

Kinetic and Mechanistic Investigation on Oxidation of L-Alanine and L-leucine by Chloramine-T (CAT) Using Chloro-complex of Ir(III) in its Nano-Concentration Range as Homogeneous Catalyst : A Comparative Study

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ABSTRACT

The kinetics and mechanism of homogeneously Ir(III) chloride catalysed oxidation of L-alanine (ala) and L-leucine (leu) by chloramine-T [CAT] have been investigated in a perchloric acidic medium in the presence of mercuric acetate as a scavenger in the temperature range 30°C-45°C. The reactions follow identical kinetics. The experimental results show the first order kinetics with respect to the oxidant [CAT] and catalyst [Ir(III)] while positive effect with respect to both of the amino acids were observed. It is found that that [Hg(OAc)₂], [H⁺] and ionic strength (μ) of the medium have insignificant effect on the rate. Chloride ion is found to positively influence the rate of reaction. The reaction between chloramine-T and substrate (ala and leu) in acid medium shows 1:1 stoichiometry. The reactions have been studied at four different temperatures between 30 to 45°C and the activation parameters have been calculated. We have proposed a mechanism involving the complex formation between catalyst, substrate and oxidant. Acetaldehyde and isopentaldehyde have been identified chromatographically and spectroscopically as the final product of oxidation of ala and leu, respectively. Based on the kinetic data, reaction stoichiometry and product analysis, a suitable reaction mechanism has been proposed and the rate law has been derived.

Keywords: Kinetics, mechanism, Ir(III) catalysis, amino acids, chloramine-T, acidic medium

I. INTRODUCTION

Amino acids are required for every metabolic process making them important for all life processes. Oxidation of amino acids is of vital importance both from the chemical point of view and its role in the mechanism of amino acids metabolism [1]. Amino acids undergo different types of reaction according to whether a particular amino acid contains non-polar groups or polar substituents. In literature, many investigations have been carried out to study the kinetics of oxidation of amino acids by various kinds of reagents under different experimental conditions [2-5]. These studies show that the mechanism of oxidation of amino acids differs for the different reaction systems as different oxidants lead to the formation of different oxidation products [6-7]. Oxidative decarboxylation and deamination of amino acids are well reported biochemical processes. The

kinetics and oxidation of amino acids have been documented with various oxidants [8-10]. Among all the amino acids, alpha- amino acids, which have both the amine and carboxylic acid groups attached to the first carbon atom, have particular importance in biochemical and pharmaceutical applications. L-alanine and L-leucine are the particular alpha- amino acids those are important for stimulating muscle protein synthesis. A few studies are available in the literature about the catalyzed oxidation of L-Leucine and L-Alanine in acidic medium.

Several oxidizing agents can be used for the metal catalyzed oxidation of L-Leucine and L-Alanine. The aromatic N-halosulfonamides is a group of mild oxidants that are widely used as oxidizing agents in both acid and alkaline solutions due to the presence of strongly polarized N-linked halogen in +1 state [11-12].

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 [13-15]. Many organic substrates were oxidized by these sulfonamides and the kinetic and mechanistic aspects of these reactions are well documented [16-18]. Sodium N-chloro-p-toluenesulfonamide or Chloramine-T (CAT; $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NClNa}\cdot 3\text{H}_2\text{O}$) is a prominent member of this group and is used as halogenating and oxidizing agent [12,19,20]. Depending upon the pH of the medium, it forms various oxidizing species and thus shows a variety of kinetic results [21-22]. Many investigations are carried out to study the oxidizing behavior of Chloramine-T and other N-halosulfonamides [23-25]. In most of the studies one of the species, RNHCl ($\text{R} = \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$), HOCl , or H_2OCl^+ , has been considered as the reactive species [26]. Chloramine-T can act as both electrophile and nucleophile according to the reaction conditions.

Different transition metal catalysts have been used in the N-haloamine oxidation of organic substrates [27]. 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 [28]. Iridium(III) chloride is an important platinum group metal ion and has been extensively used as a homogeneous catalyst in a number of redox reactions [29]. Several studies have reported the use of Ir(III) chloride as a non-toxic and homogeneous catalyst [30-31]. The experimental results show that the reaction of L-alanine and L-leucine with CAT in the acidic medium in the absence of a catalyst were very sluggish but the reaction becomes facile in the presence of Ir(III) catalyst.

The aim of the present comparative study is to determine the most probable reaction path for the kinetics of oxidation of two biologically important amino acids, viz., L-alanine and L-leucine by CAT using chloro complex of Ir(III) in its nano-concentration range as homogeneous catalyst in acidic medium with the following objectives: (i) to ascertain the reactive species of catalyst and oxidant, (ii) find the oxidative capacity of oxidant (CAT) (iii) 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.

II. MATERIAL AND PROCEDURE

A. Materials

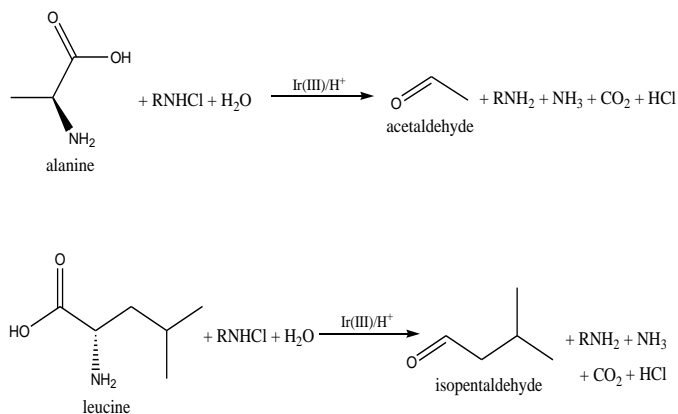
A standard aqueous solution of chloramine-T (S.D. Fine Chem. Ltd) was prepared afresh daily by dissolving its known weight in doubly distilled water and its concentration was estimated iodometrically. In order to avoid photochemical deterioration, the solution of chloramine-T was preserved in black coated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

B. Kinetic measurements or Procedure

A thermostated water bath was used to maintain the desired temperature within $\pm 0.1^\circ\text{C}$. Appropriate amount of substrate and all other reagents except chloramine-T, and enough distilled water to keep the total volume constant were taken in a reaction vessel and thermostated at 35°C for thermal equilibrium. A measured amount of Chloramine-T solution pre-equilibrated at same temperature was rapidly added to the reaction mixture. 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.

C. Stoichiometry and product analysis

In order to ascertain the stoichiometry of the reactions, different sets of experiments with varying $[\text{RNHCl}]:[\text{Amino acid}]$ ratios were performed at 35°C for 48 h and constant concentrations of all other reactants under the conditions $[\text{RNHCl}] \gg [\text{Amino acid}]$. Iodometric estimation of unconsumed $[\text{RNHCl}]$ in different sets shows that 1 mole of RNHCl was consumed to oxidize 1 mole of Amino acid (ala or leu). Accordingly, the following stoichiometric equations can be formulated:



Acetaldehyde (ethanal) in the case of L-alanine and isopentaldehyde in the case of L-leucine, were identified as the main oxidation product by the help of chromatography (TLC), conventional (spot test) method and also through 2,4-dinitrophenyl hydrazine (DNPH) derivative (Brady's test) (Scheme 1). The functional group -CHO was also confirmed by Tollen's reagent and Schiff's base. The nature of both products were further confirmed by its IR spectrum [Acetaldehyde: 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) and Isopentaldehyde: 2822 cm^{-1} due to C-H stretching, 1722 cm^{-1} due to C=O stretching and 1390 due to C-H bending (Figure 2)]. Similarly, ammonia was identified by Nessler's reagent and CO_2 was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the liberated gas through a tube containing lime water.

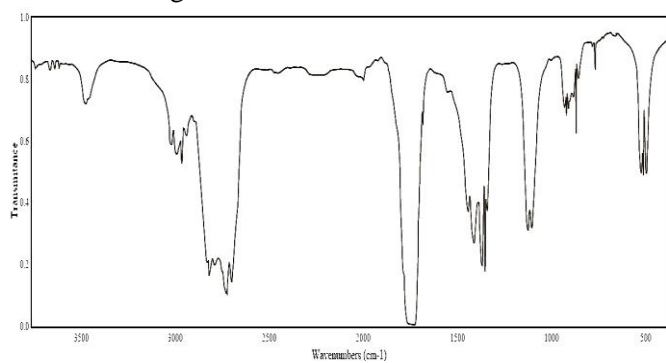


Figure 1. IR spectrum of the main product acetaldehyde

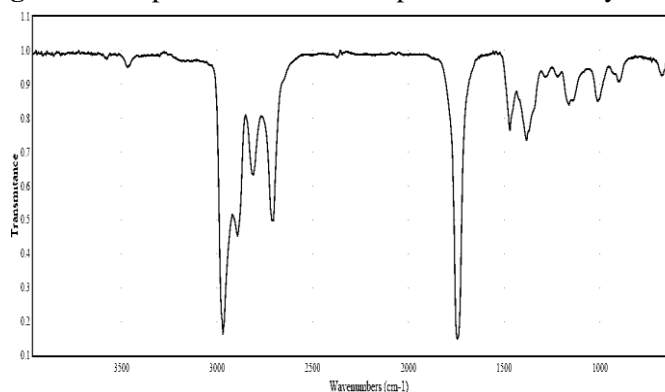
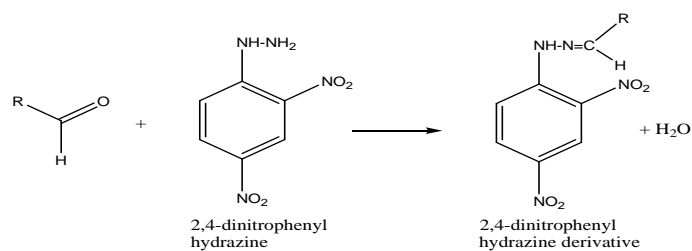


Figure. 2. IR spectrum of the main product

isopentaldehyde



Scheme 1. Preparation of 2,4-dinitrophenyl hydrazine derivative

III. RESULTS AND DISCUSSION

Kinetics of Ir(III) catalyzed oxidation of amino acids (ala and leu) by chloramine-T in acidic medium was investigated at 35°C . The kinetic results were collected at several initial concentrations (Table 1, 2). The order of reaction with respect to each reactant was determined by varying the concentration of oxidant, substrate, Ir(III) chloride (Table 1), H^+ ions, $[\text{Cl}^-]$ and mercuric acetate one by one in different sets keeping concentration of all other reactants constant at constant temperature 35°C . In each kinetic run, the initial rate (i.e., $-\text{dc}/\text{dt}$) 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:

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

Where $[\text{RNHCl}]^*$ denotes the $[\text{RNHCl}]$ at which $(-\text{dc}/\text{dt})$ was determined.

It is clear from the data given in Table 1 that, throughout the variation of Chloramine-T, the rate of the reaction increases in the same proportion in which the concentration of Chloramine-T is increased, which leads to the conclusion that the order of reaction with respect to $[\text{Chloramine-T}]$ is unity. A plot of $(-\text{dc}/\text{dt})$ versus $[\text{Chloramine-T}]$ was linear with the slope value near unity for both amino acids, which further confirms first order dependence of reaction on chloramine-T (Figure 3).

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

[Oxidant] x 10 ³ M (Chloramine-T)	[Amino acid]x 10 ² M	[Ir(III)] x10 ⁵ M	(-dc/dt)x10 ⁷ ML ⁻¹ s ⁻¹	
			L-alanine	L-leucine
0.83	1.00	6.67	1.72	2.15
1.00	1.00	6.67	2.12	2.65
1.25	1.00	6.67	2.62	3.30
1.67	1.00	6.67	3.50	4.42
2.50	1.00	6.67	5.30	6.62
5.00	1.00	6.67	10.65	13.25
1.00	0.33	6.67	1.55	2.36
1.00	0.40	6.67	1.65	2.42
1.00	0.50	6.67	1.80	2.50
1.00	0.66	6.67	1.92	2.60
1.00	1.00	6.67	2.12	2.65
1.00	2.00	6.67	2.40	2.85
1.00	1.00	2.67	0.80	1.07
1.00	1.00	4.01	1.25	1.58
1.00	1.00	5.34	1.65	2.12
1.00	1.00	6.67	2.12	2.65
1.00	1.00	8.02	2.55	3.19
1.00	1.00	9.35	3.05	3.70

Solution conditions: [Hg(OAc)₂] = 1.25 x 10⁻³ M,
[HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

The first order kinetics with respect to [Chloramine-T] was also confirmed by 'least-square method'(figure-4). The plot of (-dc/dt) versus [Ir(III)] was linear indicating first order dependence on Ir(III) in case of each amino acid (figure-5). A plot of log (-dc/dt) versus log [Ir(III)] also gives a slope which is close to the average value of first order rate constant at 35°C for the oxidation of L-Alanine and L-leucine. Increase in concentration of each

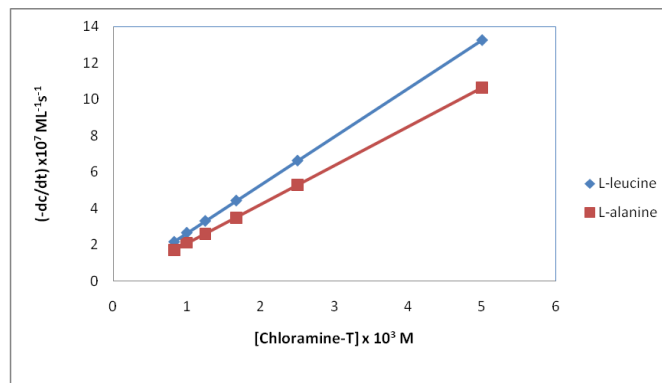


Figure 3. Plot between (-dc/dt) and [Chloramine-T] for the oxidation of Amino acid at 35^oC.

[Ir (III)] = 6.67 x 10⁻⁵ M, [amino acid] = 1.00 x 10⁻² M, [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

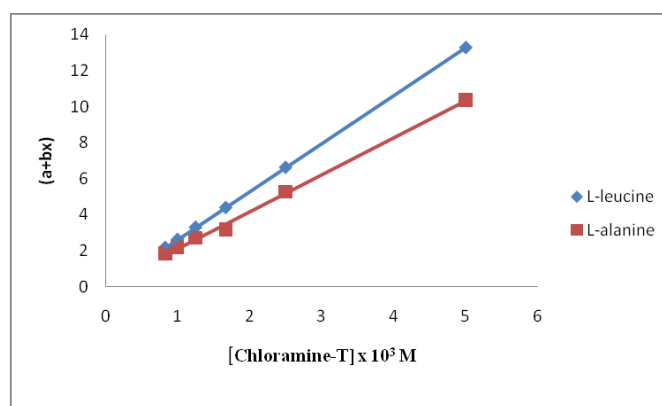


Figure 4. Plot between (a+bx) and [Chloramine-T] for the oxidation of Amino acid at 350C.

[Ir (III)] = 6.67 x 10⁻⁵ M, [amino acid] = 1.00 x 10⁻² M, [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

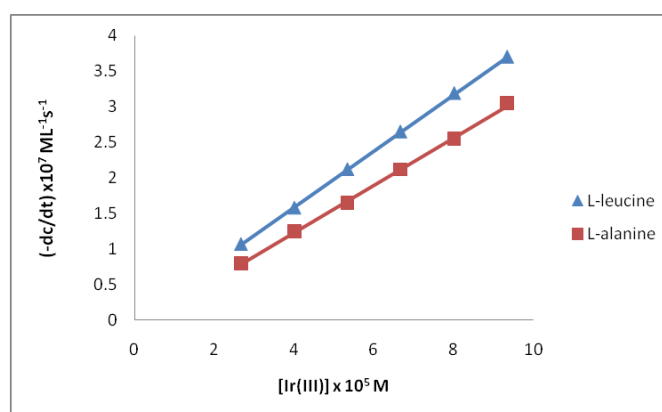


Figure 5. Plot between (-dc/dt) and [Ir(III)] for the oxidation of Amino acid at 35^oC.

[Chloramine-T] = 1.00 x 10⁻³ M, [amino acid] = 1.00 x 10⁻² M, [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M

amino acid shows positive effect (figure-6) i.e., $(-dc/dt)$ value increases with increase in concentration of substrates (Table 1).

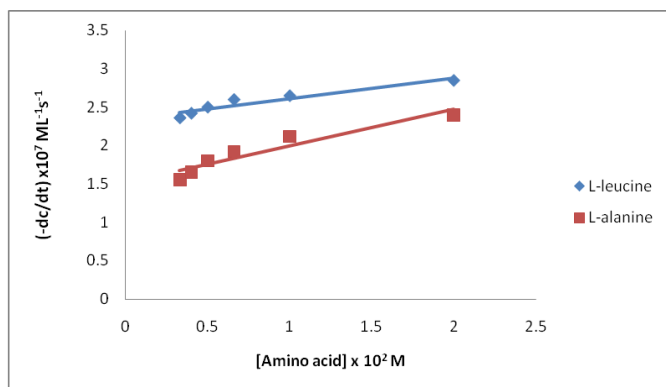


Figure 6. Plot between $(-dc/dt)$ and $[Amino\ acid]$ for the oxidation of Amino acid at $35\ ^\circ C$.

$[Ir\ (III)] = 6.67 \times 10^{-5}\ M$, $[Chloramine-T] = 1.00 \times 10^{-3}\ M$, $[Hg(OAc)_2] = 1.25 \times 10^{-3}\ M$, $[HClO_4] = 1.00 \times 10^{-3}\ M$, $[KCl] = 1.00 \times 10^{-3}\ M$.

Table 2. Effect of variation of $HClO_4$, KCl and $NaClO_4$ at $35\ ^\circ C$

$[HClO_4] \times 10^3\ M$	$[KCl] \times 10^3\ M$	$NaClO_4 \times 10^3\ M$	$(-dc/dt) \times 10^7\ ML^{-1}\ s^{-1}$	
			L-alanine	L-leucine
0.83	1.00	1.00	1.90	2.46
1.00	1.00	1.00	2.12	2.65
1.25	1.00	1.00	1.75	2.56
1.67	1.00	1.00	2.18	2.39
2.50	1.00	1.00	2.04	2.70
5.00	1.00	1.00	2.15	2.50
1.00	0.83	1.00	1.82	2.52
1.00	1.00	1.00	2.12	2.65
1.00	1.25	1.00	2.25	2.75
1.00	1.67	1.00	2.50	2.90
1.00	2.50	1.00	2.65	3.05
1.00	5.00	1.00	2.80	3.20
1.00	1.00	0.83	2.05	2.60
1.00	1.00	1.00	2.12	2.65
1.00	1.00	1.25	1.85	2.56
1.00	1.00	1.67	2.55	2.53
1.00	1.00	2.50	1.70	2.72

1.00	1.00	5.00	2.52	2.68
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Solution conditions: $[Ir\ (III)] = 6.67 \times 10^{-5}\ M$, $[Chloramine-T] = 1.00 \times 10^{-3}\ M$, $[amino\ acid] = 1.00 \times 10^{-2}$, $[Hg(OAc)_2] = 1.25 \times 10^{-3}\ M$.

Variation of $[KCl]$ concentration shows positive effect on reaction rate (Table 2). Negligible effect of mercuric acetate was found in each case which 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 [32]. 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 [33]. The reaction is unaffected by H^+ concentration with respect to each amino acid (Table 2).

To study the effect of temperature on the oxidation of L-Alanine and L-leucine, reactions were carried out at different temperatures ranging from $30-45\ ^\circ C$ keeping the concentrations of all reactants same. Activation parameters i.e., energy of Activation (E_a), Arrhenius factor (A), entropy of activation (ΔS^*), free energy of activation (ΔG^*) and enthalpy of activation (ΔH^*) were calculated and summarized (Table 3). The value of energy of activation (E_a) was found to be more for L-Alanine than L-leucine which clearly proves chloramine-T is more reactive towards L-leucine. The plots of $\log k$ versus $1/T$ for L-Alanine and L-leucine are straight line graphs with negative slopes which proves the validity of Arrhenius equation (figure-7). 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 [34]. 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 [35]. 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.

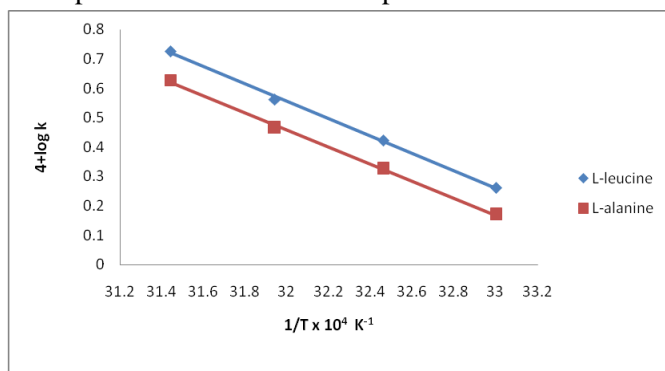


Figure 7. Arrhenius Plot of the oxidation of Amino acid at 35 C.

[Ir (III)] = 6.67 x 10⁻⁵ M, [Chloramine-T] = 1.00 x 10⁻³ M, [amino acid] = 1 x 10⁻², [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

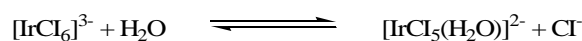
Table 3. Activation parameters for the oxidation of amino acid

Parameters	Temperature(°C)	L-alanine	L-leucine
K ₁ x 10 ⁴ s ⁻¹	30	1.48	1.83
K ₁ x 10 ⁴ s ⁻¹	35	2.12	2.65
K ₁ x 10 ⁴ s ⁻¹	40	2.92	3.65
K ₁ x 10 ⁴ s ⁻¹	45	4.25	5.32
Log A	--	11.78	11.52
E _a (kJ mol ⁻¹)	35	67.60	65.49
ΔG* (kJ mol ⁻¹)	35	72.23	71.65
ΔH* (kJ mol ⁻¹)	35	65.04	62.65
ΔS* (JK ⁻¹ mol ⁻¹)	35	-23.35	-28.30

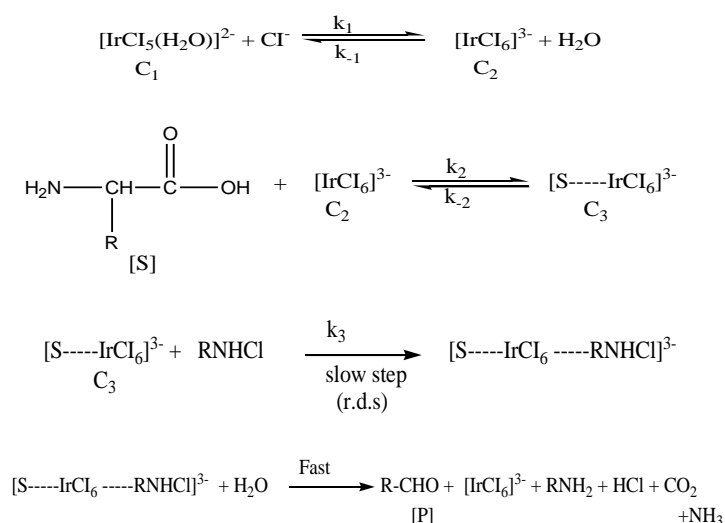
Solution conditions: [Ir (III)] = 6.67 x 10⁻⁵ M, [Chloramine-T] = 1.00 x 10⁻³ M, [amino acid] = 1.00 x 10⁻², [Hg(OAc)₂] = 1.25 x 10⁻³ M, [HClO₄] = 1.00 x 10⁻³ M, [KCl] = 1.00 x 10⁻³ M.

A. Mechanism and derivation of rate law

In acidic solution Iridium chloride exists as [IrCl₆]³⁻. It has also been reported that [IrCl₆]³⁻ is involved in equilibrium as follows [36]:



Thus either [IrCl₆]³⁻ or [IrCl₅H₂O]²⁻ may act as catalytic species [37]. If [IrCl₅H₂O]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 [IrCl₆]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:



Where,

R = -CH₃ for L-alanine

R = -CH₂-CH-(CH₃)₂ for L-leucine

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

$$\text{Rate} = \frac{-d[\text{RNHCl}]}{dt} = k_3[\text{C}_3][\text{RNHCl}] \quad (i)$$

$$[\text{Ir(III)}]_T = [\text{C}_1] + [\text{C}_2] + [\text{C}_3] \quad (ii)$$

$$\frac{d[\text{C}_1]}{dt} = k_{-1}[\text{C}_2] - k_1[\text{C}_1][\text{Cl}^-] \quad (iii)$$

$$[\text{C}_1] = \frac{k_{-1}[\text{C}_2]}{k_1[\text{Cl}^-]} \quad (iv)$$

$$[\text{C}_1] = \frac{[\text{C}_2]}{K_1[\text{Cl}^-]} \quad (v)$$

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

In same way,

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

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

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

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

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

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

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

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

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

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

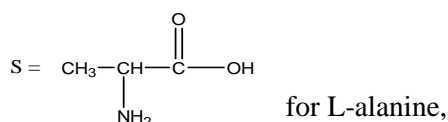
This gives

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

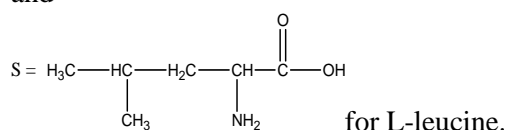
Putting the value of C_3 in equation (i), we get

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

Where,



and



Equation (vii) is the final rate law which very well explains the observed positive effects of [substrates] and $[Cl^-]$, and first order kinetics with respect to $[Ir(III)]$ and $[RNHCl]$ in the oxidation of amino acids.

IV. CONCLUSION

The following conclusions can be derived in the present study of Ir(III) catalyzed oxidation of L-alanine and L-leucine 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 and L-leucine by Chloramine-T are 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 in case of each amino acid and the oxidation products were identified (e) Activation parameters were computed from the Arrhenius plot. (f) The value of activation parameters reveals that L-leucine is more reactive than L-alanine (g) 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 and L-leucine by Chloramine-T in acidic medium.

V. ACKNOWLEDGEMENT

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