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Role of Chloro Complex of Rh(III) in The Oxidation of Valine by N- Chlorosuccinimide in Acidic Medium: A Kinetic and Mechanistic Study

**Santosh Kumar, Jaya Srivastava, Ritu Swamini Bala, Shailesh Kumar Singh,
Ashok Kumar Singh and Shahla Rahmani**[*]

*Department of Chemistry, University of Allahabad Allahabad- 211002 (UP), **INDIA**

Email: ashokeks@rediffmail.com, shahlaau@rediffmail.com

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ABSTRACT

The kinetics of oxidation of valine (val) by N-chlorosuccinimide (NCS) in the presence of chloro complex of $RhCl_3(H_2O)_3$ as an inhibitor in acidic medium at 40 ^{0}C have been investigated. The reaction is first-order with respect to [NCS] and [valine]. The reaction shows fractional negative order with respect to [Rh(III)] and [H^+] in the oxidation of valine. Nil effects of [Hg(II)], [NHS] or [Cl^-] on the reaction rate were observed. Ionic strength and dielectric constant also have nil effect. The observed kinetic data, available literature and spectroscopic evidence lead us to conclude that $NCSH^+$ and $RhCl_3(H_2O)_3$ are the reactive species of NCS and Rh(III) chloride, respectively in acidic medium. The reaction has been studied at four different temperatures and with the help of observed first-order rate constant values, various activation parameters have been calculated. The main oxidation products of the reaction were identified as isobutyraldehyde and ammonia. The proposed reaction mechanism is well supported by kinetic data, spectrophotometric evidence and positive entropy of activation

Keywords: Mechanism; Valine, N-Chlorosuccinimide, Acid medium, Rh(III)-Chloride.

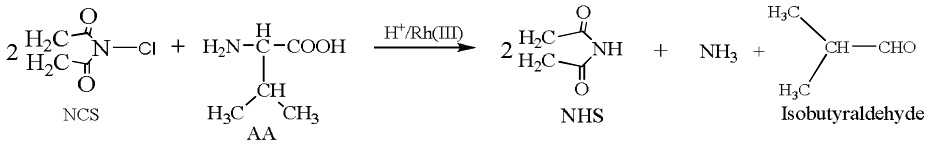
INTRODUCTION

The kinetic investigation of the oxidation of amino acids is important because of their biological significance and amino acids residues are the main constituents of proteins and the study of its sensitivity towards oxidation open up a new area to understand the mechanism involved in the protein and amino acid modifications [1]. A number of uncatalyzed [2] and catalyzed [3] kinetic studies have been reported on the oxidation of amino acid by different oxidants. The oxidation of biologically important amino acid valine is very significant because it may reveal the mechanism of amino acid metabolism. Transition metal catalyzed reactions have created great interest due to their involvement in many important industrial processes [4]. Various N-halogeno compounds [5-11] such as N-bromoacetamide (NBA), N-bromo succinimide (NBS), N-chlorosuccinimide (NCS) are reported to have diverse chemistry due to their ability to act as a source of halonium cations, hypohalite species, nitrogen anions, and strongly polarized N-linked halogens. N-Halo compounds, a group of mild oxidizing agents, have been extensively used for the catalyzed [12-16] and unanalyzed [17-20] oxidation of a variety of organic compound. The coordination chemistry of Rh(III) [21] has drawn considerable attention due to its chemical reactivity, anti-tumour activity, electronic structure and catalytic functions of its complexes with potential industrial applications. Rh(III) is reported to form a variety of complexes such as $[Rh\,Cl]^{2+}$, $[RhCl_2]^{+}$, $RhCl_3$, $[RhCl_4]^{-}$, $[RhCl_5]^{2-}$ and $[RhCl_6]^{3-}$ in the presence of HCl with varying concentration [22]. However, in view of biological importance of amino acid and also in view of scant information on the role of Rh(III)-chloride complex as an inhibitor, the present study has been undertaken.

MATERIALS AND METHODS

All the chemicals were used as supplied. A fresh standard solution of N-chlorosuccinimide was prepared daily by dissolving a known weight of N-chlorosuccinimide (Loba Chem) in double distilled water, and the solution was standardized iodometrically against standard sodium thiosulphate solution using starch as an indicator. Solution of amino acid was prepared daily by weighing and dissolving it in doubly distilled water. Stock solution of Rh(III) chloride (Rh(III)) was prepared by dissolving its sample in 3M HCl solution and the concentration of Rh(III) chloride was determined as 3.79×10^{-3}M. The solutions of $HClO_4$ (H^{+}), $Hg(OAc)_2$ (Hg(II)), succinimide (NHS), $NaClO_4$ and KCl were prepared by dissolving their samples in doubly distilled water. $NaClO_4$, $HClO_4$, $Hg(OAc)_2$ (acidified with 20% acetic acid), and KCl were used to maintain the ionic strength of the medium (μ), H^{+} ions concentration, Hg(II) concentration (used as Br^{-} ions scavenger) and Cl^{-} ion concentration respectively throughout the study. Hydrochloric acid (HCl) was used to prepare the Rh(III) chloride (used as an inhibitor) solution. All the kinetic measurements were carried out at constant temperature 40^{0} C. The reaction mixture was prepared in a black-coated conical flask (Jena) to prevent photochemical reaction. Requisite amounts of all reactant solutions, i.e. NBA, $Hg(OAc)_2$, $HClO_4$, HCl, NHS and Rh(III), were placed in the reaction vessel and equilibrated at 40 ^{0}C. The requisite volumes of standard solutions of all the reactants except amino acid were taken in black coated reaction vessel which was equilibrated at 40 °C. A measured volume of amino acid solution, also equilibrated at 40^{0} C, was added to the reaction mixture to start the reaction. The progress of the reaction was determined by measuring the unconsumed [NCS] iodometrically at regular time intervals using starch as an indicator.

Stoichiometry: The stoichiometry of the reaction was determined by allowing the reaction mixtures containing large excess of [NCS] over [Valine]. Simultaneously, a blank solution of the reaction mixture was also prepared by adding all the solutions without valine. Both the reaction mixtures were allowed to stand for 48 hours and the excess of [NCS] in both the solution was estimated by iodometry. The observed stoichiometry of the reaction was calculated as [Valine]: NCS = 1:2. The stoichiometric equation is given as follows.



Isobutyraldehyde in the case of valine were identified as the main oxidation products through kinetic and equivalence studies.

RESULTS AND DISCUSSION

In order to propose a reaction mechanism for oxidation of valine by NCS in presence of Rh(III)-chloride as an inhibitor in acid medium using $Hg(OAc)_2$ as scavenger for Br^{-} ions, a series of experiments were performed at constant temperature 40^{o}C. The initial rate of reaction in each kinetic run was determined by the plot of the remaining concentration of NCS vs. time whereas pseudo-first-order rate constant (k_1) was calculated by dividing the initial rate by the [NCS]. 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 constant at constant temperature of 40 ºC and at constant ionic strength of the medium. The values of –dc/dt were increased in the same proportion in which the [NCS] was increased, it indicates the unity order with respect to [NCS]. Unity order in [NCS] is evident from Fig 1. The observed pseudo-first order rate constant (k_1) was found to be directly proportional to the [valine] indicates the first order with respect to [valine]. A straight line passing through the origin (Fig. 2) obtained from the plot of k_1 vs. [valine] throughout 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 40^0 C (Fig.3). When the concentration of Rh(III) has been varied from 3.79 x 10^{-7}M to 3.79 x 10^{-6}M, it was found that k_1 values decrease on increasing [Rh(III)] and indicates that, the reaction follows negative fractional order with respect to Rh(III)-chloride throughout its variation (Fig.4). Successive addition of NHS and mercuric acetate (Hg^{++}) shows a negligible effect on the rate of oxidation of valine. On changing the ionic strength (μ) of the medium, the values of k_1 remain constant throughout its variation. The kinetic reaction was found to be nil effect with change in Cl^- concentration. To determine the effect of temperature on the rate in oxidation of valine, a number of experiments were performed under identical conditions at four different temperature, viz. 35, 40, 45 and 50 °C. The values of first-order rate constant, k_1, obtained at four different temperatures were utilized to calculate activation parameters such as specific rate constant (k_r), Arrhenius frequency factor (A), energy of activation (E_a), enthalpy of activation ($\Delta H^\#$), entropy of activation ($\Delta S^\#$) and Gibb's free energy of activation($\Delta G^\#$) at 40^0C (Table 1).

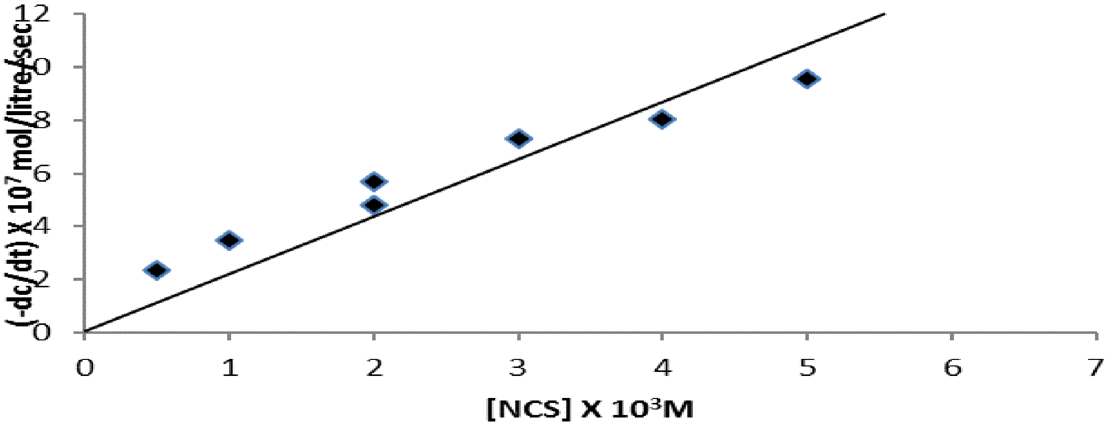


Fig 1. Plot between –d*c*/d*t* and [NCS] at 40 °C
[Valine] = 1.33×10^{-2} M; $[H^+]$ = 1.00×10^{-3} M; [NHS] = 6.50×10^{-3} M; $[Hg(OAc)_2]$ = 6.50×10^{-3}, M; [Rh(III)] = 3.79x10^{-7}M; $[NaClO_4]$ = 9.54×10^{-2} M;

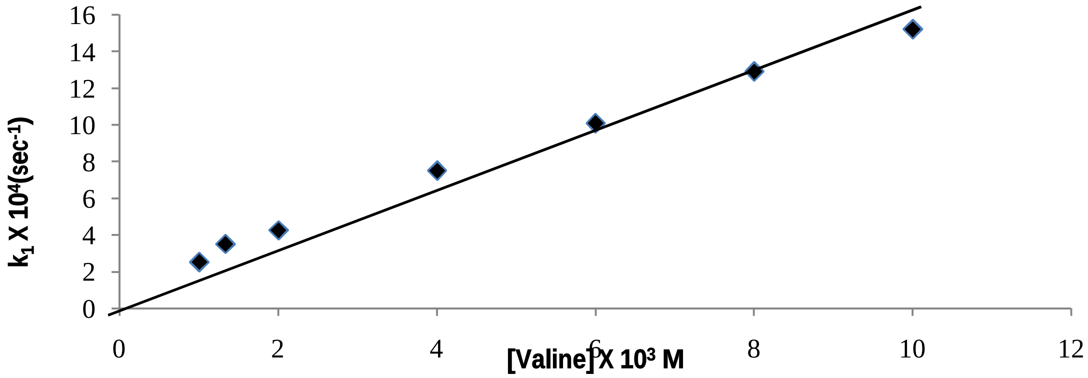


Fig 2. Plot between k_1 and [Valine] at 40 °C
[NCS] = 1.00×10^{-3} M; $[H^+]$ = 1.00×10^{-3} M; [NHS] = 1.20×10^{-3} M; $[Hg(OAc)_2]$ = 1.20×10^{-3} M; [Rh(III)] = 3.79x10^{-7}M; $[NaClO_4]$ = 9.54×10^{-2} M;

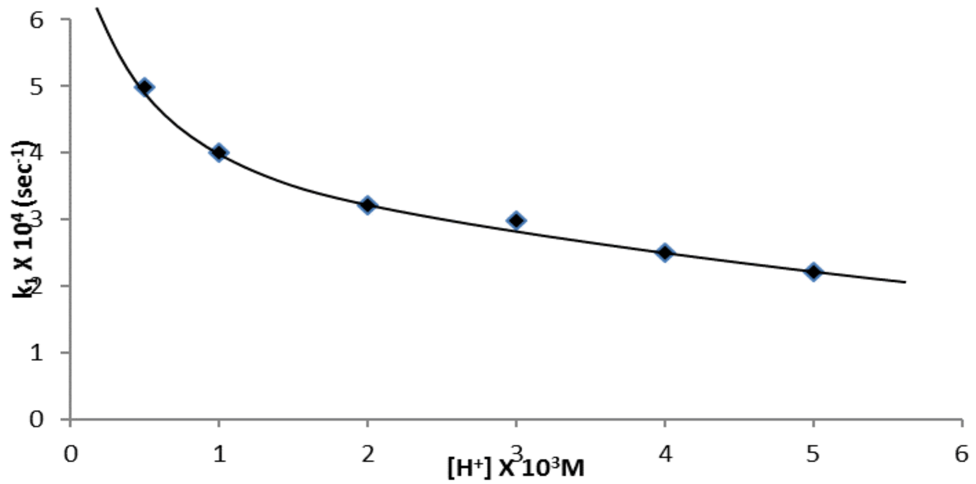


Fig 3. Plot between k_1 and [H$^+$] at 40 °C
[NCS] = 1.00×10^{-3} M; [Valine] = 1.33×10^{-2} M; [NHS] = 1.20×10^{-3} M; [Hg(OAc)$_2$] = 1.20×10^{-3} M; [Rh(III)] = 3.79x10^{-7}M; [NaClO$_4$] = 9.54×10^{-2} M;

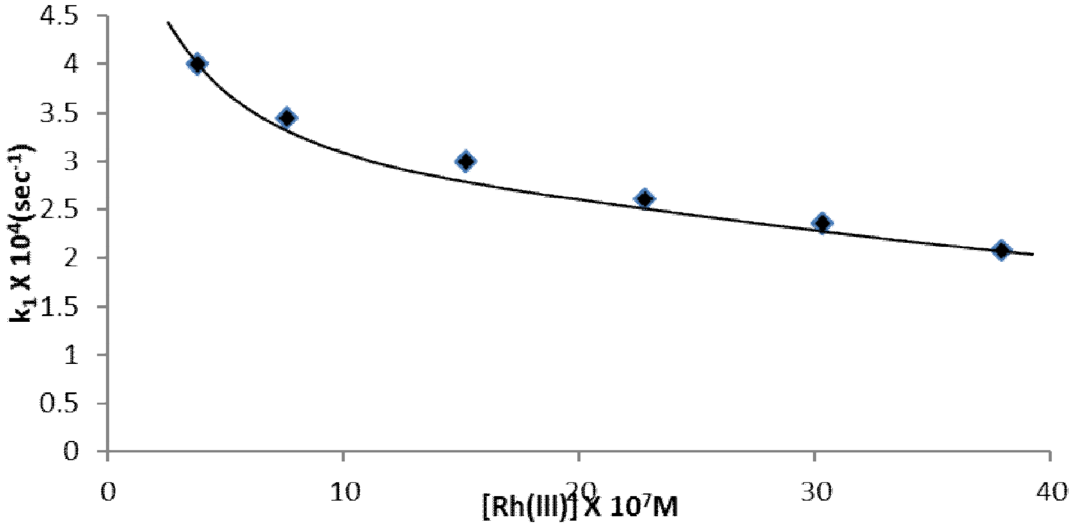


Fig.4. Plot between k_1 and [Rh(III)] at 40 °C.
[NCS] = 1.00×10^{-3} M; [Valine] = 1.33×10^{-2} M; [H$^+$] = 1.00×10^{-3} M; [NHS] = 1.20×10^{-3} M; [Hg(OAc)$_2$] = 1.20×10^{-3} M; [NaClO$_4$] = 9.54×10^{-2} M;

Table-1: Value of activation parameters of oxidation of Valine by N-chlorosuccinimide in presence of Rh(III) - chloride as an inhibitor in acidic medium at 40 ^{0}C

Compound	Ea (kJ mol^{-1})	$k_r \times10^7$ (mol^{-2}L^{2}s^{-1})	ΔH$^\#$ (kJ mol^{-1})	ΔG$^\#$ (kJ mol^{-1})	ΔS$^\#$ (JK^{-1} mol^{-1})	A (mol^{-1} dm^3 s^{-1})
Valine	131.88	3.86	129.25	115.66	43.49	2.33×10^{15}

Conditions: [NCS] = 1.00×10^{-3}M, [Valine] = 1.33×10^{-2}M, [Rh(III)] = 3.79×10^{-7}M, [H$^+$] = 1.0×10^{-3}M, μ = 0.10 M

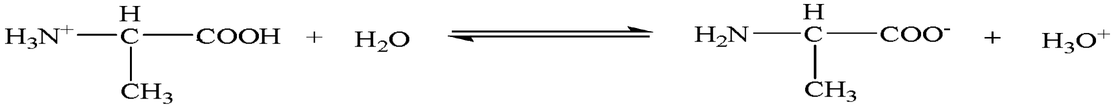
Reactive species of N-chlorosuccinimide in acidic medium: It is reported [23] that in the presence of acid, the following equilibria for NCS can be assumed to exist:

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

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

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 valine in acidic medium.

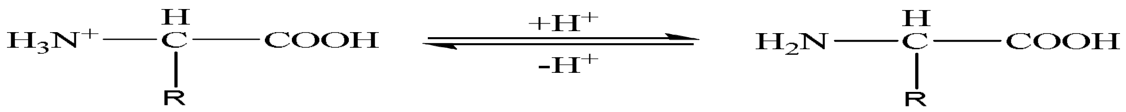
Reactive species of valine in acidic medium: It is reported [24] that alanine at pH 7.0 to carries a net negative charge with the following equilibrium shown below:



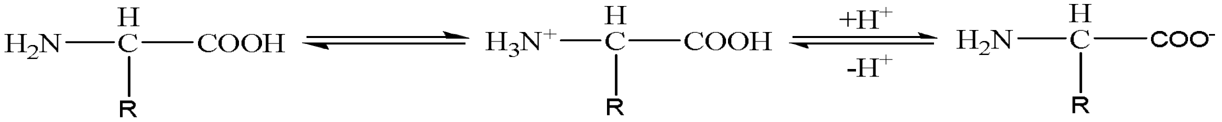
$$H_3N^+-\underset{CH_3}{\overset{H}{C}}-COOH + H_2O \rightleftharpoons H_2N-\underset{CH_3}{\overset{H}{C}}-COO^- + H_3O^+$$

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 [25] is also available where it is shown that amino acid in aqueous media exist in the following way:

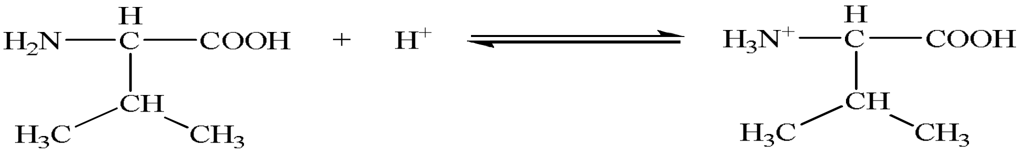


$$H_3N^+-\underset{R}{\overset{H}{C}}-COOH \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_2N-\underset{R}{\overset{H}{C}}-COOH$$



$$H_2N-\underset{R}{\overset{H}{C}}-COOH \rightleftharpoons H_3N^+-\underset{R}{\overset{H}{C}}-COOH \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_2N-\underset{R}{\overset{H}{C}}-COO^-$$

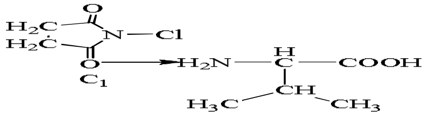
On the basis of above facts, the equilibrium as shown below can be assumed for the existence of valine in acidic medium,



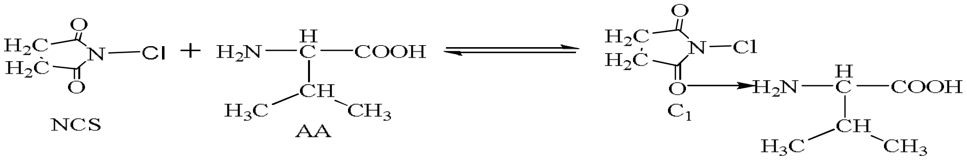
Observed inverse fractional order in $[H^+]$ indicates that valine itself can be considered as the reactive species of valine in its oxidation by NCS in acidic medium using Rh(III) as an inhibitor.

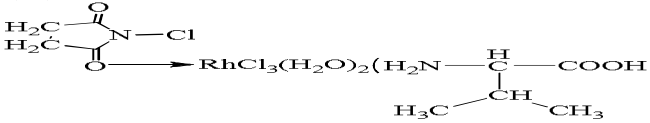
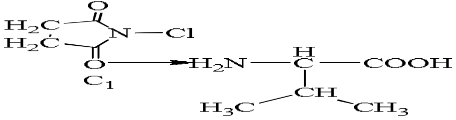
Reactive species of Rh(III) chloride in acidic medium: Various complexes formed between rhodium(III) and chloride ion in dilute hydrochloric acid solution and their isolation and characterization by the ion exchange technique is reported earlier in the literature [22]. Using the molar absorptivities of various complexes at appropriate wavelengths the approximate successive formation constants at 120°C have been determined. James and Rempel [26] in their kinetic studies of chloro complexes of rhodium as hydrogenation catalysts have reported that the anionic complexes such as $[RhCl_6]^{3-}$, $[Rh\ (H_2O)\ Cl_5]^{2-}$ and

$[Rh(H_2O)_2Cl_4]^-$ activate molecular hydrogen for the reduction of ferric ion in aqueous acid solution. According to them, cationic and neutral chloroaquorhodium(III) complexes do not catalyze the reduction of ferric ion. Harrod and Halpern [27] have carried out studies with $RhCl_3$ in 3.0-5.0*M* HCl solutions and suggested that $[RhCl_6]^{3-}$ was the predominant species in solution. However, the results obtained in this report show that the 5:1 chloro species persists over this range of HCl concentration. Studies relating to the kinetics and mechanism of Rh(III) catalyzed oxidation of styrene, stilbene and phenylacetylene by acidic periodate have also been for the oxidation of valine by NCS in acidic medium. In view of the literature reported earlier, A solution of Rh(III) chloride was prepared in 3.0 M HCl, and its concentration was determined as 3.809×10^{-3}M. This stock solution was further diluted, and in each kinetic run the Rh(III) chloride concentration was in the order of 10^{-6}M. From the literature it is clear that the attainment of equilibrium among the various complex species in the rhodium(III) chloride system is possible only under certain conditions. Considering the conditions under which the original solution of rhodium(III) chloride as well as very dilute solution of rhodium(III) chloride used in various kinetic runs were prepared, it can be concluded that the lone species, $RhCl_3(H_2O)_3$, is the reactive species of rhodium(III) chloride in the oxidation of valine by NCS in acidic medium. Support to this assumption can be given by nil effect of $[Cl^-]$ on the rate of oxidation of valine.

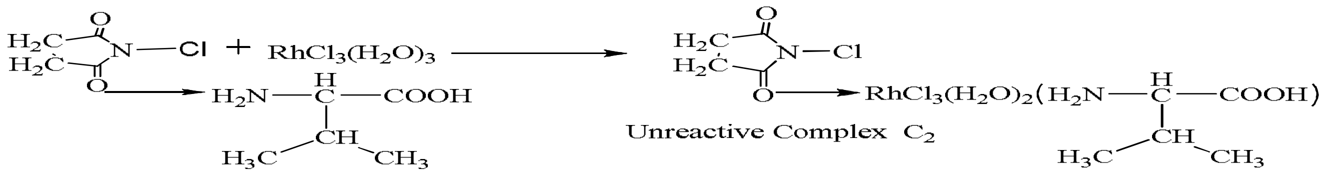
Spectral evidence for the formation of complexes in the oxidation of valine shown in the proposed reaction scheme: Efforts were made to ascertain possible formation of complexes between different reactive species during the course of reaction with the help of VARIAN CARY WIN UV–VIS spectrophotometer. For this, the spectra for various solutions of NCS, Rh(III), H^+ and amino acid were collected. When spectra for the solutions of two different concentration of in presence H^+ were collected, it was found that there is substantial increase in absorbance from 0.65 to 0.84 with the increase in [NCS] (Fig-5 (1), (2). Further spectra for the solutions containing NCS and H^+ and NCS and H^+ with two different concentration of valine were recorded with the help of UV-Visible spectrophotometer, it was found that with the increase in the concentration of valine, there is an increase in absorbance from 1.00 to 1.12 and 1.18 (Fig-5 (1), (3), and (4). This increase in absorbance with the increase in the concentration of valine can be regarded as due to more and more formation of the complex, 

according to the following equilibrium



After ascertaining the formation of a complex between reactive species of valine 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 Rh(III)-chloride. For this, the spectra for valine, NCS, H^+ solution and for valine, NCS and H^+ with three different concentration of Rh(III)-chloride were collected Fig-5 (3), (5), (6) and (7). This spectral information where an increase in absorbance from 1.18 to 1.24, 1.60 and 1.88 with the increase in Rh(III)-chloride concentration is indicated, led us to conclude that an unreactive complex of the type,  is formed between the complex, 

formed earlier and a reactive species of Rh(III) i.e., $[Rh(III)Cl_3(H_2O)_3]$ in the following way.



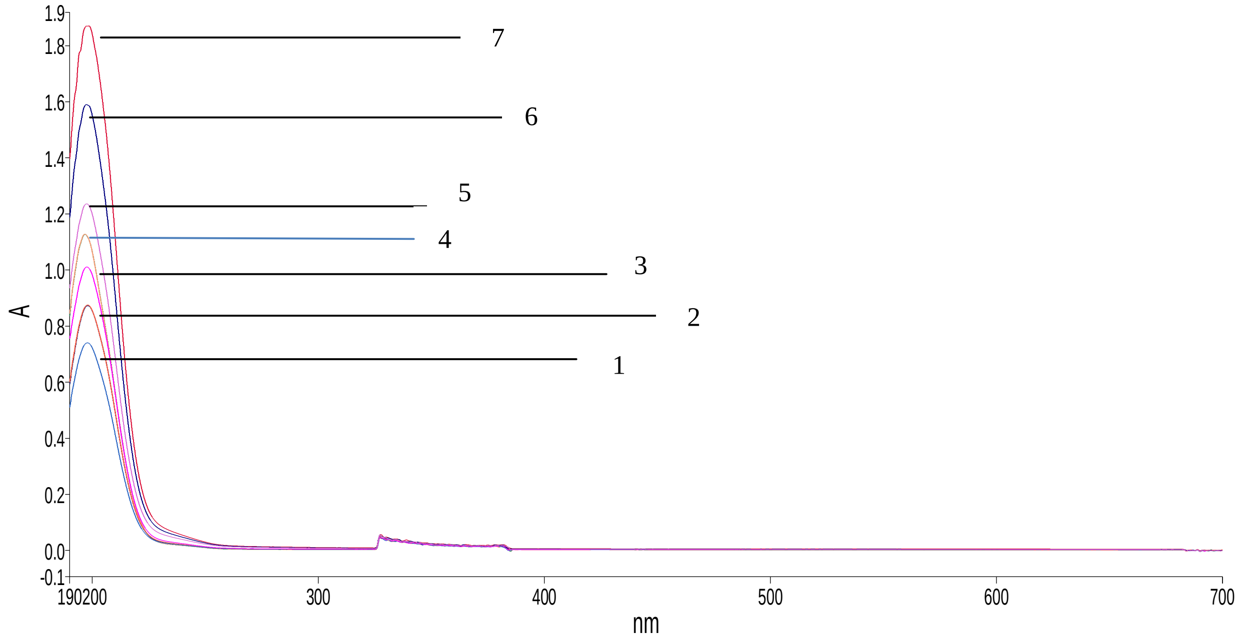
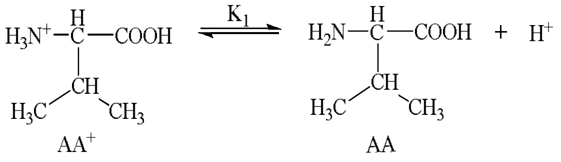


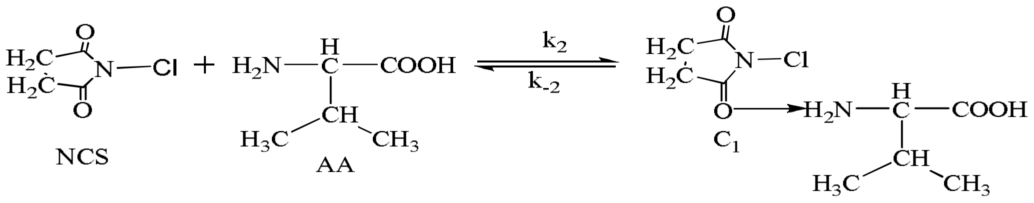
Fig 5. Spectra of solutions [1-7] recorded at room temperature

1 - [NCS] = 0.80×10^{-4} M; [H^+] = 1.0×10^{-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] = 0.5×10^{-4} M; ***4-*** [NCS] = 0.80×10^{-4} M; [H^+] = 1.0×10^{-4} M; [AA] = 1.0×10^{-4} M; ***5 -*** [NCS] = 0.80×10^{-4} M; [H^+] = 1.0×10^{-4} M; [AA] = 0.5×10^{-4} M; [Rh(III)] = 1.67×10^{-7} M; ***6-*** [NCS] = 0.80×10^{-4} M; [H^+] = 1.0×10^{-4} M; [AA] 0.5×10^{-4} M;[Rh(III)] = 5.025×10^{-7} M; ***7-*** [NCS] = 0.80×10^{-4} M; [H^+] = 1.0×10^{-4} M; [AA] 0.5×10^{-4} M; [Rh(III)] = 10.020×10^{-7} M;

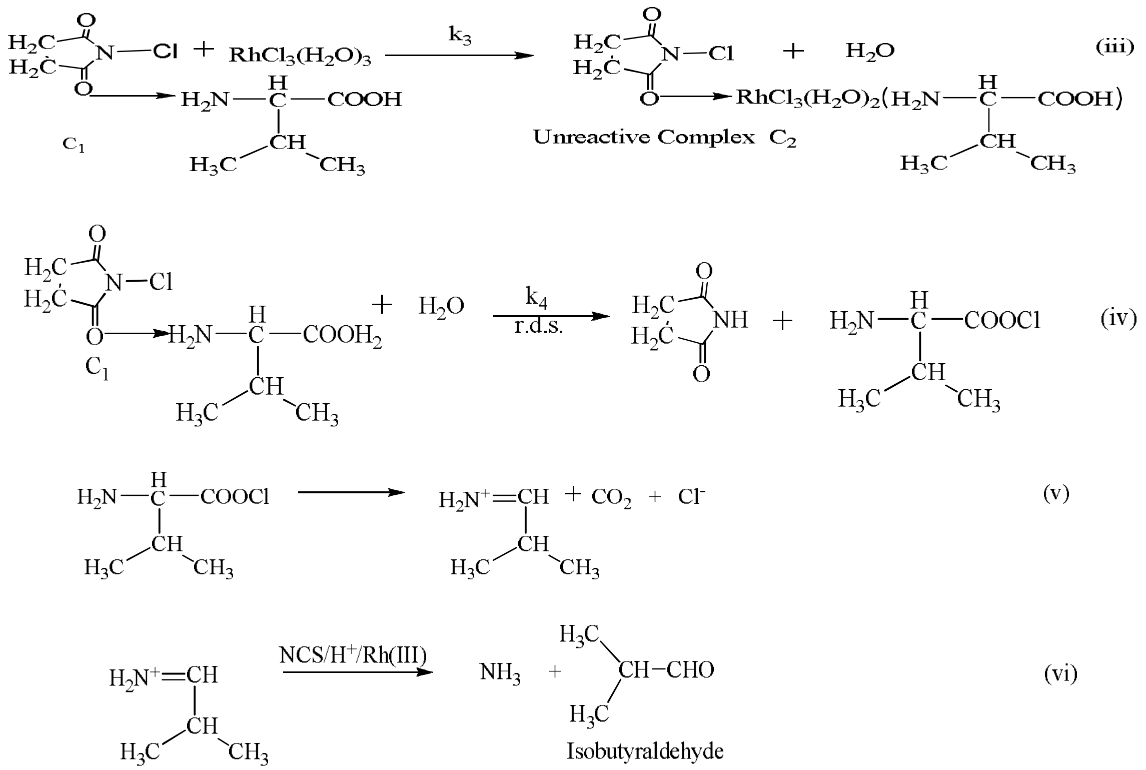
On the basis of observed kinetic data and spectroscopic evidence a suitable mechanism is proposed (Scheme-1)



(i)



(ii)



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:

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

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

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

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

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

Since at steady state $dC_{1/}dt = 0$, hence

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

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

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

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

$$[AA]_T = [AA] + [AA^+] \tag{5}$$

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

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

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

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

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

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

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

CONCLUSIONS

The following conclusions were drawn from the observed kinetic data and from the spectroscopic information collected for oxidation of valine by NCS in acidic medium and Rh(III) chloride used as inhibitor.

1. On the basis of observed negative effect of $[H^+]$ and nil effect of [NHS] on the rate of oxidation, NCS itself has been assumed as the reactive species of NCS in acidic medium.
2. The rate of oxidation of valine is unaffected by the ionic strength of the medium.
3. Isobutyraldehyde was identified as the oxidation product of the reaction under investigation.
4. Making basis to the reported literature and observed kinetic data, it has been decided that Rh(III)-chloride in the present study of oxidation of valine will take part in the reaction as $RhCl_3(H_2O)_3$.
5. 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 Rh(III) concentration on the rate of oxidation.

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AUTHOR ADDRESS

1. **Shahla Rahmani**
Department of Chemistry,
University of Allahabad Allahabad- 211002 (UP), India
E-mail: shahlaau@rediffmail.com, Tel: 09454971738, 9415279887