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Role of $IrCl_3(H_2O)_3$ in the oxidation of glycine by N-chlorosuccinimide in acidic medium: A kinetic and mechanistic study

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Abstract : The present study performs the kinetics and mechanism of oxidation of glycine by N-chlorosuccinimide (NCS) in the presence of chloro-complex of Ir(III) i.e.$IrCl_3(H_2O)_3$ in acidic medium at 40^0C using mercuric acetate as scavenger. The redox reaction shows unity order with respect to [glycine] and follows first order kinetics with respect to N-chlorosuccinimide. The reaction shows negative effects with respect to $[H^+]$ and [Ir(III)]. The rate of oxidation of glycine is not affected by the change of concentration of $[Cl^-]$, [NHS], [Hg(II)], ionic strength (μ) and dielectric constant of the medium. The reaction was studied at four different temperatures (from 308K-323K) and observed values of rate constant were used to calculate various activation parameters specially the entropy of activation ($\Delta S^{\#}$). NCS itself and $IrCl_3(H_2O)_3$ have been postulated as the reactive species of NCS and Ir(III) chloride in acidic medium, respectively. On the basis of kinetic orders, activation parameters and spectrophotometric evidence, a most probable reaction mechanism has been proposed for the oxidation of glycine in presence of Ir(III) as an inhibitor in acidic medium.
Keywords : Kinetic studies, Glycine, Ir(III)-chloride, Inhibitor, N-Chlorosuccinimide, Acidic medium.

Introduction:

Amongst various N-haloamides, N-chlorosuccinimide is reported[1] as a source of positive chlorine, hypochlorite and nitrogen ions which act both as base and nucleophile. In literature its use has been reported as an oxidizing agent as well as an analytical reagent specially in acidic medium[2]**.** In recent years the kinetics of oxidation of amino acids has been subject of extensive research due to the economical and biological importance of protein to living organisms. Besides fulfilling specific nutritional or physiological roles, Amino acids residues are the main constituents of protein and the study of its sensitivity towards oxidation open up a new area to understand the mechanism involved in the protein and amino acid modification. Protein may also have therapeutic or pharmacological action. A number of catalyzed[3-6] oxidation of amino acids has been carried out in acidic/alkaline medium by using various organic and inorganic oxidants. Transition metal catalyzed reactions have created great interest due to their chemical reactivity, antitumor activity, electronic structure and catalytic functions with involvement in many important potential industrial processes. In view of the biological importance of amino acid, and also in view of the fact that no investigation on the kinetic oxidation of glycine with NCS as an oxidant and Ir(III) chloride as inhibitor in alkaline medium has so far been made, the present study has been undertaken.

Experimental:

All the reagents used were of highest purity percentage available. Reaction mixture was prepared in black coated conical flask to prevent any photochemical reaction. All the solutions used were prepared in double distilled water to prevent any foreign ion interference. N-chlorosuccinimide (Loba Chem) was recrystalized from hot water and its purity was checked. Required amount of NCS was weighed and dissolved it in double distilled water. The prepared solution of NCS was standardised against standard solution of sodium thiosulphate (Qualigens Chemicals) iodometrically. Standard solutions of Glycine (E. Merck) was freshly prepared by exact weighing and dissolving the weighed amount in double distilled water. A solution of Ir(III) chloride (Sigma Chemicals) was prepared in HCl of known strength (10.00×10^{-2} M) and its concentration was maintained at 6.69×10^{-3} M. A weighed amount of sodium hydroxide (Qualigens Chemicals) was dissolved in double distilled water. and standardized by acid base titration.

Each kinetic run was performed at a constant temperature of 40ºC with an accuracy of ±0.1°C. In a black coated conical flask all the reactants except glycine were mixed in required quantity and hanged in thermostatic water bath maintained at 40ºC. Freshly prepared solution of substrate (glycine) was also kept in separate conical flask within the same thermostatic water bath at the same temperature. When both the solutions have acquired the temperature of the bath, measured amount of the glycine solution was pipetted out and was mixed in the conical containing reaction mixture. As soon as the amino acid solution was mixed with the reaction mixture the reaction gets initiated. To know the actual progress of the reaction, 5 ml of the reaction mixture were taken out and poured in a conical containing 5 ml of KI (4%) solution and 5 ml of $HClO_4$ solution and the liberated iodine equivalent to unconsumed NCS was titrated against hypo solution using starch as an indicator. In each kinetic run, the initial rate of reaction was calculated from the slope of the curve obtained by the plot of remaining concentration of NCS versus time.

Results and Discussion:

The kinetics of Ir(III)-catalysed oxidation of Glycine by NCS in acidic medium has been studied at 40°C. To know the effect of N-chlorosuccinimide on the rate of reaction, a number of kinetic experiments were performed by varying NCS concentration and keeping the concentration of all other reactants at constant temperature of 40ºC and at constant ionic strength of the medium. Unity order in [NCS] is evident from Fig.1 where a direct proportionality between the rate and concentration of NCS was observed. During the variation from 0.86 x 10^{-6} to 5.86 x 10^{-6} of Ir(III)-chloride, the concentrations of all other reactants were kept constant. The reaction follows negative fractional order with respect to Ir(III)-chloride throughout its variation (Fig.2). For the effect of amino acid on the rate of oxidation, the concentration of glycine was varied from 1.00×10^{-2} M to 10.00×10^{-2} M at constant concentrations of all other reactants and at constant temperature, 40°C. Fig.3 shows a plot between the values of first-order rate constant, k_1, and [Glycine]. This plot clearly shows first-order kinetics with respect to [glycine] throughout its ten fold variation. The decrease in the first-order rate constant k_1, with the increase in $[H^+]$ was observed in the variation of $[H^+]$ at constant concentration of all other reactants and at constant temperature 40°C [Fig.4]. The rate of the reaction remains unaffected by the change in $[Cl^-]$ and ionic strength of the medium. To determine the effect of temperature on the rate in NCS oxidation of glycine using Ir(III) as inhibitor, a number of experiments were performed under identical conditions at four different temperature, viz. 35, 40, 45 and 50°C. By the observed values of first order rate constant, k_1, the values of activation parameters like ΔS^*, ΔG^*, ΔH^*, E_a and A for Ir(III)-catalysed oxidation were calculated and found as -206.66 JK^{-1} mol^{-1}, 115.64 kJ mol^{-1}, 50.92 $kJmol^{-1}$, 53.55 $kJmol^{-1}$ and 2.72×10^2 mol^{-1} l s^{-1}, respectively.

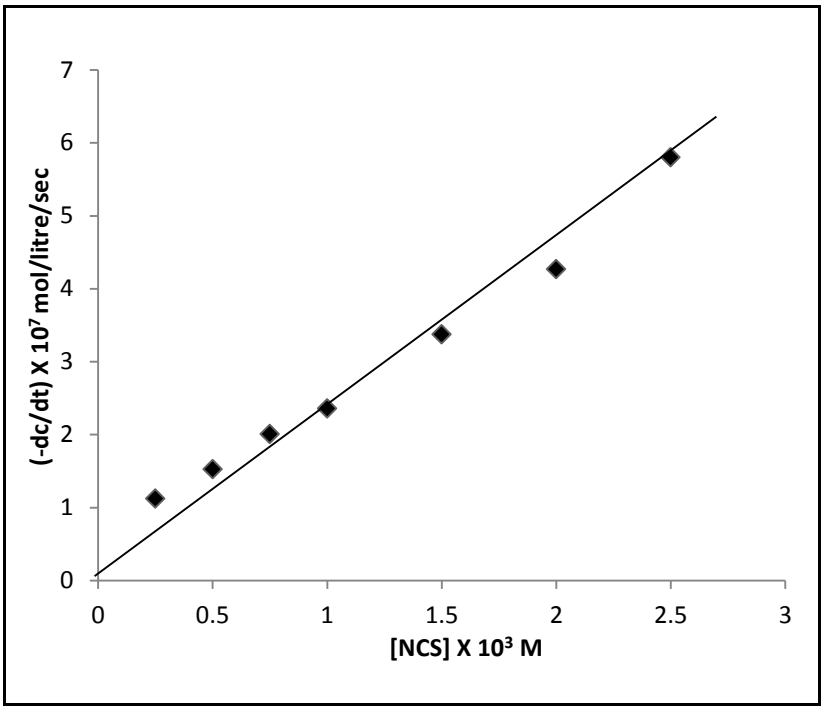


Fig.1. Plot between –d*c*/d*t* and [NCS] at 40°C

[Glycine] = 1.33×10^{-2} M; $[H^+] = 5.00\times10^{-3}$ M; [NHS] = 3.00×10^{-3} M; $[Hg(oAc)_2] = 3.00\times10^{-3}$ M; Ir(III) = $5.58\text{x}10^{-6}$M; $[NaClO_4] = 1.88\times10^{-1}$ M;

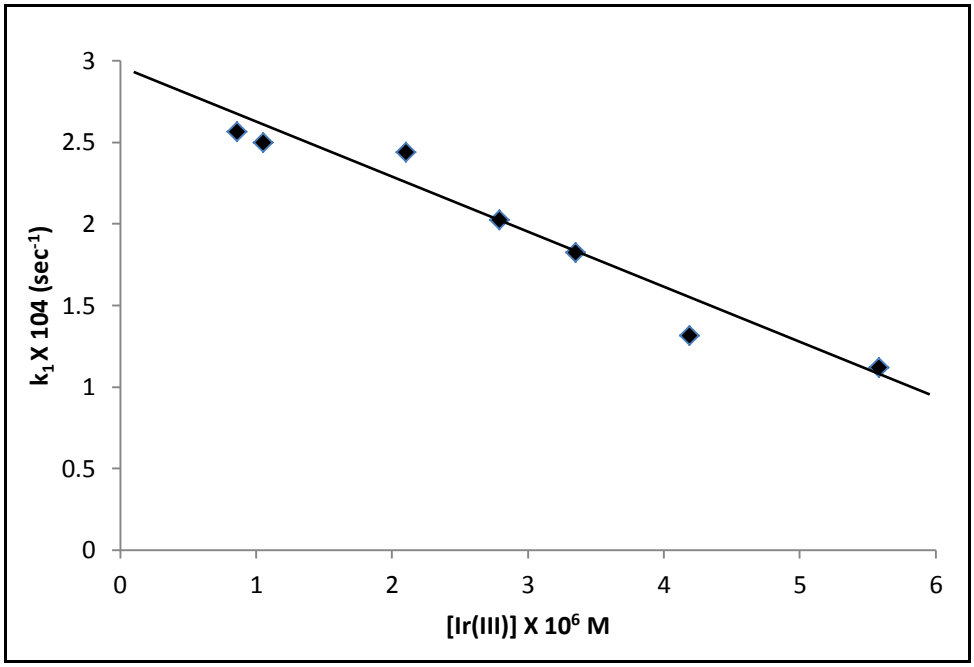


Fig. 2. Plot between k_1 and [Ir(III)] at 40°C

[NCS] = 1.00×10^{-3} M; [Glycine] = 1.33×10^{-2} M; $[H^+] = 5.00\times10^{-3}$ M; [NHS] = 1.20×10^{-3} M; $[Hg(oAc)_2] = 1.20\times10^{-3}$ M; $[NaClO_4] = 1.91\times10^{-1}$ M;

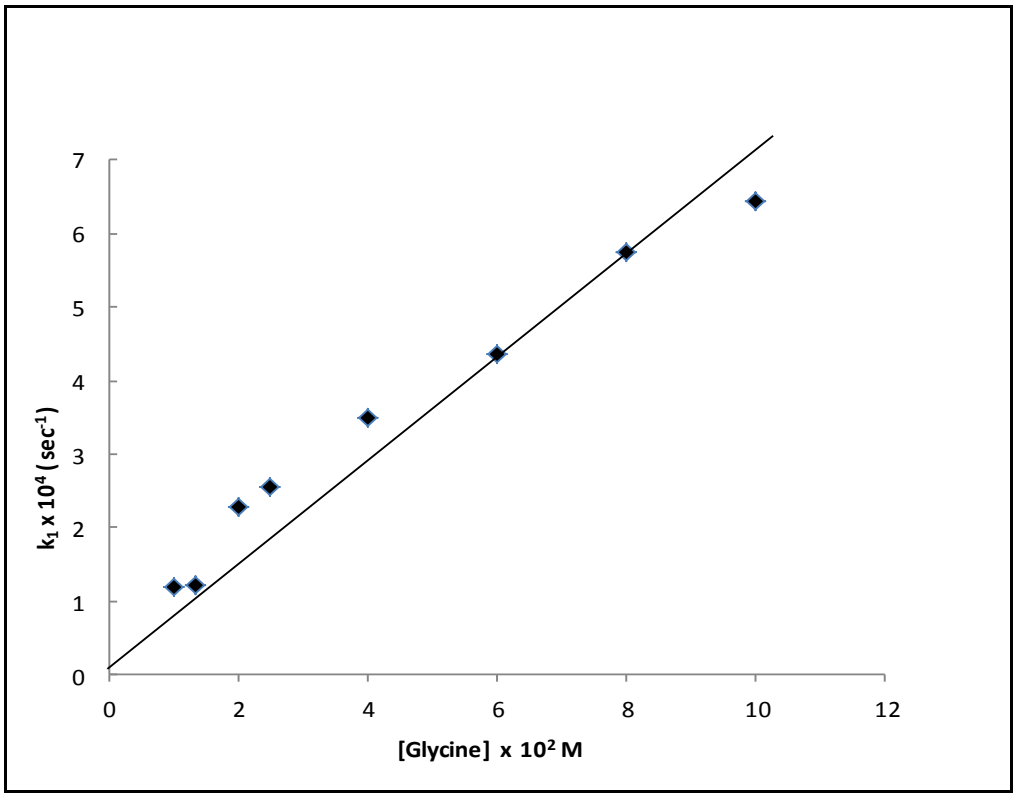


Fig. 3. Plot between k_1 and [Glycine] at 40°C

[NCS] = 1.00×10^{-3} M; [H^+] = 5.00×10^{-3} M; [NHS] = 1.20×10^{-3} M; [$Hg(oAc)_2$] = 1.20×10^{-3} M; Ir(III) = 5.58×10^{-6}M; [$NaClO_4$] = 1.91×10^{-1} M;

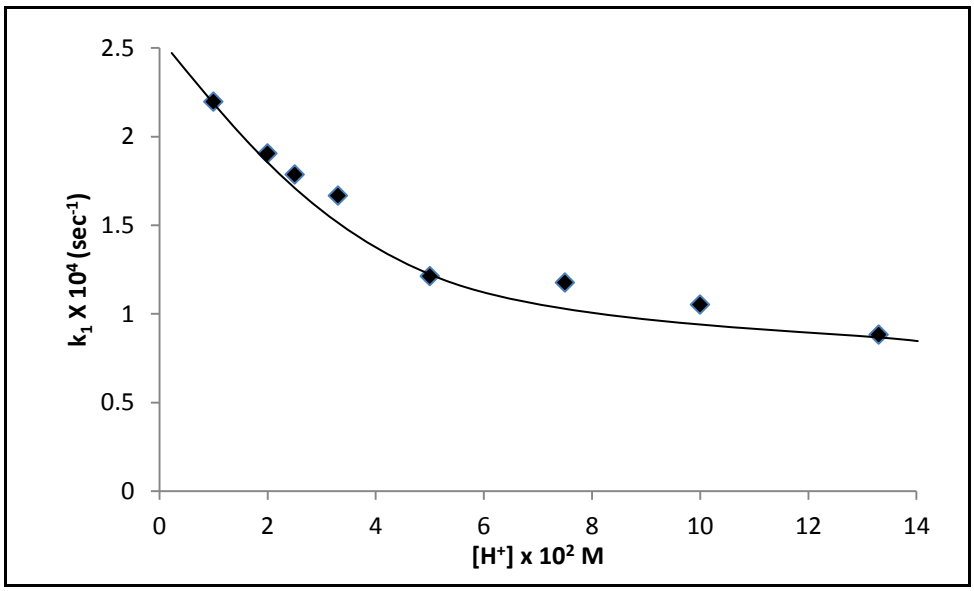


Fig. 4. Plot between k_1 and [H^+] at 40°C

[NCS] = 1.00×10^{-3} M; [Glycine] = 1.33×10^{-2} M; [H^+] = 5.00×10^{-3} M; [NHS] = 1.20×10^{-3} M; [$Hg(oAc)_2$] = 1.20×10^{-3} M; Ir(III) = 5.58×10^{-6}M; [$NaClO_4$] = 1.91×10^{-1} M;

Reactive species of N-chlorosuccinimide in acidic medium:

It is reported[7] that in the presence of acid, the following equilibria for NCS can be assumed to exist:

$$>NCl + H^+ \rightleftharpoons >\overset{+}{N}HCl$$

$$>\overset{+}{N}HCl + H_2O \rightleftharpoons >NH + H_2\overset{+}{O}Cl$$

From the equilibria indicated above, it is clear that NCS itself or ^+NHCl or H_2OCl^+ may be considered as the reactive species of NCS in acidic medium. On the basis of observed negative effect of $[H^+]$ and nil effect of [NHS] on the rate of oxidation, the species ^+NHCl or H_2OCl^+ cannot be considered as the reactive species of NCS in acidic medium. The only choice left is to assume that NCS itself is the reactive species of NCS in the oxidation of glycine in acidic medium.

Reactive species of glycine in acidic medium:

It is reported[8] that alanine at pH 7.0 to carries a net negative charge with the following equilibrium shown below:

$$^+NH_3CH(CH_3)COO^- + H_2O \rightleftharpoons NH_2CH(CH_3)COO^- + H_3O^+$$

If a small amount of HCl or any other acid is added to the alanine solution, the acid-base equilibrium is shifted in such a way that the net charge on the alanine becomes zero.

Report[9] is also available where it is shown that glycine in aqueous media exist in the following way:

$$^+NH_3CH_2COOH \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} NH_2CH_2COOH$$

$$NH_2CH_2COOH \rightleftharpoons {}^+NH_3CH_2COOH \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} NH_2CH_2COO^-$$

On the basis of above facts, the equilibrium as shown below can be assumed for the existence of glycine in acidic medium,

$$NH_2CH_2COOH + H^+ \rightleftharpoons {}^+NH_3CH_2COOH$$

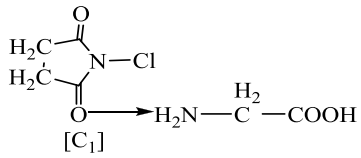
Observed inverse fractional order in $[H^+]$ indicates that glycine itself can be considered as the reactive species of glycine in its oxidation by NCS in acidic medium using Ir(III) as an inhibitor.

Reactive species of Ir(III)-chloride in acidic medium:

Reports[10,11] are available where kinetics of hydration of $IrCl_6^{3-}$ and of the addition of a Cl^- to $[Ir(H_2O)Cl_5]^{2-}$ in 1.0-2.5M $HClO_4$ (or HCl) at 50^0C have been made and visible and Ultraviolet absorption spectra of Ir(III) complexes $Ir(H_2O)_2Cl_4^-$ and $Ir(H_2O)_3Cl_3$ together with the spectra of $IrCl_6^{3-}$ and $Ir(OH_2)Cl_5^{2-}$ in 2.5F $HClO_4$ – 1.2F $NaClO_4$ were found in reasonable agreement with the results reported by Poulsen and Garner[10] and by Jorgensen[12]. Kinetic studies regarding oxidation of xylose, maltose and lactose by potassium iodate (KIO_3) in alkaline medium using Ir(III)-chloride as catalyst are also reported[13,14]**.** In each case $[IrCl_3(H_2O)OH]^-$ has been assumed as the reactive species of Ir(III)-chloride in alkaline medium. In the oxidation of formaldehyde[15], Ir(III) has been determined as the reactive species of Ir(III)-chloride in acidic medium. Efforts[16] have also been made to study the effect of HCl concentration and temperature on Ir(III) speciation at equilibrium. In this paper, the authors have observed that at room temperature and at 70^0C, Ir(III)-chloride in 0.1M HCl concentration will remain as $[IrCl_3(H_2O)_3]$ whereas in 8M HCl solution, it will remain as $[IrCl_5(H_2O)]^{2-}$ and $IrCl_6]^{3-}$ respectively. Since in the present study of oxidation of glycine the solution of Ir(III)-chloride has been prepared in 0.1M HCl hence in view of observed kinetic data and the literature reported above, it can be concluded that the starting species of Ir(III)-chloride is $IrCl_3(H_2O)_3$.

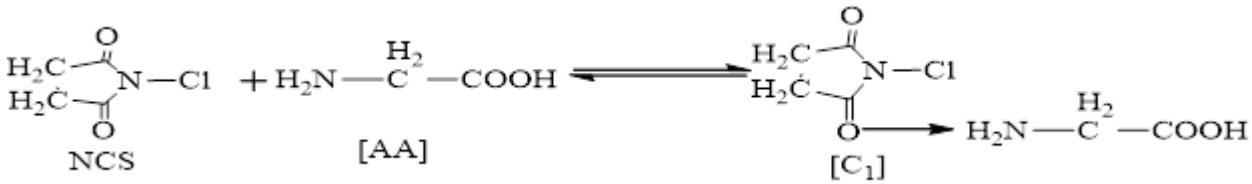
Spectral evidence collected for the formation of complexes during the course of reaction:

In the present study of oxidation of glycine by acidic solution of N-chlorosuccinimide in presence of Ir(III)-chloride as an inhibitor, there are every possibility for the formation of a complex between reactive species of glycine, and reactive species of N-chlorosuccinimide and also between the complex thus formed and reactive species of Ir(III)-chloride present in the reaction mixture. In order to verify the formation of a complex between reactive species of glycine and reactive species of NCS in acidic medium, the spectra for the solutions containing NCS and H^+ and NCS and H^+ with two different concentration of glycine were taken with the help of UV-Visible spectrophotometer (Fig.5 (peak nos. 2,3 &4)). From a perusal, it is clear that with the increase in the concentration of glycine, there is an increase in absorbance from 0.62 to 0.77 and 0.83 (Fig.5). This increase in absorbance with the increase in the concentration of glycine can be regarded as due to more and



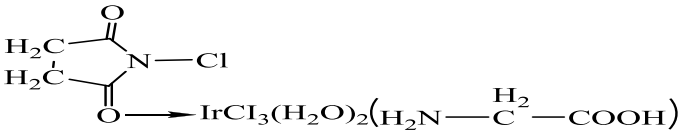
[C_1]

more formation of the complex, according to the following equilibrium.

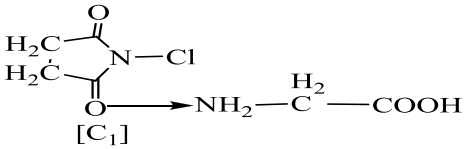


NCS [AA] [C_1]

After ascertaining the formation of a complex between reactive species of glycine and reactive species of N-chlorosuccinimide, an effort was made to probe the possibility of formation of a complex between the complex thus formed and a reactive species of Ir(III)-chloride. For this, the spectra for glycine, NCS, H^+ solution and for glycine, NCS and H^+ with two different concentration of Ir(III)-chloride were collected (Fig.5 (peak 4) and Fig.6 (peak nos. 5 &6)). This spectral information where an increase in absorbance from 0.87 to 1.00 with the increase in Ir(III)-chloride concentration is indicated, led us to conclude that an unreactive

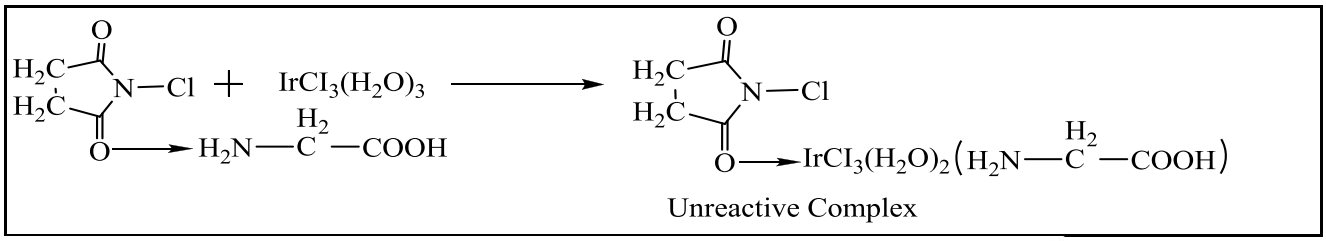


complex of the type, is formed between the complex,



[C_1]

formed earlier and a reactive species of Ir(III) ie $[Ir(III)Cl_3(H_2O)_3]$ in the following way.



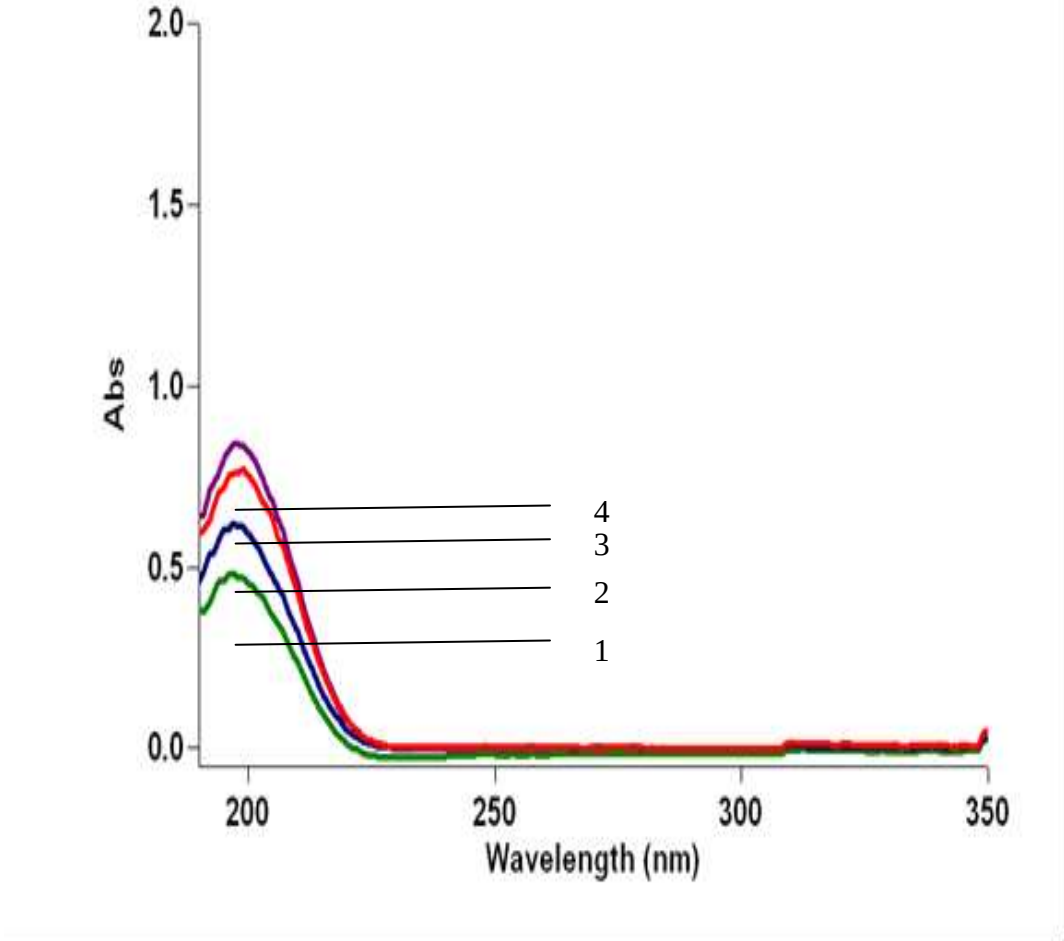


Fig. 5. Spectra of solutions [1-4] recorded at room temperature

(1) [NCS] = 0.80 × 10^{-4} M; [H^+] = 1.0 x 10^{-4} M, *(2)* [NCS] = 1.20 × 10^{-4} M; [H^+] = 1.0 × 10^{-4} M; *(3)* [NCS] = 0.80 × 10^{-4} M; [H^+] = 1.0 × 10^{-4} M; [AA] = 0.5 x 10^{-4} M; (4) [NCS] = 0.80 x 10^{-4} M; [H^+] = 1.0 x 10^{-4} M; [AA] = 1.0 x 10^{-4} M;

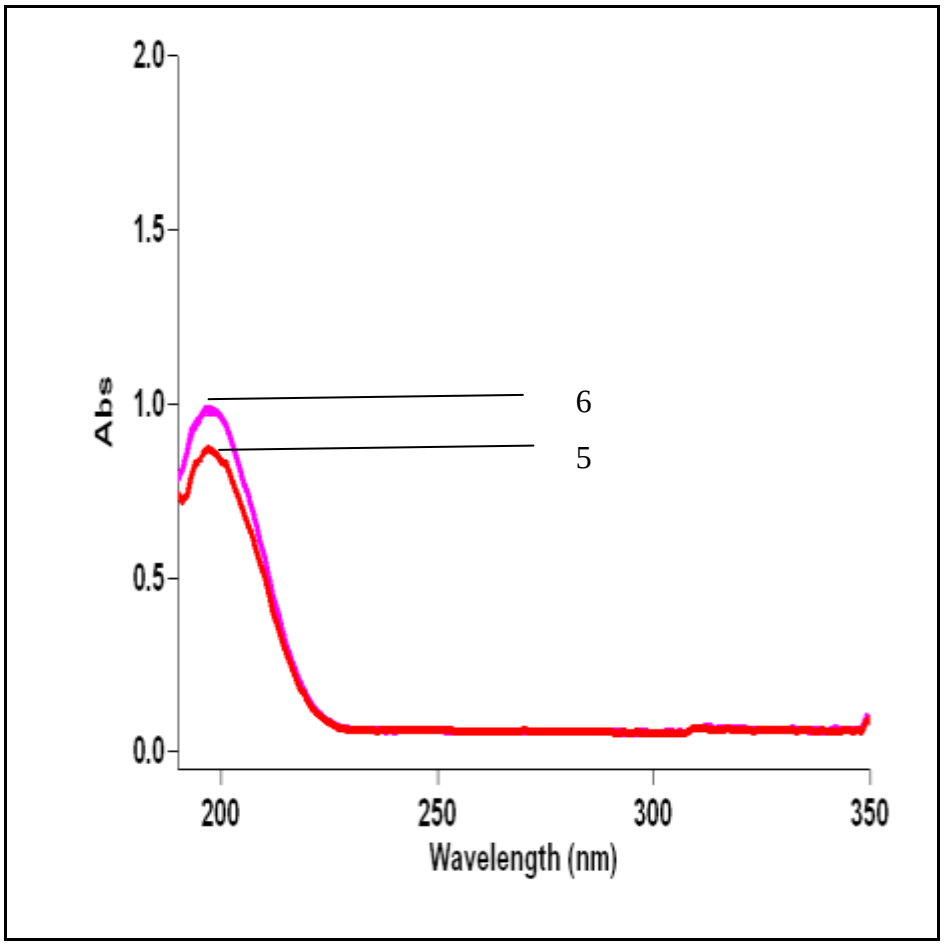


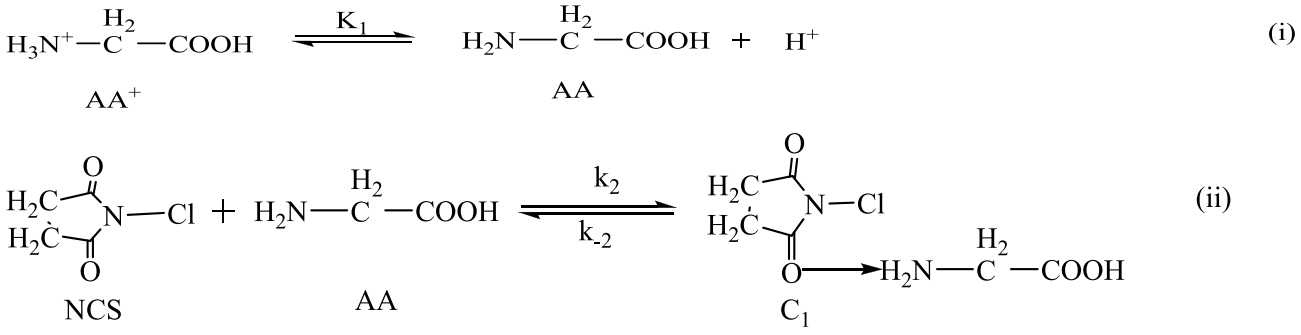
Fig. 6. Spectra of solutions [1-2] recorded at room temperature

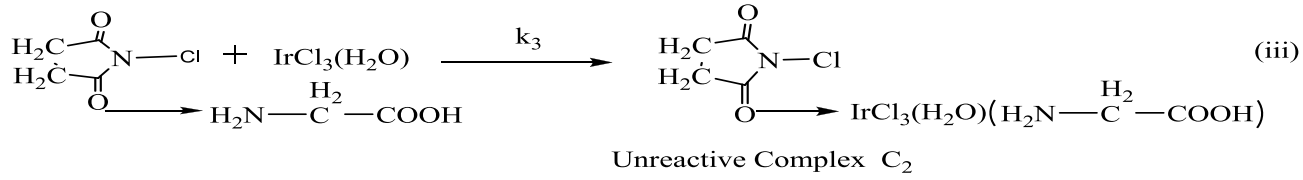
(5) [NCS] = 0.80 × 10^{-4} M; [H^+] = 1.0 x 10^{-4} M; [AA] 0.5 x 10^{-4} M; [Ir(III)] = 1.67 x 10^{-7} M;

(6) [NCS] = 0.80 × 10^{-4} M; [H^+] = 1.0 x 10^{-4} M; [AA] 0.5 x 10^{-4} M; [Ir(III)] = 5.025 x 10^{-7} M;

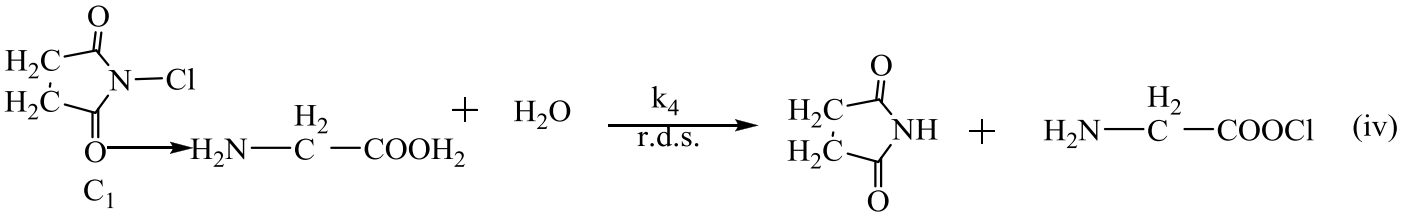
Reaction path for the oxidation of glycine:

On the basis of observed kinetic orders with respect to NCS, H^+, Ir(III) and amino acid concentration and also on the basis of spectral information collected for the formation of different complexes during the course of reaction together with the entropy of activation, a reaction scheme for the reaction under investigation can be formulated as

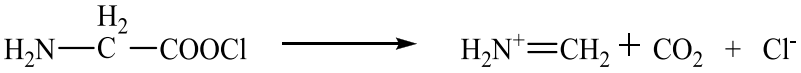




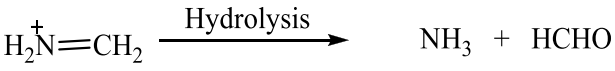
(iii)



(iv)



(v)



(vi)

Scheme-1

According to the aforesaid scheme-1 and stoichiometric data, the rate in terms of decrease in concentration of NCS can be expressed as:

$$\text{rate} = -\frac{d[NCS]}{dt} = 2k_4[C_1] \quad (1)$$

On applying the law of chemical equilibrium to step (i), we have

$$K_1 = \frac{[AA]\,[H^+]}{[AA^+]} \quad \text{or} \quad [AA^+] = \frac{[AA]\,[H^+]}{K_1} \quad (2)$$

On applying the steady- state approximation to the concentration of C_1, we have net rate formation of C_1 ie d[C]/ dt as:

$$\frac{d[C_1]}{dt} = k_2[NCS][AA] - k_{-2}[C_1] - k_3[C_1][Ir(III)] - k_4[C_1]$$

Since at study state $dC_1/dt = 0$, hence

$$0 = k_2[NCS][AA] - [C_1]\left\{k_{-2} + k_3[Ir(III)] + k_4\right\}$$

$$\text{or} \quad [C_1] = \frac{k_2[NCS][AA]}{(k_{-2} + k_3\,Ir(III) + k_4)} \quad (3)$$

On substituting the value of $[C_1]$ from Eq. (3) to Eq. (1) we get Eq. (4) as given below:

$$\text{rate} = -\frac{d[NCS]}{dt} = \frac{2k_2\, k_4[NCS][AA]}{(k_{-2} + k_3\,[Ir(III)] + k_4)} \quad (4)$$

According to the proposed reaction path, the total concentration of glycine i.e. $[AA]_T$ at any moment in the reaction can be shown as

$$[AA]_T = [AA] + [AA^+] \quad (5)$$

On substituting the value of $[AA^+]$ from Eq. (2) to Eq. (5), we get

$$[AA]_T = [AA] + \frac{[AA]\,[H^+]}{K_1}$$

$$\text{or } [AA]_T = [AA]\left(\frac{K_1 + [H^+]}{K_1}\right)$$

$$\text{or } [AA] = \frac{K_1\,[AA]_T}{K_1 + [H^+]} \quad (6)$$

Now Eq. (4) together with Eq. (6) will give Eq. (7)

$$\text{rate} = -\frac{d[NCS]}{dt} = \frac{2k_2\, k_4\, K_1[NCS][AA]_T}{(k_{-2} + k_3\, Ir(III) + k_4)\,(K_1 + [H^+])} \quad (7)$$

Eq. (7) is the final rate law and is in complete agreement with our experimental findings. **Comparative studies:**

The results of the present study of the oxidation of glycine in presence of Ir(III)-chloride were compared with the results reported for Ru(III)[17] catalysed oxidation of L-alanine and Pd(II)[18] catalysed oxidation of L-proline. As for as order with respect to the oxidant is concerned, it is first-order in the present study as well as in the other two reported studies. The role of Ir(III) as an inhibitor in the present study is contrary to the reported two studies where Pd(II) and Ru(III) were found to play the role of a catalyst. When in the present study, the effect of substrate concentration on the rate of oxidation was observed, it is found that the first-order kinetics observed in glycine concentration is different from less than unity order observed in L-alanine concentration and zero-order observed in L-proline concentration. The reported fractional positive order in $[OH]^-$ in Ru(III)[17] and Pd(II)[18]-catalysed oxidation is entirely different from observed invers fractional order in $[H]^+$ in the present study of oxidation of glycine. Observed kinetic data together with spectroscopic data show that $IrCl_3(H_2O)_3$ is the reactive species of Ir(III)-chloride in the present study of oxidation of glycine in acidic medium whereas $[Ru(H_2O)_5OH]^{2-}$ and [Pd(OH)Cl] were found as reactive species of Ru(III)[17] and Pd(II)[18] in the oxidation of L-alanine and L-proline, respectively. In view of the facts mentioned above, it can be said that the present study is different in many respect from other two studies reported earlier.

Conclusions:

The conclusions drawn from the observed kinetic data and also from the spectral information collected for the oxidation of glycine by N-chlorosuccinimide in presence of Ir(III)-chloride as an inhibitor are as follows:

1. On the basis of observed negative effect of $[H^+]$ and nil effect of [NCS] on the rate of oxidation, NCS itself has been assumed as the reactive species of NCS in acidic medium.
2. Observed invers fractional order in $[H^+]$ led us to assume that glycine itself is the reactive species of glycine in its oxidation by NCS in acidic medium.
3. Making basis to the reported literature and observed kinetic data, it has been decided that Ir(III)-chloride in the present study of oxidation of glycine will take part in the reaction as $IrCl_3(H_2O)_3$.

4. Step (iii) of the proposed reaction path where formation of unreactive complex C_2 in an irreversible process is shown, is well supported by the observed negative effect of Ir(III) concentration on the rate of oxidation.

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