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Research Article

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Kinetic and Mechanistic Study of Oxidation of L-Alanine by Acidic Solution of Chloramine-T in Presence of Chloro-Complex of Ir(III) as Homogeneous Catalyst

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Abstract: The kinetics and mechanism of homogeneously Ir(III) chloride catalyzed oxidation of L-alanine by chloramine-T [CAT] in perchloric acidic medium in the temperature range 30 to 45^{0}C have been studied. The reaction is carried out in the presence of mercuric acetate as a scavenger for chloride ion. The experimental results show first order kinetics with respect to the oxidant [CAT] and catalyst [Ir(III)] while positive effect with respect to substrate, i.e., L-alanine was observed. The reaction shows negligible effect of [$Hg(OAc)_2$], [H^+] and ionic strength of the medium. Chloride ion positively influenced the rate of reaction. The reaction between chloramine-T and L-alanine in acid medium shows 1:1 stoichiometry. To calculate activation parameters, the reactions have been studied at four different temperatures between 30 to 45ºC. A mechanism involving the complex formation between catalyst, substrate and oxidant has been proposed. Acetaldehyde has been identified chromatographically and spectroscopically as the final product of oxidation of L-alanine. Based on the kinetic data, reaction stoichiometry and product analysis, a reaction mechanism has been proposed and rate law has been derived.

Keywords: Kinetics, mechanism, Ir(III) catalysis, L-alanine, chloramine-T, acidic medium

1. INTRODUCTION

Aromatic N-halosulfonamides act as mild oxidants in both acid and alkaline solutions due to the presence of strongly polarized N-linked halogen in +1 state [1,2]. The versatile nature of N-halosulfonamides is attributed to the presence of halonium cations and nitrogen anions in their structure, which can act as both a base and a nucleophile [3-5]. Many organic substrates were oxidized by these sulfonamides and the kinetic and mechanistic aspects of these reactions are well documented [6-8]. A prominent member of this group Sodium N-chloro-p-toluenesulfonamide or Chloramine-T (CAT; p-$CH_3C_6H_4SO_2NClNa.3H_2O$) is used as haloginating and oxidizing agent [2,9,10]. Depending upon the pH of the medium, it forms various oxidizing species and thus shows a variety of kinetic results [11-12]. Several researchers have studied the oxidizing behavior of CAT [13-15] 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 [16]. It can behave as both electrophile and nucleophile depending on the reaction conditions.

Oxidation reactions are of fundamental importance in nature, and are key transformations in organic synthesis. Oxidation of amino acids is of great importance both from chemical point of view and its bearing on the mechanism of amino acids metabolism [17]. They can undergo numerous kinds of reaction depending on whether a particular amino acid contains non polar groups or polar substituents. Amino acids are used in variety of applications in biochemical research, microbiology, nutrition, pharmaceuticals and fortification of foods and feeds. Amino acids have been oxidized by a variety of reagents under different experimental conditions [18-21]. However, the mechanism differs for different reaction systems. The oxidation of amino acids is also of considerable interest as different oxidants lead to formation of different oxidation products [22-23]. Oxidative decarboxylation of amino acids is one of the well reported biochemical processes. The kinetics and oxidation of amino acids have been documented with various oxidants [24-26]. However, there are only few reports available in the literature for the oxidation of L-alanine [17,27].

Various transition metal catalysts have been used in the N-haloamine oxidation of organic substrates [28]. 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 [29]. Iridium(III) chloride is an important platinum group metal ion and has been extensively used as homogeneous catalyst in a number of redox reactions [30]. Several studies have reported the use of Ir(III) chloride as a non-toxic and homogeneous catalyst [31-32]. Preliminary experimental results indicate that the reaction of L-alanine (ala) 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 aspects of the Ir(III) catalyzed oxidation of L-alanine 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.

2. EXPERIMENTAL

2.1. Materials

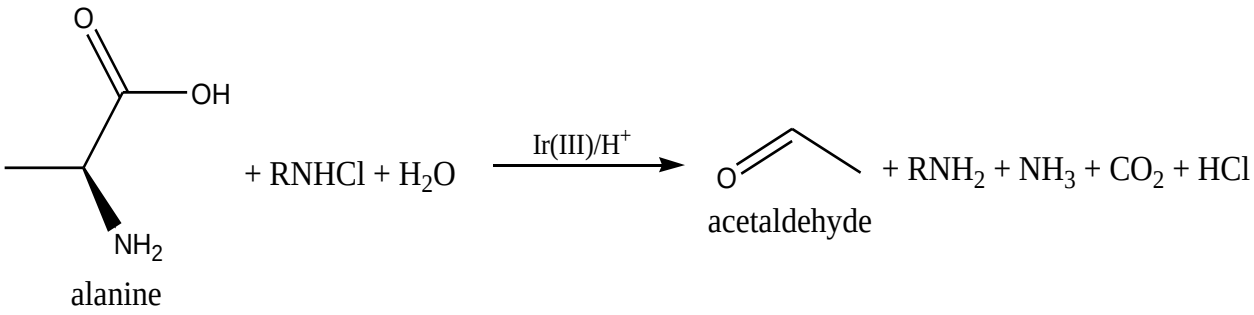
A stock standard solution of chloramine-T (S.D. Fine Chem. Ltd) was prepared by dissolving its known weight in doubly distilled water and its concentration was estimated iodometrically. In order to avoid photochemical deterioration, the solution of chloramine-T was preserved in black coated flask. The standard solution of L-alanine (E. Merck) 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.

2.2. Kinetic measurements or Procedure

The kinetic runs were carried out at 35±0.1 ^{0}C. The reaction was initiated by mixing the already thermostated solution of L-alanine 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 librated 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.

2.3 Stoichiometry and product analysis

In order to ascertain the stoichiometry of the reaction, different sets of experiments with varying [RNHCl]:[L-alanine] ratios were performed at 35 ^{0}C for 48 h and constant concentrations of all other reactants under the conditions [RNHCl] >> [L-alanine]. Iodometric estimation of unconsumed [RNHCl] in different sets shows that 1 mole of RNHCl was consumed to oxidize 1 mole of L-alanine. Accordingly, the following stoichiometric equation can be formulated



Acetaldehyde (ethanal), the main product in the oxidation of L-alanine was identified by the help of chromatography (TLC), conventional (spot test) method and also through 2,4-dinitrophenyl hydrazine (DNPH) derivative (Brady's test). The nature of acetaldehyde further confirmed by its IR spectrum (2730 cm^{-1} due to C-H stretching , 1733 cm^{-1} due to C=O stretching and 1370 due to C-H bending) (Figure 1). Similarly, ammonia by Nesseler's reagent and CO_2 was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through tube containing lime water.

3. RESULT AND DISCUSSION

Kinetics of Ir(III) catalyzed oxidation of L-alanine by chloramine-T in acidic medium was investigated at 35 ^{0}C. The kinetic results were collected at several initial concentrations (Table1,2). The order of reaction with respect to each reactant was determined by varying the concentration of oxidant, L-

alanine, 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 35^0C. 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:

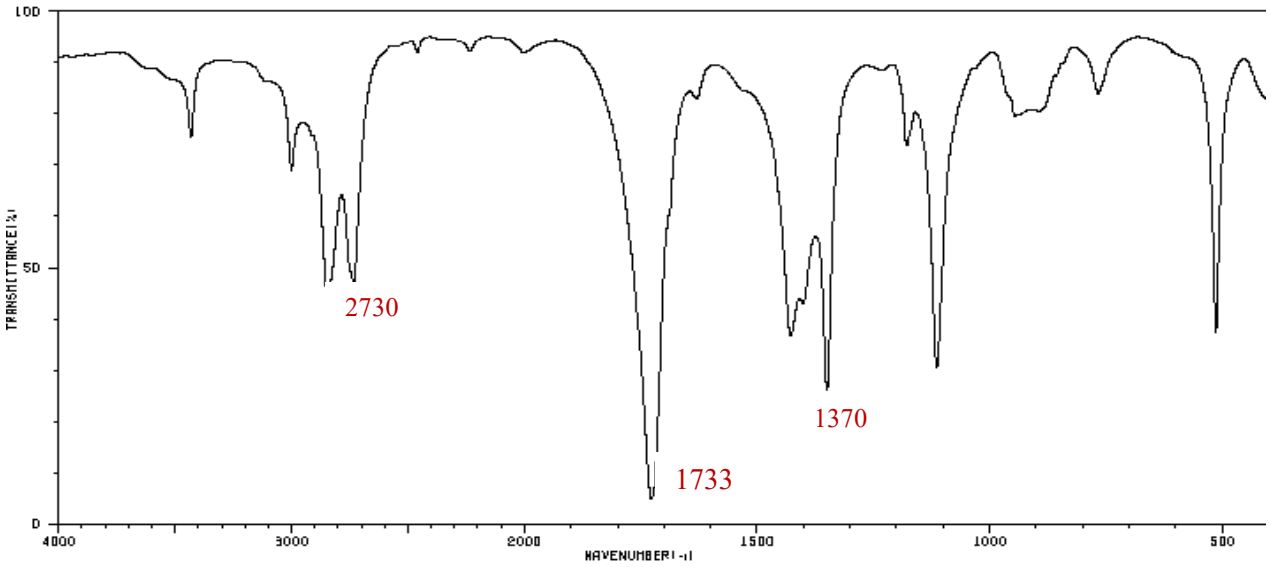
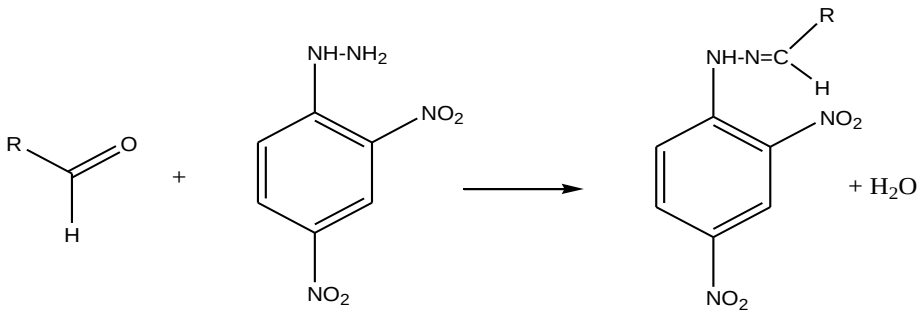


Figure 1. IR-spectrum of the main product acetaldehyde



2,4-dinitrophenyl hydrazine

2,4-dinitrophenyl hydrazine derivative

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

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

Table 1. Effect of variation of oxidant, L-alanine, Ir (III) at 35^0

[Oxidant] x 10^3 M (Chloramine-T)	[Substrate]x 10^2 M (L-alanine)	[Ir(III)] x 10^5 M	(-dc/dt)x10^7 $ML^{-1}s^{-1}$
0.83	1.00	6.67	1.72
1.00	1.00	6.67	2.12
1.25	1.00	6.67	2.62
1.67	1.00	6.67	3.50
2.50	1.00	6.67	5.30
5.00	1.00	6.67	10.65
1.00	0.33	6.67	1.55
1.00	0.40	6.67	1.65
1.00	0.50	6.67	1.80
1.00	0.66	6.67	1.92
1.00	1.00	6.67	2.12
1.00	2.00	6.67	2.40
1.00	1.00	2.67	0.80
1.00	1.00	4.01	1.25
1.00	1.00	5.34	1.65
1.00	1.00	6.67	2.12
1.00	1.00	8.02	2.55
1.00	1.00	9.35	3.05

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

Solution conditions: [Ir (III)] =6.67 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3} M,

[L-alanine] = 1.00 x 10^{-2}, $[Hg(OAc)_2]$ = 1.25 x 10^{-3} M.

A plot of (-dc/dt) versus [Chloramine-T] was linear with the slope value (0.97) near unity, which further confirms first order dependence of reaction on chloramine-T (figure 2). The first order kinetics with respect to [Chloramine-T] was also confirmed by 'least-square method' (figure 3). The plot of log (-dc/dt) versus log [Ir(III)] was linear indicating first order dependence on Ir(III). (figure 4). A plot of (-dc/dt) versus [Ir(III)] also gives a slope which is close to the average value of first order rate constant at 35^0C. Increase in concentration of L-alanine shows positive effect (figure 5) i.e., (-dc/dt) value increases with increase in concentration of substrate (Table 1). Variation of [KCl] concentration shows positive effect on reaction rate (Table 2). Negligible effect of mercuric acetate eliminates the probability of its

involvement either as a catalyst or as an oxidant. Hence, the function of mercuric acetate is to act as scavenger for any chloride ion formed in the reaction [33]. 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

Table 2. Effect of variation of $HClO_4$, KCl and $NaClO_4$ at 35^0

$[HClO_4]$ 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	1.90
1.00	1.00	1.00	2.12
1.25	1.00	1.00	1.75
1.67	1.00	1.00	2.18
2.50	1.00	1.00	2.04
5.00	1.00	1.00	2.15
1.00	0.83	1.00	1.82
1.00	1.00	1.00	2.12
1.00	1.25	1.00	2.25
1.00	1.67	1.00	2.50
1.00	2.50	1.00	2.65
1.00	5.00	1.00	2.80
1.00	1.00	0.83	2.05
1.00	1.00	1.00	2.12
1.00	1.00	1.25	1.85
1.00	1.00	1.67	2.55
1.00	1.00	2.50	1.70
1.00	1.00	5.00	2.52

solution of chloramine-T quick formation of RNHCl has been reported [34]. The reaction is unaffected by H^+ concentration (Table 2).

[Ir (III)] = 6.67 x 10^{-5} M, [L-alanine] = 1.00 x 10^{-2} M, $[Hg(OAc)_2]$ = 1.25 x 10^{-3} M,

$[HClO_4]$ =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

[Ir (III)] = 6.67 x 10^{-5} M, [L-alanine] = 1.00 x 10^{-2} M, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M,

[$HClO_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

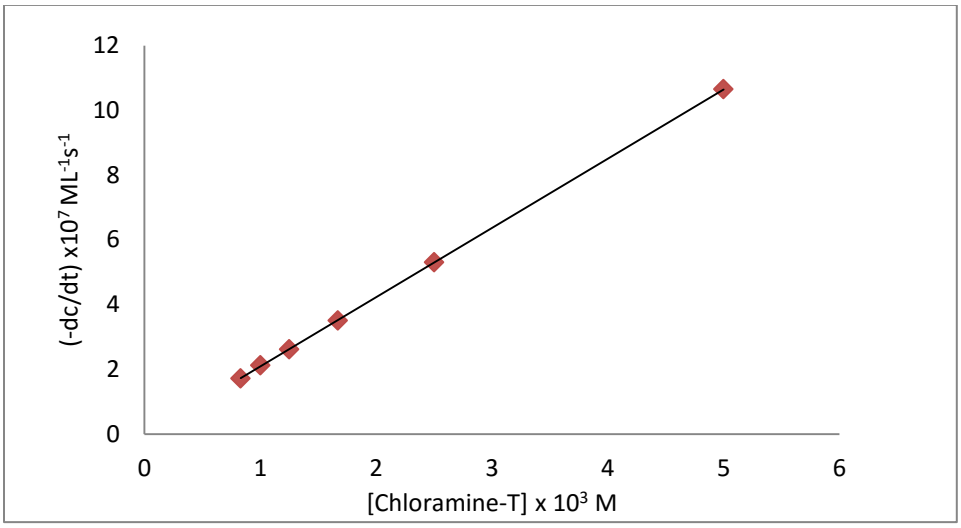


Figure 2. Plot between (-dc/dt) and [Chloramine-T] for the oxidation of L-alanine at 35 ^{0}C.

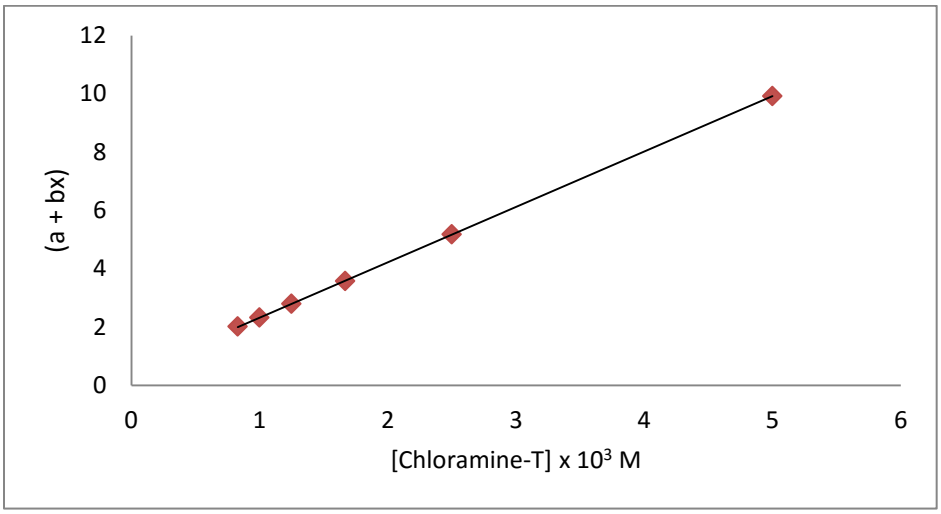


Figure 3. Plot between (a + bx) and [Chloramine-T] for the oxidation of L-alanine at 35 ^{0}C.

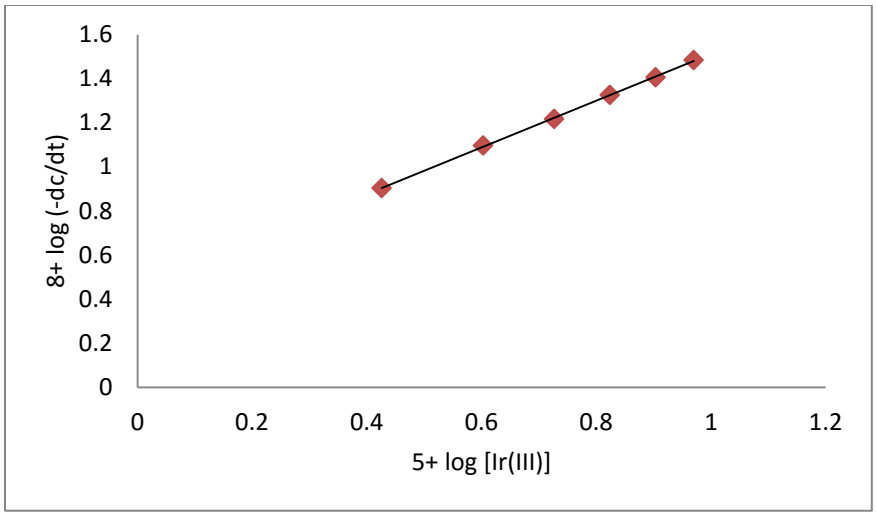


Figure 4. Plot between log (-dc/dt) and log Ir[(III)] for the oxidation of [L-alanine]at 35 ^{0}C . [L-alanine] = 1.00 x 10^{-2} M, [Chloramine-T] = 1.00 x 10^{-3}, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M, [$HClO_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

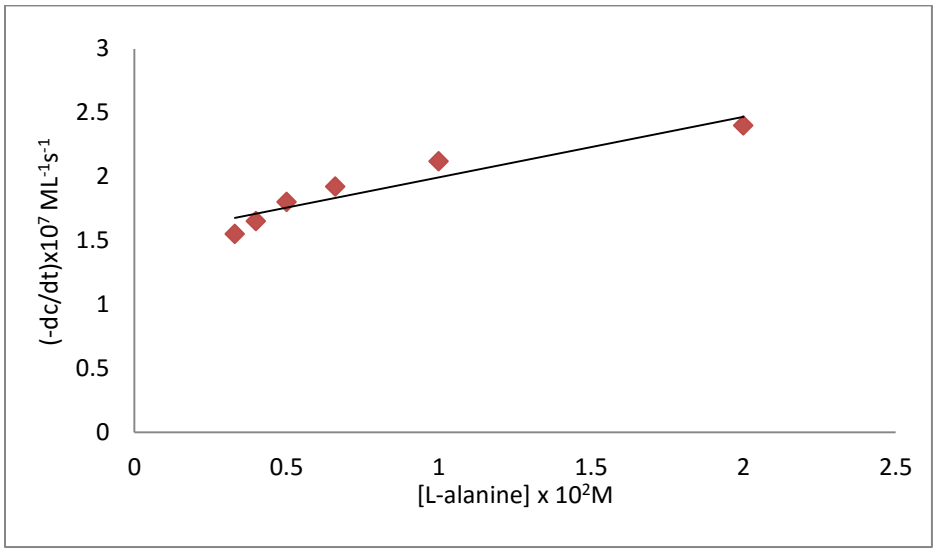


Figure 5. Plot between (-dc/dt) and [L-alanine] for the oxidation of [L-alanine] at 35 ^{0}C . [Ir (III)] = 6.67 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3}, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M, [$HClO_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

The kinetic measurements were also taken in the temperature range of 30-45^{0}C and the specific rate constants were obtained at 30^0, 35^0, 40^0 and 45^{0}C. These specific rate constants were used to draw a plot of log k versus 1/T (figure 6) which was linear. The various activation parameters were calculated from the slope of curves obtained from the Figure-6. 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 [35]. 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 [36].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 L-alanine

Parameters	Temperature(^{0}C)	L-alanine
K_1x 10^4 s^{-1}	30	1.48
K_1x 10^4 s^{-1}	35	2.12
K_1x10^4 s^{-1}	40	2.92
K_1x 10^4 s^{-1}	45	4.25
Log A	--	11.78
ΔE* (k J mol^{-1})	35	67.60
ΔG* (k J mol^{-1})	35	74.80
ΔH * (k J mol^{-1})	35	73.08
ΔS* ($JK^{-1}mol^{-1}$)	35	-5.56

Solution conditions: [Ir (III)] = 6.67 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3} M,

[L-alanine] = 1.00 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.

3.1 Mechanism and derivation of rate law

In acidic solution Iridium chloride exists as $[IrCI_6]^{3-}$. It has also been reported that $[IrCI_6]^{3-}$ is involved in equilibrium as follows [37]:

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

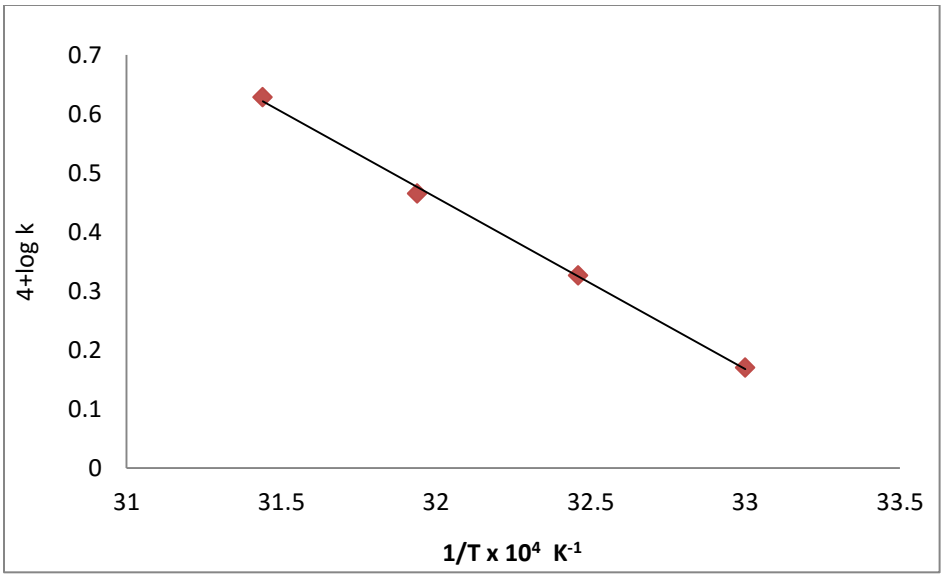
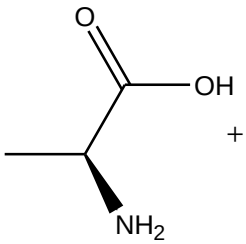


Figure 6: Arrhenius plot for the oxidation of L-alanine. [Ir (III)] = 6.67 x 10^{-5} M , [Chloramine-T] = 1.00 x 10^{-3} M, [L-alanine] = 1.00 x 10^{-2} , $[Hg(OAc)_2]$ = 1.25 x 10^{-3} M, $[HClO_4]$ =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

Thus either $[IrCl_6]^{3-}$ or $[IrCl_5H_2O]^{2-}$ may act as catalytic species [38]. If $[IrCl_5H_2O]^{2-}$ 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 $[IrCl_6]^{3-}$ 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:

$$\underset{C_1}{[IrCl_5(H_2O)]^{2-}} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C_2}{[IrCl_6]^{3-}} + H_2O$$



[S]

$$+ \quad \underset{C_2}{[IrCl_6]^{3-}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{C_3}{[S\text{-----}IrCl_6]^{3-}}$$

$$[S\text{-----}IrCI_6]^{3-} + \underset{C_3}{} RNHCl \underset{\text{slow step (r.d.s)}}{\overset{k_3}{\rightleftharpoons}} [S\text{-----}IrCI_6\text{ -----}RNHCl]^{3-}$$

$$[S\text{-----}IrCI_6\text{ -----}RNHCl]^{3-} + H_2O \overset{\text{Fast}}{\rightleftharpoons} \underset{[P]}{CH_3\text{-}CHO} + [IrCI_6]^{3-} + RNH_2 + HCl + CO_2 + NH_3$$

Where,

[S] = Substrate i.e. L-alanine

[P] = Product i.e. acetaldehyde

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

$$Rate = \frac{-d[RNHCl]}{dt} = k_3[C_3][RNHCl] \quad (i)$$

$$[Ir(III)]_T = [C_1] + [C_2] + [C_3] \quad (ii)$$

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

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

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

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

In same way,

$$\frac{d[C_2]}{dt} = k_{-2}[C_3] - k_2[S][C_2]$$

$$[C_2] = \frac{k_{-2}\,[C_3]}{k_2\,[S]}$$

$$[C_2] = \frac{[C_3]}{K_2\,[S]} \qquad (vi)$$

(where $K_2 = k_2/k_{-2}$)

Putting the value of $[C_2]$ in equation (v), we get :

$$[C_1] = \frac{[C_3]}{K_1\,K_2\,[S][Cl^-]}$$

$$[Ir(III)]_T = [C_1] + [C_2] + [C_3]$$

$$= \frac{[C_3]}{K_1\,K_2\,[S][Cl^-]} + \frac{[C_3]}{K_2\,[S]} + [C_3]$$

$$= [C_3]\left[\frac{1}{K_1\,K_2\,[S][Cl^-]} + \frac{1}{K_2\,[S]} + 1\right]$$

$$= [C_3]\left[\frac{1 + K_1\,[Cl^-] + K_1\,K_2\,[S][Cl^-]}{K_1\,K_2\,[S][Cl^-]}\right]$$

This gives

$$[C_3] = \frac{[Ir(III)]_T\,K_1\,K_2\,[S][Cl^-]}{1 + K_1\,[Cl^-] + K_1\,K_2\,[S][Cl^-]}$$

Putting the value of C_3 in equation (i), we get

$$Rate = \frac{K_1\,K_2\,k_3\,[Ir(III)]_T[S][Cl^-][RNHCl]}{1 + K_1\,[Cl^-] + K_1\,K_2\,[S][Cl^-]}$$

4. CONCLUSION

The following conclusions can be derived in the present study of Ir(III) catalyzed oxidation of L-alanine 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 L-alanine 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 1:1 and the oxidation products of L-alanine 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 L-alanine by Chloramine-T in acidic medium.

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The authors declare no conflict of interest

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