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Kinetics of Ir(III) Catalyzed Oxidative Decarboxylation and Deamination of L-phenylalanine by Chloramine-T: A Mechanistic Approach

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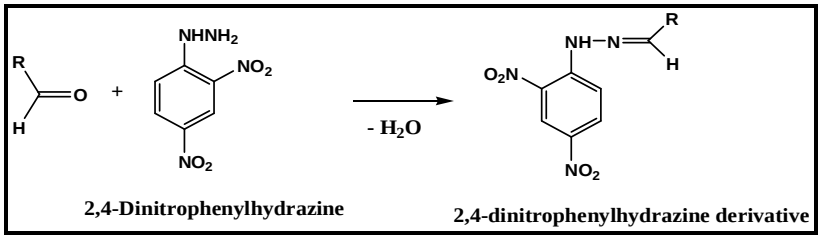
ABSTRACT

The kinetics and mechanism of homogeneously Ir(III) chloride catalyzed oxidation of L-Phenylalanine by chloramine-T [CAT] has been investigated in perchloric acidic medium in presence of mercuric acetate as a scavenger in the temperature range 30ºC-45ºC. 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-Phenylalanine was observed. The reaction shows negligible effect of [$Hg(OAc)_2$], [H^+] and ionic strength(μ)of the medium. Chloride ion positively influenced the rate of reaction. The reaction between chloramine-T and substrate (L-Phenylalanine) 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. Phenyl acetaldehyde has been identified chromatographically and spectroscopically as the final product of oxidation of L-Phenylalanine. Based on the kinetic data, reaction stoichiometry and product analysis, a reaction mechanism has been proposed and rate law has been derived.

Graphical Abstract



Preparation of 2, 4-dinitrophenyl hydrazine derivative

Keywords: Kinetics, Mechanism, Ir(III) catalysis, Amino acids, Chloramine-T, Acidic medium.

INTRODUCTION

Oxidation of amino acids is of great importance both from chemical point of view and its bearing on the mechanism of amino acids metabolism [1]. 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. Many reports are available in the recent literature one the kinetics of oxidation of amino acids by variety of reagents under different experimental conditions [2-5]. 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 [6-7]. L-Phenylalanine (L-Phe) is an electrically neutral essential amino acid, which participate in building of many proteins especially in animal and is required for normal functioning in humans. It forms active sites of enzymes and helps in maintaining their proper conformation by keeping them in proper ionic states. So, oxidation of L-Phenylalanine may help in understanding some aspects of enzyme kinetics. L-Phenylalanine, supplementation helps in the suppression of pain and aids weight loss through the suppression of appetite. It is converted into tyrosine, which in turn converted into L-DOPA, the metabolic precursor of such other vitally important molecules as, dopamine, norepinephrine (noradrenalin), and epinephrine (adrenaline). 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 [8-10].

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 [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]. A prominent member of this group Sodium N-chloro-p-toluene sulfonamide or Chloramine-T (CAT; $p\text{-}CH_3C_6H_4SO_2NClNa.3H_2O$) is used as haloginating and oxidizing agent [19-20]. Depending upon the pH of the medium, it forms various oxidizing species and thus shows a variety of kinetic results [21-22]. Several researchers have studied the oxidizing behavior of CAT [23-25] and numerous studies focus on the mechanistic aspects of the redox reactions in acidic media.

Various transition metal, Pd(II) catalyzed oxidative degradation of paracetamol by chloramine-T in acidic and alkaline media oxidation of organic substrates [26]. 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 [27-28]. Iridium(III) chloride is an important platinum group metal ion and has been extensively used as 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]. Preliminary experimental results indicate that the reaction of L-Phenylalanine, with CAT in the acidic medium without a catalyst were very sluggish but the reaction becomes facile in the presence of Ir(III) catalyst.

The aim of the present study is to propose the most probable reaction path for the kinetics of oxidation of biologically important amino acid (L-Phenylalanine) by CAT using chloro complex of Ir(III) in its nano-concentration range as homogenous 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.

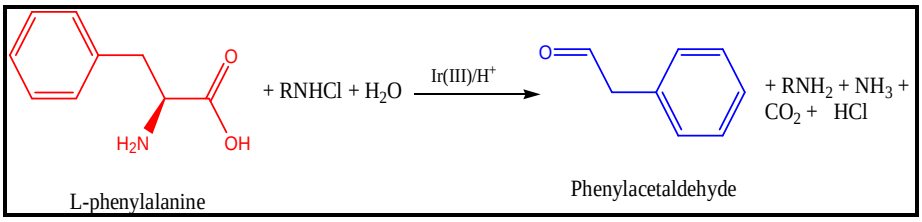
MATERIALS AND METHODS

A standard aqueous solution of chloramine-T (S.D. Fine Chem. Ltd) was prepared a fresh 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 L-phenylalanine (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.

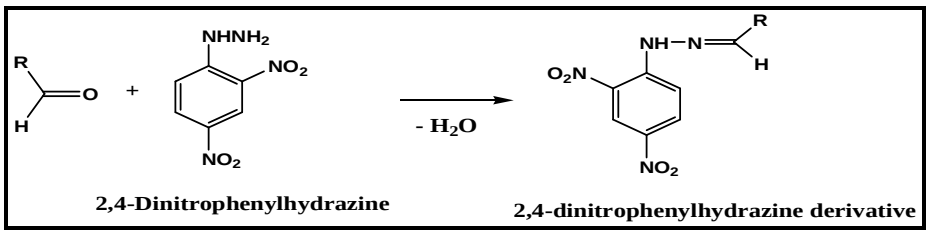
Kinetic measurements or Procedure: A thermostatic water bath was used to maintain the desired temperature within ±0.1ºC. Appropriate amount of substrate and all other reagents except chloramine-T, and enough distilled water to keep the total volume constant were taken in a reaction vessel and thermo stated at 35ºC for thermal equilibrium. A measured amount of chloramine-T solution pre-equilibrated at same temperature was rapidly added to the reaction mixture. Aliquots (5 mL) of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5 mL of 4% KI solution and 5 mL 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.

Stoichiometry and product analysis: In order to ascertain the stoichiometry of the reactions, different sets of experiments with varying [RNHCl]: [L-Phenylalanine] ratios were performed at 35ºC for 48 h and constant concentrations of all other reactants under the conditions [RNHCl] >>[L-Phenylalanine]. Iodometric estimation of unconsumed [RNHCl] in different sets shows that 1 mole of RNHCl was consumed to oxidize 1 mole of L-Phenylalanine. Accordingly, the following stoichiometric equations can be formulated



Stoichiometric equation

Phenyl acetaldehyde the main product in the oxidation of L-Phenylalanine was identified 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 phenyl acetaldehyde further confirmed by its IR spectrum (2920 cm^{-1} due to C-H (sp^3), 3030 cm^{-1}C-H(aromatic) stretching, 1498, 1602 cm^{-1} due to aromatic C=C stretching, 1724 cm^{-1} due to C=O stretching and 1454 cm^{-1} due to C-H bending) (Fig. 1). 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 tube containing lime water.



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

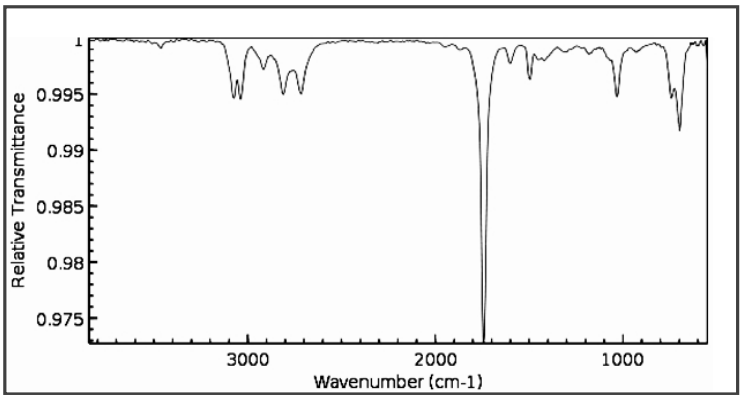


Figure 1. IR spectrum of the main product Phenyl acetaldehyde.

RESULTS AND DISCUSSION

Kinetics of Ir(III) catalyzed oxidation of L-Phenylalanine by chloramine-T in acidic medium was investigated at 35ºC. The kinetic results were collected at several initial concentrations (Table 1 and 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, [Cl^-] and mercuric acetate one by one in different sets keeping concentration of all other reactants constant at constant temperature 35ºC. 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:

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

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

Table 1. Effect of variation of oxidant, L-Phenylalanine, Ir(III) at 35°C

[Oxidant] x 10^3 M (Chloramine-T)	[Substrate]x 10^2 M (L-Phenylalanine)	[Ir(III)] x 10^5	(-dc/dt)x10^7 $ML^{-1}s^{-1}$
0.83	1.00	6.67	2.60
1.00	1.00	6.67	3.15
1.25	1.00	6.67	4.05
1.67	1.00	6.67	5.12
2.50	1.00	6.67	7.72
5.00	1.00	6.67	14.45
1.00	0.33	6.67	1.90
1.00	0.40	6.67	2.15
1.00	0.50	6.67	2.50
1.00	0.66	6.67	2.92
1.00	1.00	6.67	3.15
1.00	2.00	6.67	3.45
1.00	1.00	2.67	1.21
1.00	1.00	4.01	1.85
1.00	1.00	5.34	2.42
1.00	1.00	6.67	3.15
1.00	1.00	8.02	3.74
1.00	1.00	9.35	4.56

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.

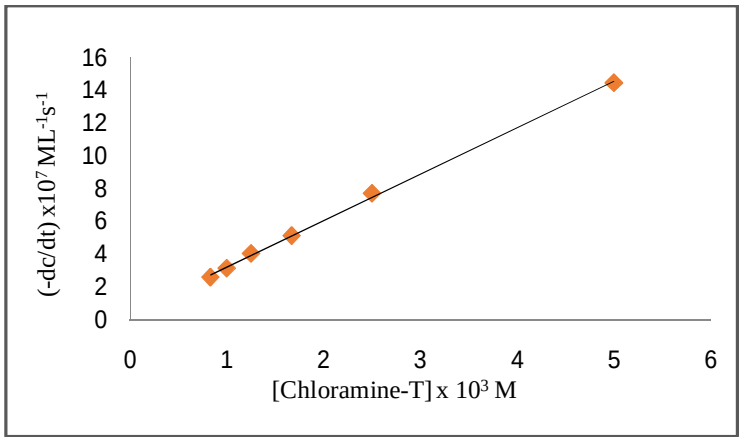


Figure 2. Plot between (-dc/dt) and [Chloramine-T] for the oxidation of L-Phenylalanine at 35°C. [Ir (III)] = 6.67 x 10^{-5} M, [L-Phenylalanine] = 1.00 x 10^{-2} M, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M,[$HClO_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

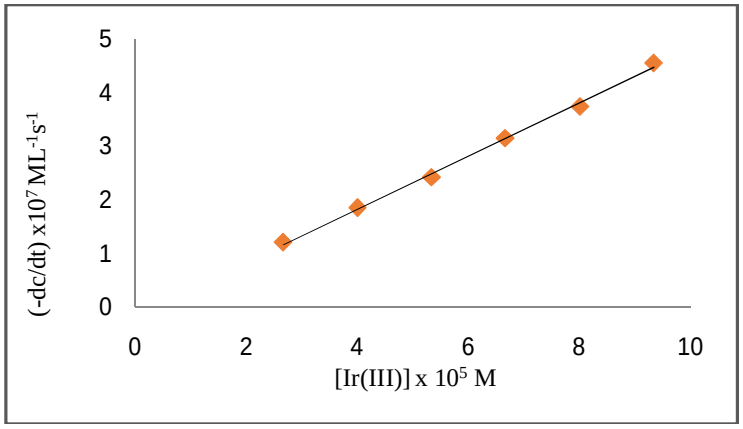


Figure 3. Plot between (-dc/dt)and [Ir(III)] for the oxidation of L-Phenylalanine at 35°C.[Chloramine-T] = 1.00 x 10^{-3}M, [L-Phenylalanine] = 1.00 x 10^{-2} M, [$Hg(OAc)_2$] = 1.25 x 10^{-3}M,[$HClO_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

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 35ºC. Increase in concentration of L-Phenylalanine shows positive effect (figure-4) i.e., (-dc/dt) value increases with increase in concentration of substrate (Table 1).

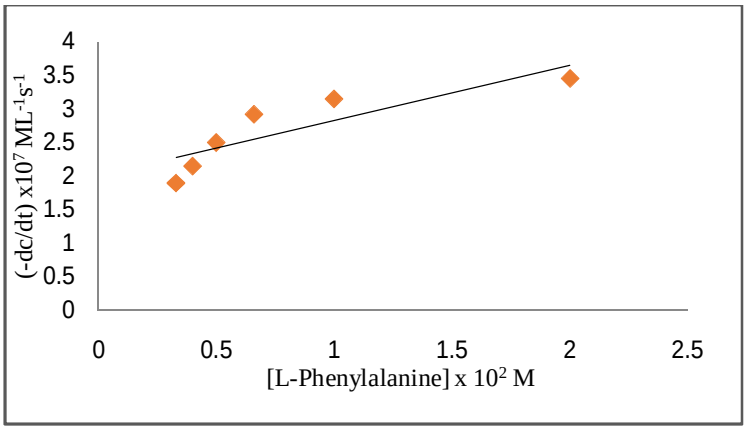


Figure 4. Plot between (-dc/dt) and [L-Phenylalanine] for the oxidation of L-Phenylalanine at 35°C. [Ir (III)] = 6.67 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3}M, [$Hg(OAc)_2$] = 1.25 x 10^{-3} M,[$HClO_4$] =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

Variation of [KCl] concentration shows positive effect on reaction rate (Table 2). Negligible effect of mercuric acetate was found in oxidation of L-Phenylalanine 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 (Table 2).

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

$[HClO_4] \times 10^3$ M	$[KCl] \times 10^3$M	$NaClO_4 \times 10^3$M	$(-dc/dt) \times 10^7 ML^{-1}s^{-1}$
0.83	1.00	1.00	2.75
1.00	1.00	1.00	3.15
1.25	1.00	1.00	2.72
1.67	1.00	1.00	2.12
2.50	1.00	1.00	3.04
5.00	1.00	1.00	2.45
1.00	0.83	1.00	2.76
1.00	1.00	1.00	3.15
1.00	1.25	1.00	3.45
1.00	1.67	1.00	3.75
1.00	2.50	1.00	4.12
1.00	5.00	1.00	4.76
1.00	1.00	0.83	2.15
1.00	1.00	1.00	3.15
1.00	1.00	1.25	3.50
1.00	1.00	1.67	2.75
1.00	1.00	2.50	2.20
1.00	1.00	5.00	2.70

Solution conditions: [Ir (III)] =6.67 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3} M, [L-Phenylalanine] = 1.00 x 10^{-2}, $[Hg(OAc)_2]$ = 1.25 x 10^{-3} M.

To study the effect of temperature on the oxidation of L-Phenylalanine, reactions were carried out at different temperatures ranging from 30-45ºC keeping the concentrations of all reactants same 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 5) which was linear. The various activation parameters were calculated from the slope of curves obtained from the figure 5. The values of activation parameters i.e., energy of Activation (Ea), Arrhenius factor (A), entropy of activation (ΔS*), free energy of activation (ΔG*) and enthalpy of activation (ΔH*) were calculated and summarized (Table 3).

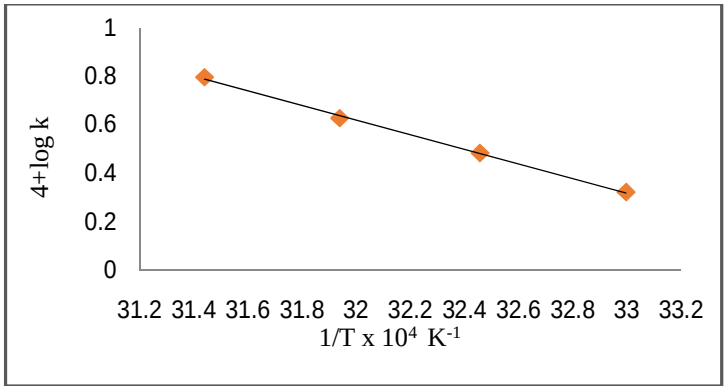


Figure 5. Arrhenius Plot of the oxidation of L-Phenylalanineat 35°C. [Ir (III)] = 6.67 x 10^{-5} M, [Chloramine-T] = 1.00 x 10^{-3}M, [L-Phenylalanine] = 1 x $10^{-2,}$ $[Hg(OAc)_2]$ = 1.25 x 10^{-3} M, $[HClO_4]$ =1.00 x 10^{-3} M, [KCl] = 1.00 x 10^{-3} M.

Table 3. Activation parameters for the oxidation of L-Phenylalanine

Parameters	Temperature(°C)	L-Phenylalanine
$K_1 x\ 10^4\ s^{-1}$	30	2.10
$K_1 x\ 10^4\ s^{-1}$	35	3.15
$K_1 x 10^4\ s^{-1}$	40	4.24
$K_1 x\ 10^4\ s^{-1}$	45	6.24
Log A	--	10.90
ΔE* (k J mol^{-1})	35	61.47
ΔG* (k J mol^{-1})	35	71.20
ΔH * (k J mol^{-1})	35	58.91
ΔS* ($JK^{-1}mol^{-1}$)	35	-40.21

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

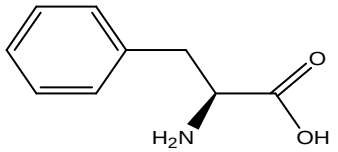
Moderate ΔH* and ΔS* values are favourable for electron transfer reaction. The value of ΔH* was due to energy of solution changes in transition state. The high positive value of ΔG* represents highly solvated transition state. The negative value of ΔS* indicates that the intermediate complex is more 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.

Mechanism and derivation of rate law: In acidic solution Iridium chloride exists as $[IrCl_6]^{3-}$. It has also been reported that $[IrCl_6]^{3-}$ is involved in equilibrium as follows [36]:

$$[IrCl_6]^{3-} + H_2O \rightleftharpoons [IrCl_5(H_2O)]^{2-} + Cl^-$$

Thus either $[IrCl_6]^{3-}$ or $[IrCl_5H_2O]^{2-}$ may act as catalytic species [37]. 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:

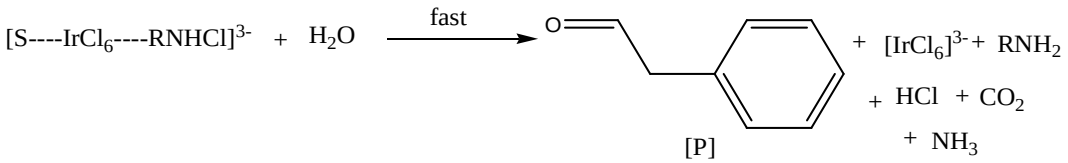
$$\underset{C_1}{[IrCl_5(H_2O)]^{2-}} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{C_2}{[IrCl_6]^{3-}} + H_2O$$



[S]

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

$$\underset{C_3}{[S\text{-----}IrCl_6]^{3-}} + RNHCl \xrightarrow[\text{slow step (r.d.s)}]{k_3} [S\text{-----}IrCl_6\text{ -----}RNHCl]^{3-}$$



Where,[S] = Substrate i.e. L-Phenylalanine, [P] = Product i.e. L-Phenyl acetaldehyde

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

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

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

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

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

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

Where, $K_1 = k_1/ k_{-1)}$

In same way,

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

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

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

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

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

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

APPLICATION

In this study to improve the synthesis of 2-phenylacetaldehyde as an oxidized compound and furthermore applied the synthesis of Schiff base 2,4-dinitrophenyl hydrazine. This study also useful for the optimum of time, conversion of desired product, determination of yield and all operation of parameter for production of large scale synthesis of aldehyde. Schiff base is beneficial for human health, synthesis of chelating agents and organic synthesis.

CONCLUSION

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

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