Ir(III) CATALYZED OXIDATION OF SOME POLYHYDRIC ALCOHOLS AND AMINO ACIDS BY CHLORAMINE-T: A KINETIC AND MECHANISTIC STUDY

ABSTRACT

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The word “kinetic” is originated from greek word “kinetikos” meaning to move[1]. In branch of Physics, the study of motion(mechanics) is divided into kinematics, which deals with the description of motion, and kinetics, which deals with the effects of forces on motion. Whereas in the branch of chemistry, such a distinction is not made and chemical kinetics refers to study of the time dependent rate of change of the chemical composition of materials. The chemical composition of a material can be described, macroscopically, in terms of thermodynamic state variables such as temperature, pressure, or chemical potential. For a molecular point of view, chemical kinetics involve the study of chemical reactions in which one or more molecules undergo a transformation to form a new molecule or molecules. At thermodynamic equilibrium, the macroscopic state variables listed above remain unchanged but molecular transformations still occur and the equilibrium values of the state variables are defined by the kinetics of those transformations. The amount of time required for a single molecular transformation is typically on the order of a femto second while changes in the properties of materials are usually on a much longer time scale.

Chemical kinetics is of great importance in chemical and pharmaceutical industries. Since the mechanism of a reaction is closely linked with kinetics, and since mechanism is a major topic of inorganic, organic and biological chemistry, the subject of kinetics provides a unifying framework for these conventional branches of chemistry. Catalysis, solid state chemistry and surface chemistry heavily rely on the understanding of the kinetic techniques and analysis. With the evolution of computers and computing techniques, dramatic advances have taken place in quantum mechanical calculations of the potential energy and in theoretical descriptions of rates of reaction. As a result, kinetics is significantly contributing to the rapidly growing subjects such as atmospheric chemistry and environmental studies.

Temperature studies provide important information about the nature of the activated complex as obtained from the values of activation parameters (ΔS^*, ΔG^*, ΔH^* etc.). Making use of these thermodynamic parameters, the proposed mechanism can be justified.

The kinetic studies have also been useful in working out the conditions for obtaining the maximum yield of several industrial products. It is natural that the majority of kinetic investigations deal with the reaction whose rates can be measured easily, without the use of special methods. During recent years, due to the development of new electronic techniques, a good deal of work has been devoted to the study of reactions that are difficult to study by conventional methods. For instance, the reactions occurring at very high hydrostatic pressures or temperatures and reaction occurring at very high velocity.

The role of catalyst was widely recognized in modern chemical industry and has therefore been subjected to qualitative and quantitative studies. The reactions in solution are rather complicated than those in gaseous phase due to the uncertainty of the reacting species and their activities or their salvation by the solvent molecules. Among several type of reactions occurring in solution, redox reactions [2] are most frequently investigated from the kinetic point of view.

Kinetics has an answer to many difficult analytical problems [3-5]. Kinetics also help in mixture analysis [6], enzyme analysis and use of enzyme in the determination of rate dependence on substrate concentration by the direct use of kinetic data [7]. Kinetic studies are also very useful in polymer chemistry and for determining the greater stability conditions for better yields of desired polymer [8-9]. The most widely studied reactions in solutions are the electron transfer reactions between an oxidant and reductant [10]. The reaction involving catalytic oxidation reactions plays an important role in a chemical process. A large number of researchers have worked in the field of oxidant reduction processes [11-14].

The manner in which the rate of a reaction varies with the concentration of reacting species is usually the slowest step which is also the rate determining step. Reaction mechanisms are derived concepts which can be changed or modified if some new information is indicated by stating the order of the reaction. For multistep reactions the kinetic study is limited to new facts that are observed [15].

The rate law can be derived for various mechanisms. A comparison of experimentally observed rate law then allows one to make some choice among apparently reasonable mechanism. Only that mechanism which gives the rate law of

the form determined by experiments may be considered as possible mechanism for the reaction.

Aims and objectives of the present work

In the present thesis an attempt has been made to investigate the kinetics of oxidation of some polyhydric alcohols (ethylene glycol, mannitol, D-sorbitol) and amino acids (leucine, alanine and phenylalanine) by acidified solution of chloramine-T in the presence of iridium(III) chloride as a homogeneous catalyst and mercuric acetate as a scavenger for chloride ion (likely to be produced in the reaction) in acidic medium.

The main aims and objectives of the present investigation may be summarized as follows:-

1. To study the effect of oxidant (Chloramine-T) variation on the rate of reaction in acidic medium.
2. To investigate the effect of change in concentration of catalyst (iridium(III) chloride), substrate and mercuric acetate on the rate of reaction and determine the order of reaction with respect to each of them in acidic medium.
3. To study the effect of $[H^+]$, $[Cl^-]$ and ionic strength and calculate its effect on the reaction rate.
4. To study the effect of temperature on the reaction rate.
5. To calculate the thermodynamic activation parameters viz. Ea, ΔG^*, ΔS^*, ΔH^* and logA for various reactions.
6. To derive rate law for the reaction and give mechanistic steps conforming to the rate law.
7. All the above studies have been made for six different compounds.

Materials and methodology

All the reagents used were of highest purity available.

An aqueous solution of substrate, oxidant (chloramine-T), sodium perchlorate and mercuric acetate (E. Merck) were prepared by dissolving the weighed amount of sample in double distilled water. Perchloric acid (60%) of (E. Merck) grade was

used as a source of H^+ ions. Sodium perchlorate (E. Merck) was used to maintain the ionic strength of medium. Reaction stills were blackened from outside to prevent photochemical effect.

The stock solution of chloramine-T (E. Merck) was prepared by dissolving the weighed amount of sample [0.5688] in triple distilled water, standardized iodometrically and stored in dark coloured bottle.

The stock solution of iridium(III) chloride (Johnson Matthey) was prepared by dissolving the sample in dilute HCl of known strength (0.018N).and was stored in black painted bottle to prevent photochemical decomposition.

Appropriate quantities of solution of mercuric acetate, perchloric acid, KCl, substate and $IrCl_3$ were placed in a 100 cm^3 jena glass vessel. The requisite amount of double distilled water was added, so that the total volume of the reaction mixture was 50 cm^3 after adding the substrate. The reaction mixture was then placed in a thermostated water bath maintained at desired temperature ± 0.1ºC.

The mixture was allowed to attain the bath temperature and reaction was then initiated by adding the requisite amount of oxidant solution and progress of reaction was followed by determining chloramine-T (oxidant) iodometrically in aliquots withdrawn after regular time intervals, by using starch as an indicator.

A brief outline of kinetic results obtained in Ir(III) catalyzed oxidation of polyhydric alcohols by chloramine-T in acidic medium.

The title reaction yielded the following kinetic informations:

1. The reaction follows first order kinetics with respect to oxidant i.e., chloramine-T.
2. Zero order dependence of the reaction on the substrate (ethylene glycol, mannitol and D-sorbitol) was observed.
3. Negligible effect of $[H^+]$ on the rate of reaction was observed in all the reactions performed.
4. First order kinetics with respect to catalyst i.e., Ir (III) chloride was observed.
5. Insignificant effect of ionic strength of the medium on the reaction rate was observed.
6. Addition of mercuric acetate did not bring about any appreciable change in the reaction velocity.
7. Addition of chloride ion to the reaction mixture caused positive change in the reaction velocity.
8. Addition of acetic acid showed positive effect on the rate of reaction.
9. Increase in the temperature showed marked effect on the reaction velocity.
10. Two moles of chloramine-T oxidized one mole of substrate (ethylene glycol, mannitol and D-sorbitol).
11. The main product of oxidation of all polyhydric alcohols was the corresponding acid.

Mechanism of Ir(III) catalyzed oxidation of polyhydric alcohols by chloramine-T in acidic medium:

The possible reactive oxidizing species of Chloramine-T and catalyzing species of iridium(III) chloride has been identified as RNHCl and $[IrCl_6]^{3-}$ respectively and considering the observed kinetic informations about the effect of $[H^+]$, $[Cl^-]$, [substrate], addition of mercuric acetate, effect of change in ionic strength of the medium on the rate of reaction in oxidation of substrate, the following reaction scheme may be suggested.

Consider equilibrium (1) which exists in the catalyst Ir(III):

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

Positive effect with respect to Cl^- in the present investigation suggests that the equilibrium would shift to the right. Therefore $[IrCl_6]^{3-}$ is the active species of Ir(III) chloride in acidic media.

$$\underset{[C_2]}{[IrCl_6]^{3-}} + RNHCl \xrightarrow[\text{slow step r.d.s}]{k_2} \underset{[C_3]}{[IrCl_6 \text{-----} RNHCl]^{3-}} \qquad (2)$$

$$[C_3] + RCH_2OH \xrightarrow{\text{Fast}} [IrCl_5H]^{3-} + \underset{\displaystyle R\text{-}\overset{\displaystyle RNCl}{\overset{|}{C}}\text{H-OH}}{} + HCl \qquad (3)$$

$$[IrCl_5H]^{3-} + RNHCl \longrightarrow [IrCl_6]^{3-} + RNH_2 \qquad (4)$$

$$\underset{\displaystyle R\text{-}\overset{\displaystyle RNCl}{\overset{|}{C}}\text{H-OH}}{} + H_2O \longrightarrow R\text{-}COOH + RNH_2 + HCl \qquad (5)$$

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

$$\frac{-d[RNHCl]}{dt} = k_2[C_2]\,[RNHCl]$$

$$\text{Rate} = k_2[C_2]\,[RNHCl] \qquad (6)$$

$$[Ir(III)]_T = [C_1] + [C_2] \qquad (7)$$

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

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

$$[C_1] = \frac{[C_2]}{K_1[Cl^-]} \qquad (K_1 = k_1/k_{-1})$$

By putting the value of $[C_1]$ in equation (7), we get

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

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

$$[Ir(III)]_T = [C_2]\left(\frac{1 + K_1[Cl^-]}{K_1[Cl^-]}\right) \qquad (8)$$

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

By putting the value of $[C_2]$ in equation (6), we get

$$\boxed{\text{Rate} = \frac{K_1 k_2[Ir(III)]_T[RNHCl][Cl^-]}{1 + K_1[Cl^-]}} \qquad (9)$$

The rate law derived fully explains first order dependence of the reaction rate on chloramine-T, Ir(III) chloride and zero order dependence of the reaction rate on

substrate viz., ethylene glycol, mannitol and D-sorbitol. The rate law also shows positive effect with respect to potassium chloride.

A brief outline of kinetic results obtained in Ir(III) catalyzed oxidation of amino acids by chloramine-T in acidic medium.

The title reaction yielded the following kinetic informations:-

1. The reaction follows first order kinetics with respect to oxidant i.e., chloramine-T.
2. Fractional positive order with respect to amino acids.
3. First order kinetics in Iridium(III) chloride was observed.
4. Zero order dependence on perchloric acid was observed in the oxidation of leucine, alanine and phenylalanine.
5. Positive effect of chloride ion was also observed for all the reactions.
6. Addition of mercuric acetate did not influence the rate of reaction.
7. Zero effect of variation of ionic strength of the medium was observed.
8. Addition of acetic acid did not show any influence on the rate of reaction.
9. Increase in the temperature showed marked effect on the rate of reaction.
10. One mole of chloramine-T oxidized a mole of substrate (leucine, alanine and phenylalanine).
11. The main product of oxidation of both amino acids is corresponding aldehyde.

Mechanism of Ir(III) catalyzed oxidation of amino acids by chloramine-T in acidic medium:

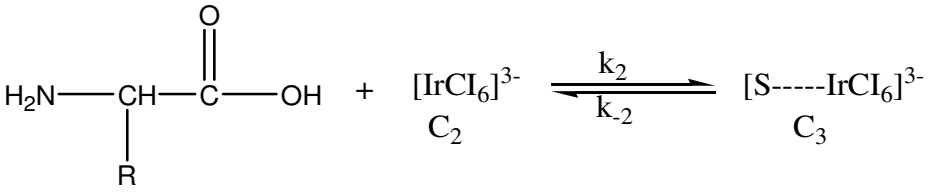
The possible reactive oxidizing species of Chloramine-T and catalyzing species of Iridium(III) chloride has been identified as RNHCl and $[IrCl_6]^{3-}$ respectively and considering the observed kinetic informations about the effect of $[H^+]$, $[Cl^-]$, [substrate], addition of mercuric acetate, effect of change in ionic strength

of the medium on the rate of reaction in oxidation of substrate, the following reaction scheme may be suggested.

Cl^- exist as the following equilibrium in acidic solution of Ir(III) chloride.

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

Positive effect with respect to Cl^- in the present investigation suggests that the equilibrium would shift to right. Therefore, $[IrCl_6]^3]$ is the active species of iridium(III) chloride in acidic medium.



(2)

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

$$[S\text{-----}IrCl_6\text{ -----}RNHCl]^{3-} + H_2O \xrightarrow{\text{Fast}} \underset{[P]}{CH_3\text{-}CHO} + [IrCl_6]^{3-} + RNH_2 + HCl + CO_2 + NH_3 \qquad (4)$$

Now considering the above steps and applying the steady-state treatment with reasonable approximation

$$\frac{-d[RNHCl]}{dt} = k_3[C_3]\,[RNHCl]$$

$$\text{Rate} = k_3[C_3]\,[RNHCl] \qquad (5)$$

$$[Ir(III)]_T = [C_1] + [C_2] + [C_3] \quad (6)$$

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

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

$$[C_1] = \frac{[C_2]}{K_1[Cl^-]} \qquad (K_1 = k_1/k_{-1}]) \quad (7)$$

In the same way,

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

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

$$[C_2] = \frac{[C_3]}{K_2[S]} \qquad (K_2 = k_2/k_{-2})$$

Putting the value of $[C_2]$ in equation (7), we get

$$[C_1] = \frac{[C_3]}{K_1K_2[Cl^-][S]}$$

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

$$= \frac{[C_3]}{K_1K_2[Cl^-][S]} + \frac{[C_3]}{K_2[S]} + [C_3]$$

$$= [C_3]\left(\frac{1}{K_1K_2[Cl^-][S]} + \frac{1}{K_2[S]} + 1\right)$$

$$[Ir(III)]_T = [C_3]\left(\frac{1+K_1[Cl^-]+K_1K_2[Cl^-][S]}{K_1K_2[Cl^-][S]}\right)$$

$$[C_3] = \frac{[Ir(III)]_T K_1K_2[Cl^-][S]}{1+K_1[Cl^-]+K_1K_2[Cl^-][S]}$$

By putting the value of $[C_3]$ in equation (5), we can find

$$\text{Rate} = \frac{K_1K_2k_3[\text{Ir(III)}]_T[Cl^-][S][RNHCl]}{1+K_1[Cl^-]+K_1K_2[Cl^-][S]} \qquad (8)$$

Thus the rate law derived fully explains first order dependence of the reaction rate on chloramine-T, Ir(III) chloride. The rate law also shows positive effect with respect to substrate and potassium chloride. There is negligible effect of mercuric acetate, addition of heavy water and ionic strength of the medium. Addition of acetic acid shows positive effect.

Reactive species of Chloramine-T in acidic medium

Chloramine-T acts as a mild oxidant in both acidic and alkaline media. In general, CAT undergoes a two-electron change in its reactions to form the reduction products, PTS ($p\text{-}CH_3C_6H_4SO_2NH_2$ or RNH_2) and sodium chloride. The aqueous solution of chloramine-T behaves as a strong electrolyte [16], and, depending on the pH, its results in different types of reactive species. The possible oxidizing species in an acidified CAT solution are the conjugate free acid (RNHCl), dichloramine-T ($RNCl_2$), hypochlorous acid (HOCl) and H_2OCl^+.

Chloramine-T exists as a free acid (RNHCl) in acidic media. The dissociation constant of RNHCl at a pH 4.5 is 2.8×10^{-5} reported by Morris *et al.* [17]. Further, RNHCl can undergo disproportionation or hydrolysis according to following reactions:

$$2RNHCl \rightleftharpoons RNCl_2 + RNH_2$$

$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl$$

In case of polyhydric alcohol, HOCl acts as the most reactive species of CAT in the reaction, which gives a rate law capable of explaining all the kinetic observations and other effects. In case of amino-acids, it was found that $RNCl^-$ is a strong base and therefore, likely to be fully protonated even if only an equivalent amount of acid is present and exist as RNHCl.

Reactive species of Iridium(III) chloride in acidic media

Iridium(III) chloride is an important platinum group metal ion and has been extensively used as homogeneous catalyst in a number of redox reactions [18]. Several studies have reported the use of Ir(III) chloride as a non-toxic and homogeneous catalyst [19]. The acidic solution of Iridium chloride exists as $[IrCl_6]^{3-}$. It has also been reported that $[IrCl_6]^{3-}$ is involved in equilibrium as follows :

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

Either $[IrCl_6]^{3-}$ or $[IrCl_5H_2O]^{2-}$ may act as catalytic species. If $[IrCl_5H_2O]^{2-}$ is taken as catalytic species the rate law would require negative effect of chloride ion. In present investigation, the positive effect of chloride ion on the oxidation rate is observed. 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.

Calculation of the activation parameters

In this section an attempt has been made to calculate the different activation parameters. For this, the reaction has been studied at four different temperatures and with the help of observed rate/rate constant, the energy of activation (E_a), specific rate constant (k_r), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*), free energy of activation (ΔG^*) and Arrhenius frequency factor (A) have been computed for different reactions. The activation parameter have been calculated with the help of following equations:-

(i) $$k_r = \frac{-dc/dt}{[RNHCl]^{n_1}[S]^{n_2}[Ir(III)]^{n_3}[H^+]^{n_4}}$$

(ii) $$\frac{\Delta S^*}{4.576} = \log k_r - 10.573 - \log T + \frac{E_a}{4.576T}$$

All values are in calories

(iii) $\Delta H^* = E_a - RT$

(iv) $\Delta G^* = \Delta H^* - T\Delta S^*$

(v) $\log A = \log k_r + \frac{E_a}{2.303RT}$

The calculated values of various activation parameters for different redox systems are as follows:-

Activation parameters of Ir(III) catalyzed oxidation of some polyhydric alcohols and amino acids by chloramine-T in acidic medium:

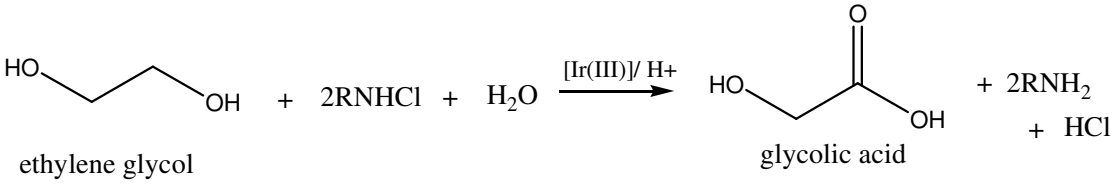
Substrate	Temperature Coefficient	E_a kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* JK mol^{-1}	ΔG^* kJ mol^{-1}	Log A
Ethylene glycol	2.10	54.93	52.40	-60.09	71.16	9.82
Mannitol	1.97	50.56	47.99	-74.08	70.58	9.13
D-Sorbitol	1.99	42.90	40.33	-98.05	70.51	7.88
Leucine	2.00	65.49	62.65	-28.30	71.65	11.52
Alanine	1.97	67.60	65.04	-23.35	72.23	11.78
Phenylalanine	2.01	61.47	58.91	-40.21	71.20	10.90

Stoichiometry and reaction products

1(a) Ir(III) catalyzed oxidation of some polyhydric alcohols by chloramine-T in acidic medium.

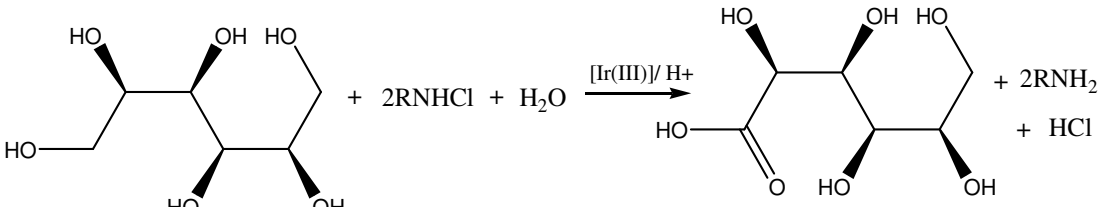
In oxidation of ethylene glycol, mannitol and D-sorbitol, it has been observed that two moles of chloramine-T were required to oxidize one mole of substrate in presence of acidic solution of Ir(III) chloride as catalyst. Accordingly the following stoichiometric equations could be formulated as:-

(i) For Ethylene Glycol:-



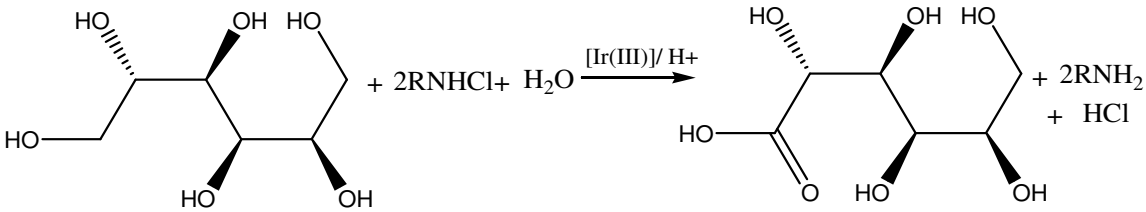
ethylene glycol — glycolic acid

(ii) For Mannitol:-



D-mannitol — Mannonic acid

(iii) For D-Sorbitol:

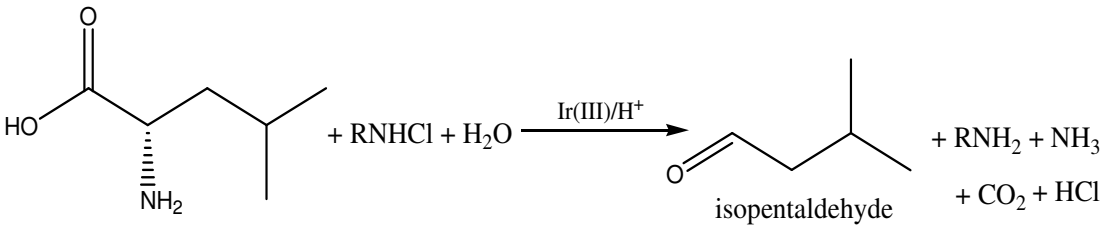


D-Sorbitol — D-Gluconic acid

1(b) Ir(III) catalyzed oxidation of Amino Acids by Chloramine-T in acidic medium:

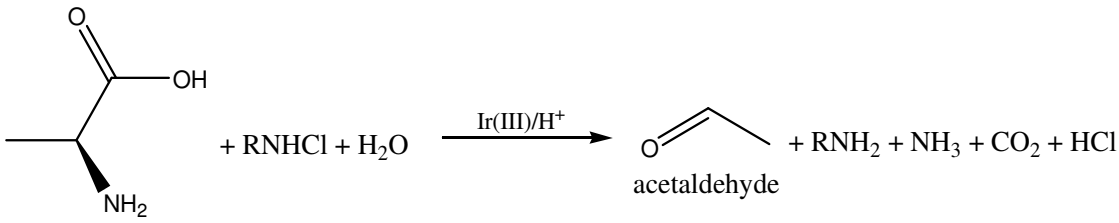
The stoichiometric studies on oxidation of leucine, alanine and phenylalanine by chloramine-T in presence of $HClO_4$ reveals that one mole of chloramine-T was required to oxidize one mole of substrate [amino acid]. On the basis of the above experimental findings, the overall reaction for the oxidation of reducing substrate has been given as follows:

(i) For Leucine:



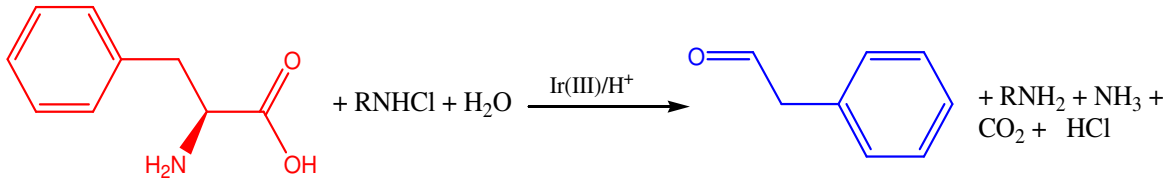
leucine isopentaldehyde

(ii) For Alanine:



alanine acetaldehyde

(ii) For Phenylalanine:



L-phenylalanine Phenylacetaldehyde

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