.00	3.34	0.10	13.31	16.18
1.00	2.00	3.34	0.20	12.02	9.86
1.00	2.00	3.34	0.30	9.01	7.38
1.00	2.00	3.34	0.50	5.75	5.11
1.00	2.00	3.34	0.70	3.75	4.02
1.00	2.00	3.34	0.90	3.30	3.35

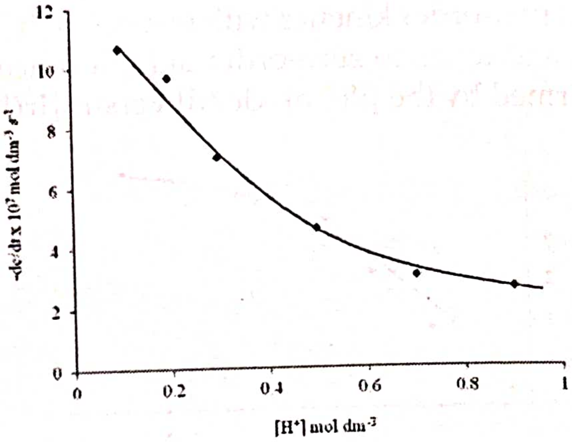


Fig. 4: Plot of Rate versus [H$^+$] at T = 308K.
[CAT] = 1.00 x 10^{-3} mol dm^{-3}, [EDA] = 2.00 x 10^{-2} mol dm^{-3} and [Ir(III)]= 3.34 x 10^{-6} mol dm^{-3}.

The reaction rate decreased with increasing [$HClO_4$] (Fig. 4). The variation of [Cl$^-$], solvent and ionic strength of medium did not affect the reaction velocity. Effect of temperature on the reaction rate was determined by keeping constant concentration of other constituents of the reaction mixture (Table 2). The values of different activation parameters such as activation energy (E_a), enthalpy of activation (ÄH$^{\#}$) and entropy of activation ("S$^{\#}$) were determined from the temperature effect on rates.

Table 2: Effect of Temperature and Corresponding Activation Parameter on the Rate of Oxidation of EDA.

Temperature (K)	k_1 x 10^{4}s^{-1}(Cal)
298	2.90
303	4.64
308	5.64
313	6.25
Ea (kJ mol $^{-1)}$	23.6
ΔH(kJ mol $^{-1}$)	21.03
ΔS (JK^{-1} mol $^{-1}$)	-40.47
ΔG(kJ mol $^{-1}$)	8.57
log A	4.13
k_r x 10^{-3} (s^{-1})	0.3749

3.2 *Test for Free Radicals*

To test the presence of free radicals in the reaction, the reaction mixture containing CAT, EDA, Ir(III) chloride and perchloric acid with acryl amide was placed in an inert atmosphere for 24 h. When the reaction mixture was diluted with methanol, it was found that there was no precipitate in the reaction mixture [9,10,15]. This clearly showed free radicals were not formed in the redox reaction under investigation.

4. Discussion

4.1 Reactive Species of CAT

CAT acts as a mild oxidant in both acidic and alkaline media. In general, CAT undergoes two-electron change in its reactions forming the reduction products, PTS (p-$CH_3C_6H_4SO_2NH_2$ or RNH_2) and sodium chloride. The oxidation potential of CAT-RNH_2 redox couple varies with pH of the medium (E_o is 1.14 V at pH 0.65, 0.778 V at pH 7.0, 0.614V at pH 9.7 and 0.50 V at pH 12) and decrease with increase in pH of the medium. The existence of similar equilibria in acid and alkaline solution of CAT has been reported by Morris *et al.* [22], Ruff and Kucsman [23], Bishop and Jennings [24], Hardy and Johnston [25], and Higuchi *et al.* [26]. Aqueous solution of chloramine-T (RNClNa) behaves as a strong electrolyte [23] and depending on the pH, it furnishes different types of reactive species. The possible oxidizing species in acidified CAT solution are the conjugate free acid (RNHCl), dichloramine-T ($RNCl_2$), hypochlorous acid (HOCl) and possibly H_2OCl^+ and in alkaline solutions RNHCl, HOCl, $RNCl^-$ and OCl^-.

4.2 Reactive Species of Iridium

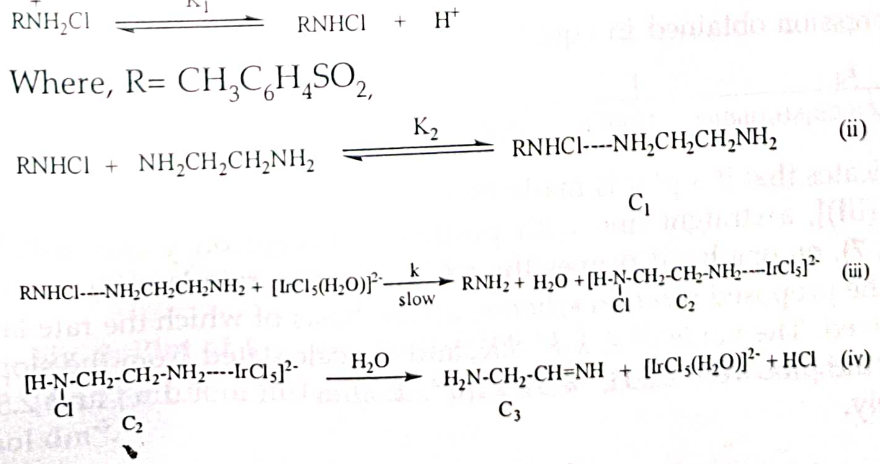
It is known that $IrCl_3$ in hydrochloric acid gives $[IrCl_6]^{3-}$ species [27]. It has also been reported that iridium (III) and iridium (I) ions are the stable species of iridium [28]. Further, the aquation of $[IrCl_6]^{3-}$ gives $[IrCl_5H_2O]^{2-}$, $[IrCl_4(H_2O)_2]^-$ and $[IrCl_3(H_2O)_3]$ species [29-30]. This equilibrium may be shown by general equation.

$$IrCl_6^{3-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [IrCl_5(H_2O)]^{2-} + Cl^-$$

In case of negligible effect of chloride ions on the reaction rate in the present study indicate that $[IrCl_5(H_2O)]^{2-}$ can be considered as the reactive species. Therefore, considering our experimental results, $[IrCl_5(H_2O)]^{2-}$ has been considered to be the reactive species of iridium (III) chloride in the present study.

Considering the reactive species of catalyst, oxidant and with the help of above experimental findings, the probable reaction mechanism is proposed (Scheme I)

Reaction scheme I:



$$\overset{+}{R}NH_2Cl \overset{K_1}{\rightleftharpoons} RNHCl + H^+ \quad (i)$$

Where, R= $CH_3C_6H_4SO_2$,

$$RNHCl + NH_2CH_2CH_2NH_2 \overset{K_2}{\rightleftharpoons} \underset{C_1}{RNHCl\text{---}NH_2CH_2CH_2NH_2} \quad (ii)$$

$$RNHCl\text{---}NH_2CH_2CH_2NH_2 + [IrCl_5(H_2O)]^{2-} \xrightarrow[slow]{k} RNH_2 + H_2O + \underset{C_2}{[H\text{-}\underset{Cl}{N}\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{---}IrCl_5]^{2-}} \quad (iii)$$

$$\underset{C_2}{[H\text{-}\underset{Cl}{N}\text{-}CH_2\text{-}CH_2\text{-}NH_2\text{---}IrCl_5]^{2-}} \xrightarrow{H_2O} \underset{C_3}{H_2N\text{-}CH_2\text{-}CH{=}NH} + [IrCl_5(H_2O)]^{2-} + HCl \quad (iv)$$

$$H_2N\text{-}CH_2\text{-}CH{=}NH \xrightarrow[-NH_3]{H_2O} H_2NCH_2CHO \xrightarrow[-RNH_2]{RNH_2Cl} NH_2CH_2COOH \qquad (v)$$

Considering the fact that 1 mole of EDA is oxidized by 2 moles of CAT.

$$\text{Rate} = 2\,k\,[C_1] \qquad (1)$$

On the basis of steps (i) to (v), Eq. (2) can be obtained in the following forms, respectively:

$$\text{Rate} = \frac{2\,k\,K_1K_2\,[H_2NCH_2CH_2NH_2]\,[R\overset{+}{N}H_2Cl]\,[Ir(III)]}{[H^+]} \qquad (2)$$

Applying steady state approximation

$$0 = \frac{dC_1}{dt} = k_2\,[RNHCl]\;[NH_2CH_2CH_2NH_2] - k_{-2}\,[C_1] - k\,[C_1]\,[Ir(III)] \qquad (3)$$

$$\text{Rate} = \frac{kk_2K_1\,[R\overset{+}{N}H_2Cl]\;[NH_2CH_2CH_2NH_2]\;[Ir(III)]}{[H^+]\,\left(k_{-2} - k\,[Ir(III)]\right)} \qquad (4)$$

At any time of the reaction, the total concentration of CAT, i.e., $[CAT]_T$ can be shown as

$$[CAT]_T = [R\overset{+}{N}H_2Cl] + [RNHCl] + [C_1] \qquad (5)$$

On substituting the value of $[C_1]$ in Eq. (5) we get Eq. (6)

$$= [R\overset{+}{N}H_2Cl] + \frac{K_1[R\overset{+}{N}H_2Cl]}{[H^+]} + \frac{K_1k_2\,[R\overset{+}{N}H_2Cl]\;[NH_2CH_2CH_2NH_2]}{[H^+]\,\left(k_{-2} - k\,[Ir(III)]\right)} \qquad (6)$$

$$[R\overset{+}{N}H_2Cl] = \frac{[H^+]\,[CAT]_T\left(k_{-2} - k\,[Ir(III)]\right)}{k_{-2}K_1 + K_2k\;[NH_2CH_2CH_2NH_2] + k\,[Ir(III)]} \qquad (7)$$

$$\text{Rate} = \frac{2kk_2K_1\,[NH_2CH_2CH_2NH_2]\;[Ir(III)]\,[CAT]_T}{k_{-2}K_1 + K_2k\;[NH_2CH_2CH_2NH_2] + k\;[H^+]\;[Ir(III)]} \qquad (8)$$

$$\frac{\text{Rate}}{[CAT]_T} = k_{obs} = \frac{2\,kk_2K_1\,[NH_2CH_2CH_2NH_2]\,[Ir(III)]}{k_{-2}K_1 + K_1k_2[NH_2CH_2CH_2NH_2] + k\;[H^+]\;[Ir(III)]} \qquad (9)$$

The rate expression obtained in equation (8) can be re-written as

$$\frac{1}{k_{obs}} = \frac{k_{-2}}{2\,kk_2\,[NH_2CH_2CH_2NH_2]\,[Ir(III)]} + \frac{1}{k\,[Ir(III)]} + \frac{[H^+]}{K_1k_2\,[NH_2CH_2CH_2NH_2]} \qquad (10)$$

Eq. (10), indicates that if a plot is made between $[CAT]_T]$/rate and 1/[EDA] or $[H^+]$ or 1/[Ir(III)], a straight line with positive intercept on y-axis will be obtained (**Fig. 6, 7**), on one hand proves the validity of the rate law (8) and on the other hand the proposed reaction scheme, on the basis of which the rate law (8) has been derived. The value of k, k_2K_1, kK_2 and k_{-2} calculated from the slope and intercept of the plot were 0.331, 4.54×10^{-3}, 1.00×10^{-7} mol dm^{-3} and 2.59×10^{-13} respectively.

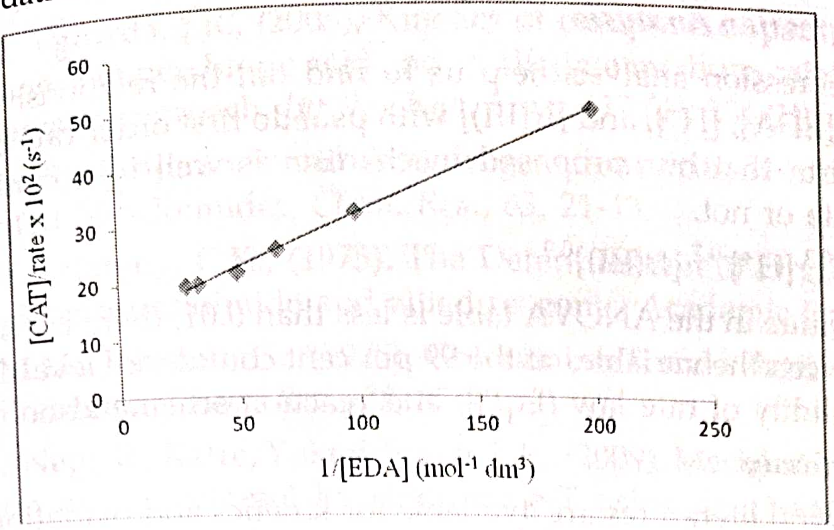


Fig. 6: Plot of 1/[EDA] versus [CAT]/rate at T = 308K. [$HClO_4$] = 0.50 mol $dm^{-3}$and [Ir(III)]= 3.34 x 10^{-6} mol dm^{-3}.

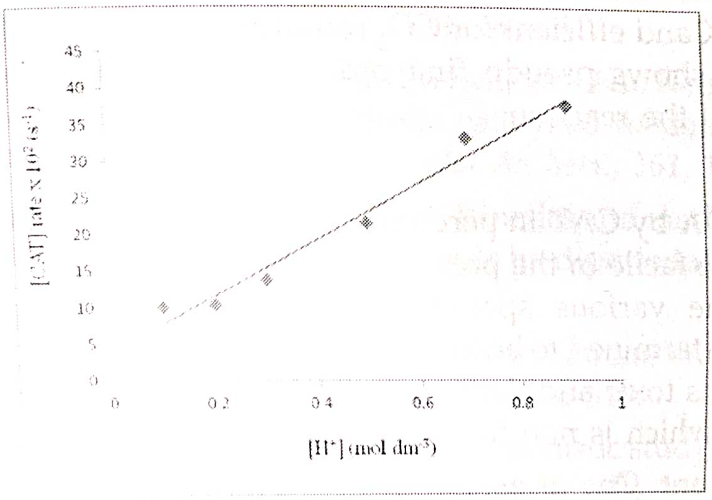


Fig. 7: Lot [H^+] versus [CAT]/rate at T = 308K. [EDA] = 2.00 x 10^{-2} mol $dm^{-3}$and [Ir(III)]= 3.34 x 10^{-6} mol dm^{-3}.

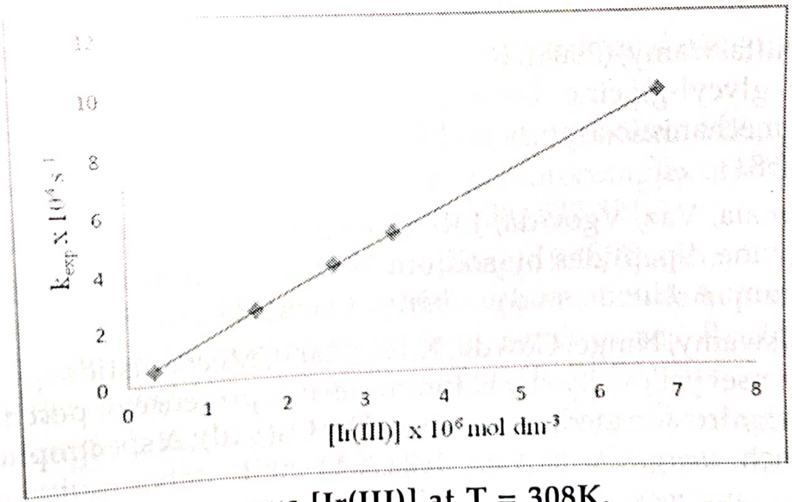


Fig. 8: Plot of k_{obs} versus [Ir(III)] at T = 308K. [CAT] = 1.00 x 10^{-3} mol dm^{-3}, [EDA] = 2.00 x 10^{-2} mol dm^{-3}, [$HClO_4$] = 0.50 mol dm^{-3}.

4.3 Multiple Regression Analysis

Multiple regression analysis help us to find out the relationship between dependent (i.e., [EDA], [H^+], and [Ir(III)] with psuedo first order rate constant k_1) to sure or confirm that our proposed mechanism is well in accordance with experimental data or not.

$$k_1 = k\,[EDA]^{0.3}\,[H^+]^{-0.7}\,[Ir(III)]^{0.9}$$

Since the P-value in the ANOVA table is less than 0.01, there is a statistically relationship between the variables at the 99 per cent confidence level. This study also supports validity of rate law (Eq. 8) and reaction scheme also.

4.4 Comparative Study

There are several literatures are available for kinetics and oxidation study of EDA, i.e., removal of carbon dioxide by EDA [31] and super critical waste water treatment by oxidation process [13]. On doing comparison of present work with above work, it is concluded that, EDA followed second order rate constant, 15770 $m^3/(kmols)$ at 303 K and efficient for CO_2 removal or CO_2 capturing solvent and in present work it shows pseudo first order and generate non toxic product glycine as poduct of the reaction.

5. Conclusion

Oxidation of EDA by CAT in perchloric acid medium was found to be very sluggish, but became facile in the presence of a micro-quantity of Ir(III) chloride catalyst. Among the various species of Ir(III) chloride in acidic medium, $[IrCl_5(H_2O)]^{2-}$ was determined to be the catalytic species. As we already discussed that EDA's vapour is toxic and dangerous for human health, so we also got its oxidation product which is non toxic (glycine).

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