

## KINETIC AND MECHANISTIC STUDIES OF $\text{Ru}^{3+}$ CATALYSED OXIDATION OF ALANINE BY VANADIUM (V) IN SULPHURIC ACID MEDIUM

Maheshwar Prasad Sah

Department of Chemistry, S. M. College, Bhagalpur-812001, Bihar, Patna, India.

### ABSTRACT

Kinetic studies of oxidation of alanine by vanadium(v) in presence of  $\text{Ru}^{3+}$  catalyst in sulphuric acid medium has been carried out. The main oxidation products of alanine have been identified as ammonia and formic acid. A simple titrimetric method has been used. The effect of ionic strength,  $[\text{SO}_4^{2-}]$ ,  $[\text{HSO}_4^-]$ ,  $[\text{H}^+]$  and temperature were carried out and these effects are also in support of the mechanism proposed. The activation parameters have been determined. The rate law has been evaluated as

$$\frac{-d[\text{V}^{5+}]}{dt} = \frac{k_1 k_2 k_3 [\text{H}_2\text{O}] [\text{alanine}] [\text{Ru}^{3+}] [\text{V}^{5+}]}{k_{-1} k_{-2} + k_{-1} k_3 [\text{H}_2\text{O}] + k_2 k_3 [\text{H}_2\text{O}] [\text{Ru}^{3+}]}$$

**Keywords:** Alanine, vanadium(v), kinetics, mechanism, oxidation, catalysis.

### INTRODUCTION

Alanine is a non-essential amino acid that plays a key role in the glucose-alanine cycle between muscle tissue liver. In amino acid degrading-tissues such as muscle, amino groups are pulled as glutamate by transamination reactions. The amino group of glutamate is transferred to pyruvate via alanine aminotransferase, forming alanine and  $\alpha$ -ketoglutarate. Alanine is passed into the blood and transported to the liver. This reaction is reversed in the liver where pyruvate can be used in gluconeogenesis to form glucose, which may return to other tissues through the circulatory system, increased alanine levels correlates with higher blood pressure, energy intake, cholesterol levels and body mass index<sup>1</sup>. Vanadium(v) is widely used for the oxidation of the organic<sup>2-4</sup> and inorganic compounds. In various compounds vanadium occurs in seven oxidation states<sup>6</sup>. Vanadium, one of the most important metal for modern technology, so that compounds of vanadium are used in metallurgy, ceramic industry, pharmaceutical industrial processes, space technology etc. Vanadium is essential for cell growth at the level of  $\mu\text{g dm}^{-3}$ , but at higher concentrations it can be toxic. The toxicity of vanadium increases with increase in oxidation state<sup>7,8</sup>. The mechanism of oxidation of alanine may be quite complicated due to the formation of different species of vanadium(v) in

acid media<sup>6</sup>. Survey of literature reveals that there are no report on the kinetics of oxidation of alanine by vanadium(v) in presence of ruthenium(III) catalyst in sulphuric acid medium.

The aim of this investigation to understand the behaviour of the active species of vanadium(v) in sulphuric acid medium in presence of ruthenium(III) catalyst and to propose the most probable reaction mechanism for the kinetics of oxidation of biologically important alanine. The investigation also aims to provide the kinetic orders with respect to each reactant of the reaction.

### EXPERIMENTAL

#### MATERIALS

All the reagents used are of analytical reagent grade. Stock solution of alanine was prepared by dissolving it in double distilled water. Stock solutions of sodium perchlorate, sodium bisulphate and sodium sulphate were prepared in double distilled water. Ruthenium(III) chloride solution was prepared in HCl of known strength. Solution of vanadium(v) was prepared in double distilled water by dissolving appropriate amount of ammonium metavanadate and sulphuric acid standardized by ferrous ammonium sulphate solution using barium diphenylamine sulphonate as redox

indicator<sup>3</sup>. Sulphuric acid and sodium perchlorate solutions were used to maintain the required acidity and ionic strength respectively.

#### METHODS

All solutions were thermally equilibrated at 40<sup>o</sup> C in a thermostated water bath. After half an hour the required amounts solutions of ammonium metavanadate, Ruthenium(III), sodium sulphate, sodium bisulphate and sulphuric acid solutions were added together into a conical flask, followed by the addition of required volume of double distilled water. The reaction mixture was then placed in a thermostated water maintained at 40 (±0.6)<sup>o</sup> C. The reaction was initiated by the addition of the measured amount of alanine solution into the solution containing ammonium metavanadate, Ruthenium(III), sodium sulphate, sodium bisulphate and sulphuric acid, placed separately in the water bath thermostat at 40<sup>o</sup> C. As soon as the half of the alanine solution passed out from the pipette, the stop watch was started to record the time. The kinetic studies were carried out by quenching the aliquot of the reaction mixture in measured excess of ferrous ammonium sulphate solution against standard vanadium(v) solution using barium diphenylamine sulphonate as redox indicator<sup>3</sup>.

#### Polymerization test

To perform polymerization test, acrylonitrile was added to the partially oxidized reaction mixture. No gel formation was observed even on addition of large excess of methanol. This indicates that the absence of free radical intermediates in the reaction mixture.

#### Stoichiometry and product analysis

The stoichiometry of reaction was determined by mixing a known concentrations of reaction mixtures in which the concentration of ammonium metavanadate solution was present in large excess amount than alanine. The conical flask containing the reaction mixtures were placed in water bath thermostat at 60<sup>o</sup> C for 12 hours or till completion of the reaction. Titrimetric method was used for the estimation of the amount of unreacted vanadium(v) with standard Fe<sup>2+</sup> solution using barium diphenylamine sulphonate as redox indicator. Estimation of unconsumed vanadium(v) showed that one mole of alanine consumes 7 moles of vanadium(v). Ammonia and formic acid were identified as main product. The ammonia<sup>9</sup> formic acid<sup>10</sup> were confirmed by the Nessler's reagent and Fehling's solution respectively.

## RESULTS AND DISCUSSION

### Order of reaction with respect to [Alanine]

The kinetics of oxidation of alanine using ruthenium(III) as catalyst have been investigated at 313 K. The concentration of alanine was varied from 3.125 x 10<sup>-3</sup> mol dm<sup>-3</sup> to 25.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> at [V<sup>5+</sup>] = 5.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>. [Ru<sup>3+</sup>] = 5.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 5.0 x 10<sup>-1</sup> mol dm<sup>-3</sup>, temperature = 313 K and I = 1.535 mol dm<sup>-3</sup>. The pseudo first constants, k<sub>obs</sub> were found to be constant, indicating the first order dependence of the reaction with respect to [Alanine]. The plot of log k<sub>obs</sub> versus log [Alanine] is linear with slope equal to 1.035 indicating the reaction is first order with respect to [Alanine] (Figure 1.).

$$k_{obs} = k_s [\text{Alanine}] \dots(1)$$

The values of k<sub>s</sub> obtained in the 5.0 x 10<sup>-1</sup> mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> are (8.4132 ± 0.562) x 10<sup>-2</sup> mol<sup>-1</sup> dm<sup>3</sup>s<sup>-1</sup>, (14.4132 ± 1.092) x 10<sup>-2</sup> mol<sup>-1</sup> dm<sup>3</sup>s<sup>-1</sup>, (25.6132 ± 0.517) x 10<sup>-2</sup> mol<sup>-1</sup> dm<sup>3</sup>s<sup>-1</sup> and (47.52 ± 0.492) x 10<sup>-2</sup> mol<sup>-1</sup> dm<sup>3</sup>s<sup>-1</sup> at 308 K, 313 K, 318 K and 323 K respectively.

### Order of reaction with respect to [V<sup>5+</sup>]

The reactions were studied at varying concentrations of [V<sup>5+</sup>] in the range from 2.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> to 12.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> at [Alanine] = 2.5 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [Ru<sup>3+</sup>] = 5.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sub>2</sub>SO<sub>4</sub>] = 5.0 x 10<sup>-1</sup> mol dm<sup>-3</sup>, temperature = 313 K and I = 1.542 mol dm<sup>-3</sup>. The average pseudo first order rate constant (k<sub>obs</sub>) was found to be (11.8587 ± 0.102) x 10<sup>-4</sup>s<sup>-1</sup>, indicates that the reaction is first order with respect to [V<sup>5+</sup>].

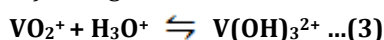
$$-d[V^{5+}] / dt = k_{obs} [V^{5+}]$$

$$-d \ln[V^{5+}] / dt = k_{obs} \dots(2)$$

### Effect of [H<sup>+</sup>] on the rate of reaction

In order to find out the effect [H<sup>+</sup>] on the rate of reaction, the concentration of [H<sup>+</sup>] was varied between 5.0 x 10<sup>-1</sup> mol dm<sup>-3</sup> to 20.0 x 10<sup>-1</sup> mol dm<sup>-3</sup> but at constant [V<sup>5+</sup>], [Alanine], [Ru<sup>3+</sup>], temperature and ionic strength of 5.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, 2.5 x 10<sup>-3</sup> mol dm<sup>-3</sup>, 5.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, 313 K and 3.035 mol dm<sup>-3</sup> respectively. The order with respect to sulphuric acid concentration was determined from the plot (Zucker Hammet)<sup>11</sup> of log k<sub>obs</sub> versus log [H<sup>+</sup>] (Figure 4.) and found to be less than unity (0.472). The plot of log k<sub>obs</sub> versus H<sub>0</sub> (Hammet acidity function)<sup>11</sup> was found to be linear with plot equal to -0.3062, shows that the rate of reaction increases with increase in [H<sup>+</sup>] (Figure 3.). The plot of log (k<sub>obs</sub> + H<sub>0</sub>) versus log a<sub>H2O</sub> was found to be linear with slope equal to 18.645 defines a parameter ω, indicates that the water molecule acts as a proton transfer agent<sup>12</sup> at rate determining step

(Figure 6.). The value of  $H_0$  has been collected from Long and Paul<sup>13</sup>. In strongly acidic medium vanadium(v) exists<sup>6</sup> only in the form of  $VO_2^+$ . In higher acid concentration,  $VO_2^+$  ion is converted into  $V(OH)_3^{2+}$  as given below:



It has been observed that with increase in  $[H^+]$ , increases the rate of reaction (Figure 4.). The  $[H^+]$  dependence of rate constant of oxidation of alanine is most probably due to the protonation of  $VO_2^+$  in the fast step (3) to produce  $V(OH)_3^{2+}$ , which subsequently combines with alanine to form Complex<sub>1</sub> (9). Plot of  $k_s$  versus  $[H^+]$  was found to be linear with positive intercept (Figure 5.), therefore,  $k_H$  is given as:

$$k_H = m [H^+] + n \dots(4)$$

Where,  $m = 8.23 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$  and  $n = 14.992 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ .

Since the order with respect to  $[H^+]$  was found to be less than unity (0.472), suggests that the protonated species  $V(OH)_3^{2+}$  of vanadium(v) is assumed to be active species.

#### Effect of $[Ru^{3+}]$

To find out the effect of  $[Ru^{3+}]$ , the reactions were studied at different concentrations of  $[Ru^{3+}]$  within the range  $2.5 \times 10^{-1} \text{ mol dm}^{-3}$  to  $10.5 \times 10^{-1} \text{ mol dm}^{-3}$  but at constant constant  $[V^{5+}]$ , [Alanine],  $[H_2SO_4]$ , temperature and ionic strength of  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $5.0 \times 10^{-1} \text{ mol dm}^{-3}$ , 313 K and  $1.568 \text{ mol dm}^{-3}$  respectively. It has been observed that the rate of reaction increases with  $[Ru^{3+}]$ , showing positive catalytic effect of  $[Ru^{3+}]$ . Reported earlier<sup>14</sup> that in acid media ruthenium(III) chloride exist in the form of  $[RuCl_6]^{3-}$ . A plot of  $\log k_{obs}$  versus  $\log [Ru^{3+}]$  was found to be linear with slope equal to 0.084, showing the positive catalytic effect of  $[Ru^{3+}]$  on the rate of reaction (Figure 7.). These findings were also confirmed by the linear plot of catalytic ratios (Table 2.) versus  $[Ru^{3+}]$ , with slope equal to 26.0938 (Figure 8.). It has been observed from the experimental results that the dependence of rate on  $[Ru^{3+}]$  can be expressed as:

$$k_{obs} = \frac{k_1 k_2 k_3^* [Alanine] [Ru^{3+}]}{k_{-1} k^* + k_2 k_3^* [Ru^{3+}]} \dots(5)$$

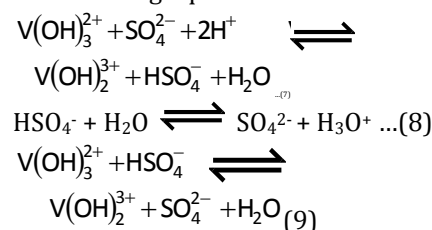
$$\frac{1}{k_{obs}} = \frac{k_{-1} k^*}{k_1 k_2 k_3^* [Alanine] [Ru^{3+}]} + \frac{1}{k_1 [Alanine]} \dots(6)$$

Where  $k_3^* = k_3 [H_2O]$  and

$$k^* = k_{-2} + k_3^*$$

#### Effect of $[SO_4^{2-}]$ and $[HSO_4^-]$ on the rate of reaction

$[SO_4^{2-}]$  and  $[HSO_4^-]$  show retarding effect on the rate of reaction at constant ionic strength (Table 1.). It is most probably due to the conversion of reactive species  $V(OH)_3^{2+}$  of vanadium(v) to unreactive species  $V(OH)_2^{3+}$  in accordance with the following equilibria:



#### Effect of Ionic strength on the rate of reaction

The effect of ionic strength on the rate of reaction was studied at different concentrations of sodium perchlorate within the range  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  to  $20.0 \times 10^{-3} \text{ mol dm}^{-3}$ . It was observed that the rate constant of reaction is independent of ionic strength of the medium (Table 2.). The independence of the rate constant on ionic strength indicates that at least one of the reacting species was molecular in nature at rate determining step<sup>15</sup>.

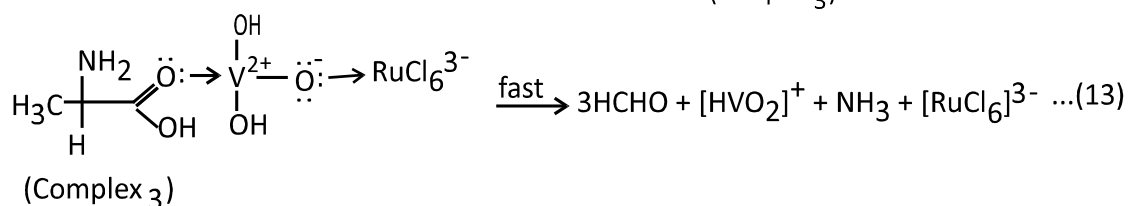
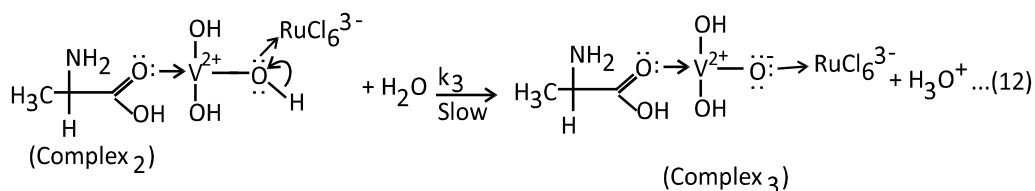
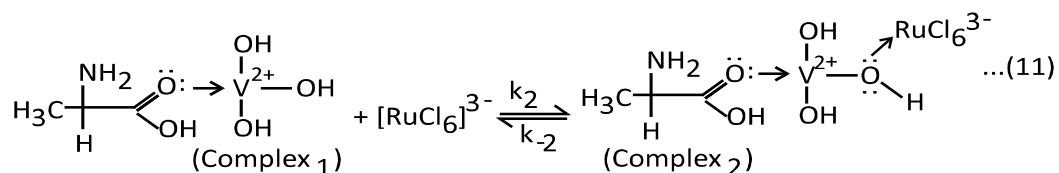
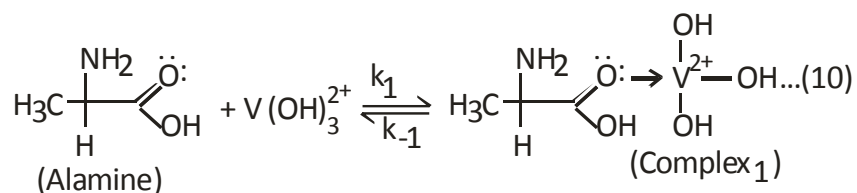
#### Effect of temperature on the rate of reaction

The rate constant of the reaction was measured at four different temperatures, 308 K, 313 K, 218 K and 323 K at constant  $[V^{5+}]$ , [Alanine],  $[Ru^{3+}]$ ,  $[H_2SO_4]$  and ionic strength of  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $5.0 \times 10^{-1} \text{ mol dm}^{-3}$ , and  $1.535 \text{ mol dm}^{-3}$  respectively. The rate constant of the reaction was found to increase with increase in temperature. The activation parameters were determined from the values of rate constant. The Arrhenius plot i. e. the slope of the plot  $\log k_{obs}$  versus  $1/T$  (Figure 9.) has been used to calculate the energy of activation ( $E_a$ ). From the Eyring's plot,  $\log (k_{obs}/T)$  versus  $1/T$  (Figure 10.), the value of enthalpy of activation ( $\Delta H^\ddagger$ ) and from which entropy of activation ( $\Delta S^\ddagger$ ) and Gibbs free energy of activation ( $\Delta G^\ddagger$ ) were calculated (Table 2.). The negative value of entropy of activation and positive value of Gibbs free energy of activation indicates the formation of more ordered activated complex and transition state is highly solvated as compared to the reactive species<sup>15,16</sup> and at rate determining step the reaction is slow and involves high energy of activation (Table 2.).

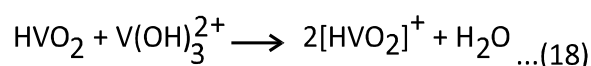
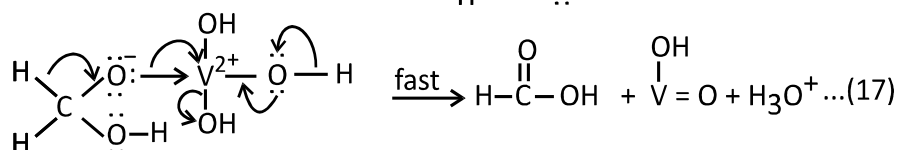
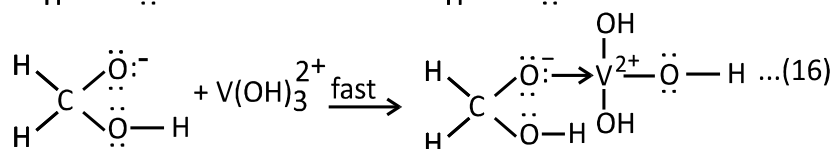
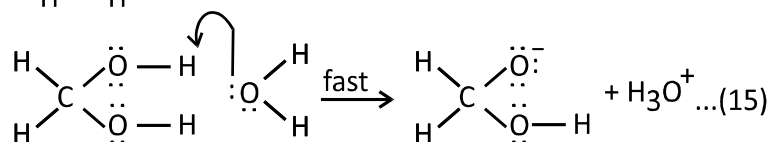
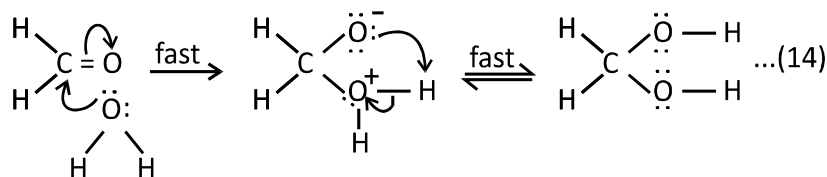
**Mechanism**

On the basis of experimental findings mentioned above in sulphuric acid medium in presence of

ruthenium(III) catalyst, the following reaction mechanism has been proposed:



6



In sulphuric acid medium, vanadium(v) oxidises the alanine through unstable intermediate complexes followed by the cleavage of C-C bond.  $V(OH)_3^{2+}$ , the reactive species of vanadium(v) combines with OH group of alanine to form Complex<sub>1</sub>.  $[RuCl_6]^{3-}$  combines with Complex<sub>1</sub> to form Complex<sub>2</sub>. Complex<sub>2</sub> liberates proton and converted into Complex<sub>3</sub>. This is the slow and rate determining step and at this step  $H_2O$  molecule acts as a proton transfer agent. The highly unstable Complex<sub>3</sub> decomposes to form formaldehyde,  $[HVO_2]^+$  with the liberation of  $NH_3$  and  $[RuCl_6]^{3-}$  is regenerated. The highly unstable hydrated form of aldehyde liberates proton followed by the combination of  $V(OH)_3^{2+}$ , to form reaction product. There was no evidence in favour of the formation of the said proposed complexes, but on the basis of above mentioned experimental results the proposed mechanism cannot be invalidate. Reported<sup>2</sup> the formation of activated complexes between  $V^{5+}$ , D-galactose and  $Ag^+$ .

From the above mechanism, the rate law can be derived as follows:

$$\frac{-d[V^{5+}]}{dt} = \frac{k_1 k_2 k_3 [H_2O][Alanine][Ru^{3+}][V^{5+}]}{k_{-1} k_{-2} + k_{-1} k_3 [H_2O] + k_2 k_3 [H_2O][Ru^{3+}]} \quad (19)$$

The above rate law (19) explains the first order dependence of rate on each in  $[V^{5+}]$  and  $[Alanine]$  and fractional order on dependence on  $[Ru^{3+}]$ . The equation (19) could be written as

$$\frac{-\ln[V^{5+}]}{dt} = k_{obs} = \frac{k_1 k_2 k_3 [H_2O][Alanine][Ru^{3+}]}{k_{-1} k_{-2} + k_{-1} k_3 [H_2O] + k_2 k_3 [H_2O][Ru^{3+}]} \quad (20)$$

$$k_{obs} = \frac{k_1 k_2 k_3^* [Alanine][Ru^{3+}]}{k_{-1} k_{-2} + k_{-1} k_3^* + k_2 k_3^* [Ru^{3+}]} \quad (21)$$

Where,  $k_3^* = k_3 [H_2O]$

$$k_{obs} = \frac{k_1 k_2 k_3^* [Alanine][Ru^{3+}]}{k_{-1} (k_{-2} + k_3^*) + k_2 k_3^* [Ru^{3+}]}$$

$$k_{obs} = \frac{k_1 k_2 k_3^* [Alanine][Ru^{3+}]}{k_{-1} k^* + k_2 k_3^* [Ru^{3+}]} \quad (22)$$

Where,  $k^* = k_{-2} + k_3^*$

$$k_{obs} = \frac{p [Alanine][Ru^{3+}]}{q + r [Ru^{3+}]} \quad (23)$$

Where,  $p = k_1 k_2 k_3^*$ ,  $q = k_{-1} k^*$  and  $r = k_2 k_3^*$

By taking reciprocal of equation (23)

$$\frac{1}{k_{obs}} = \frac{q + r [Ru^{3+}]}{p [Alanine][Ru^{3+}]} \quad (24)$$

$$\frac{1}{k_{obs}} = \frac{q}{p [Alanine][Ru^{3+}]} + \frac{r}{p [Alanine]} \quad (25)$$

Where, p, q and r are constants and expressed in terms of different rate constants. The slope, intercept on  $1/k_{obs}$  axis and extrapolated intercept on  $1/[Ru^{3+}]$  axis, give the values of  $q/p[Alanine]$ ,  $r/p[Alanine]$  and  $-1/q$  respectively. At constant  $[V^{5+}]$ , a plot of  $1/k_{obs}$  versus  $1/[Alanine]$  was linear with small intercept (45.02692) on  $1/k_{obs}$  axis, offering support for complex formation (Figure 2).

## CONCLUSION

The negative value of  $\Delta S^\ddagger$  and positive value of  $\Delta G^\ddagger$  suggest the formation of more ordered activated complex and transition state is highly solvated as compared to the reactive species. The high value of energy of activation ( $E_a$ ) suggests that the reaction is slow at rate determining step. The slope obtained from J. F. Bunnett plots equal to 18.645 indicates that the water molecule acts as a proton transfer agent at rate determining step.

## ACKNOWLEDGEMENT

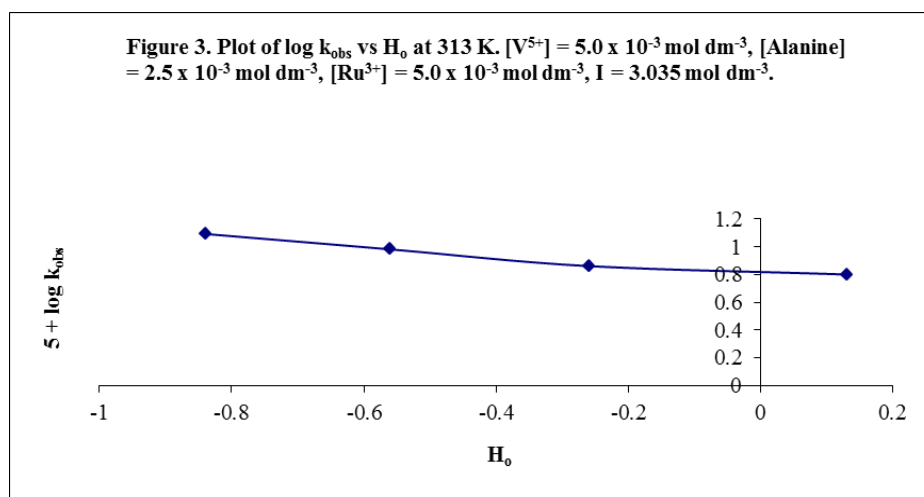
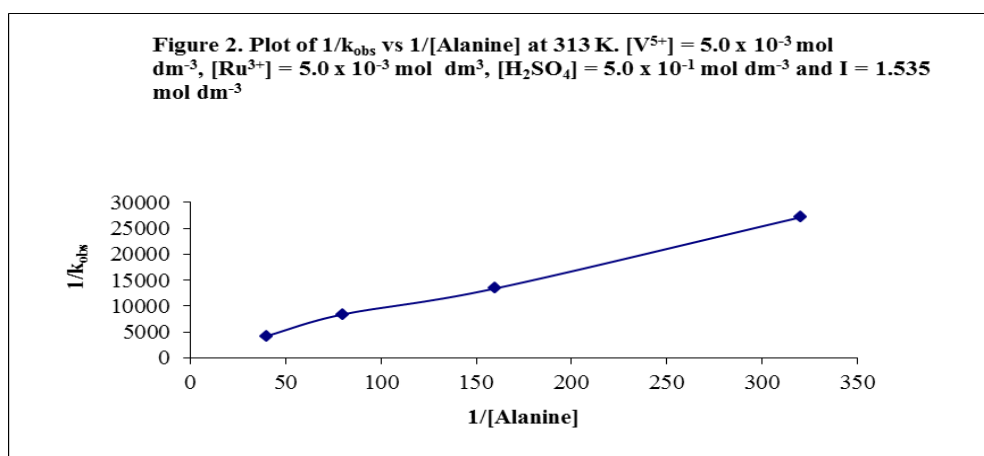
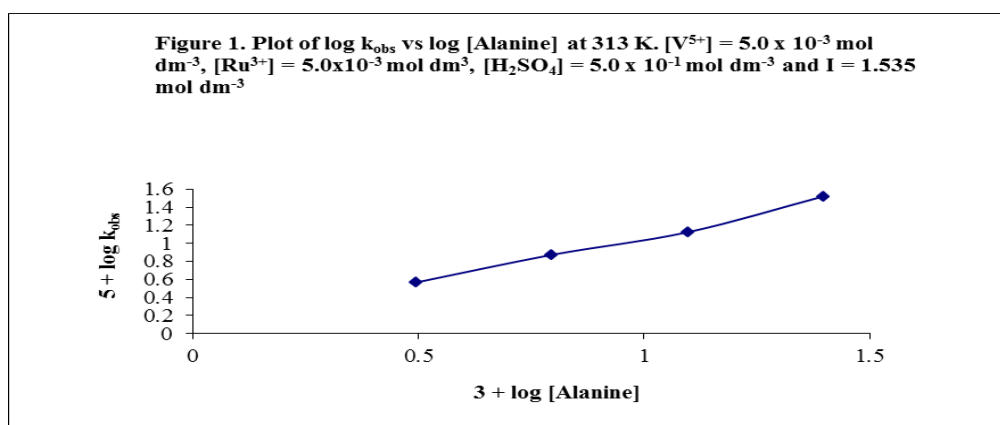
The author is thankful to Dr. L. Thakur, Retired Professor and Head, P. G. Department of Chemistry, T. M. Bhagalpur University, Bhagalpur for good suggestions.

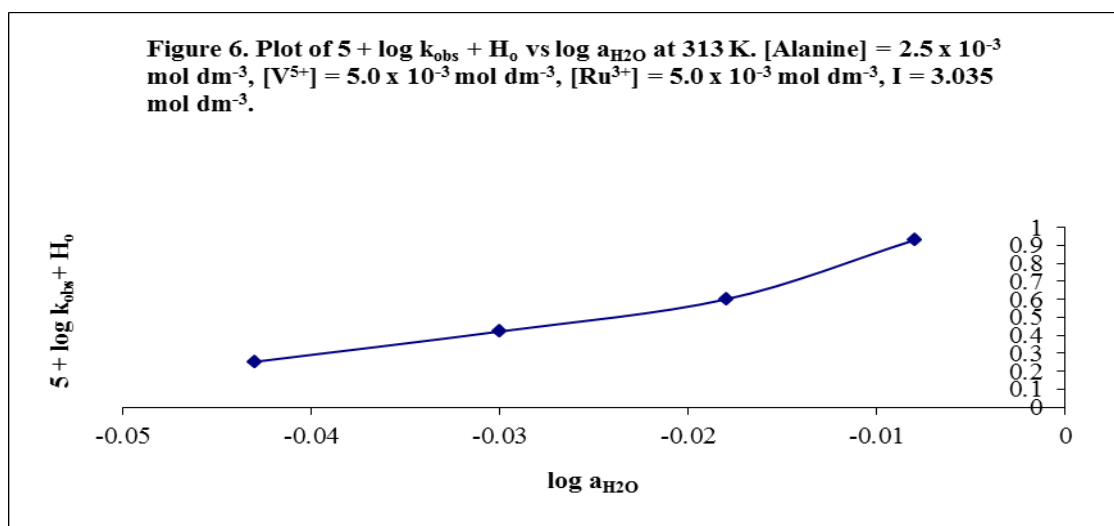
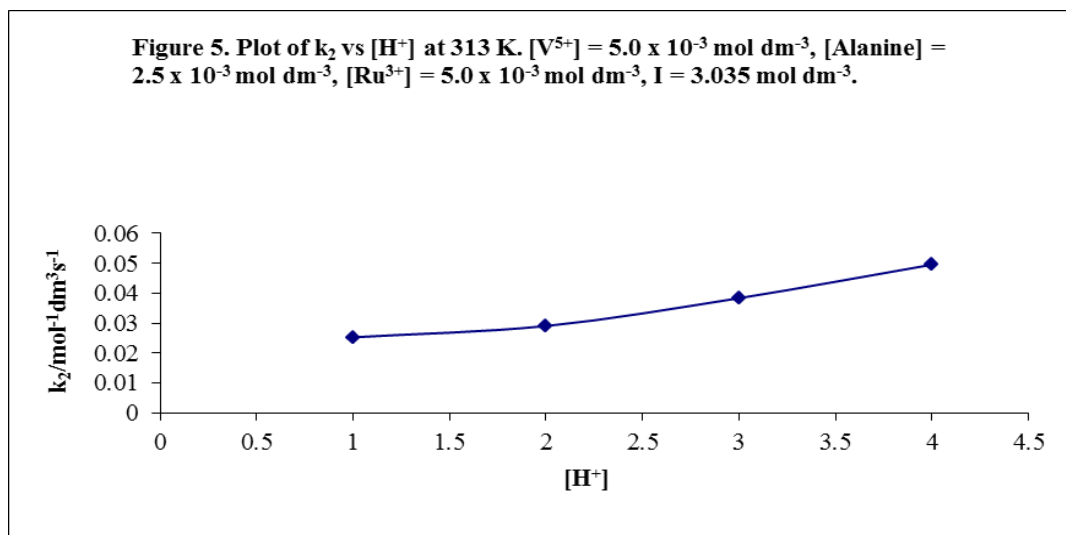
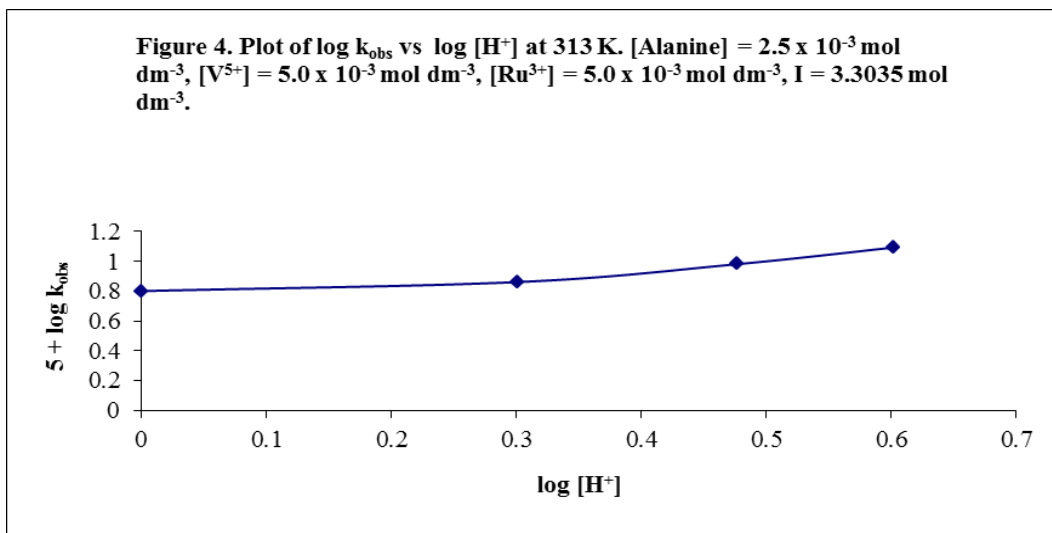
**Table 1: Effect of  $[Na_2SO_4]$  and  $[NaHSO_4]$  on reaction rate**

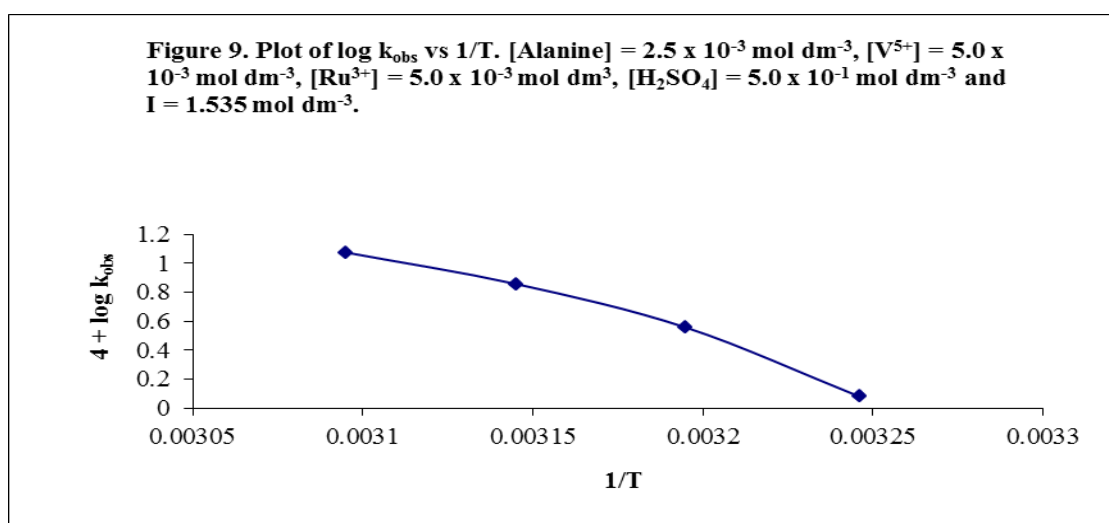
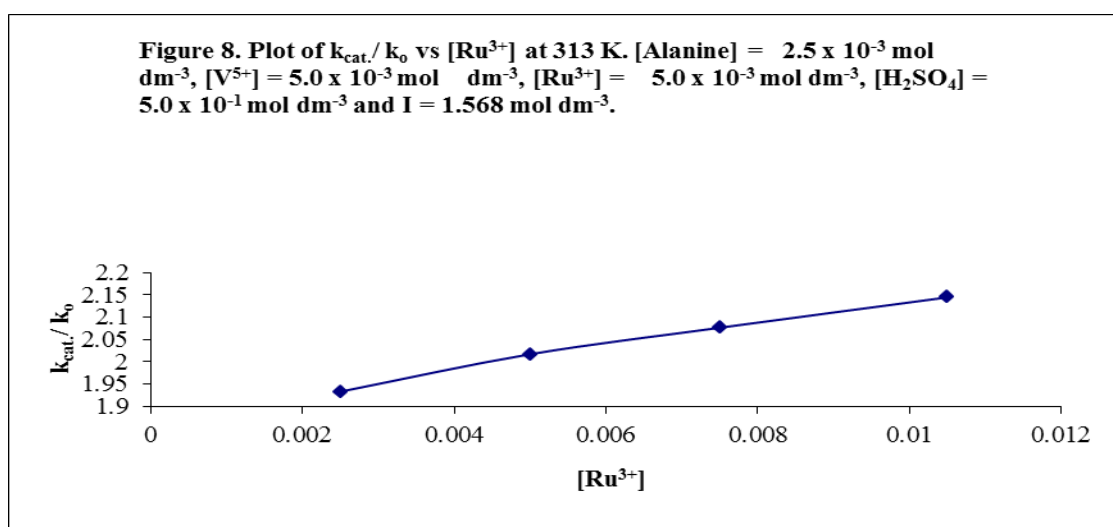
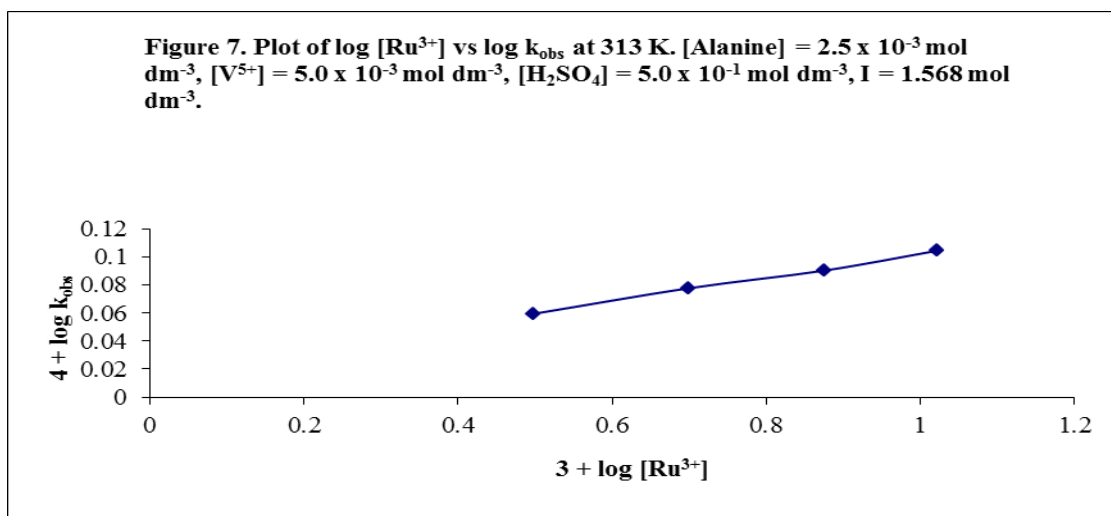
$[Alanine] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ , $[V^{5+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ , $[H_2SO_4] = 5.0 \times 10^{-1} \text{ mol dm}^{-3}$ , $[Ru^{3+}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ and Temperature = 313 K.				
I/mol dm <sup>-3</sup> = 1.565				
$[Na_2SO_4] \times 10^3 / \text{mol dm}^{-3}$	2.5	5.0	7.5	10.0
$[NaClO_4] \times 10^3 / \text{mol dm}^{-3}$	22.5	15.0	2.5	0.0
$k_{obs} \times 10^5 / \text{s}^{-1}$	30.43 ± 0.29	27.35 ± 0.23	23.97 ± 0.43	19.52 ± 0.45
I/mol dm <sup>-3</sup> = 1.545				
$[NaHSO_4] \times 10^3 / \text{mol dm}^{-3}$	2.5	5.0	7.5	10.0
$[NaClO_4] \times 10^3 / \text{mol dm}^{-3}$	7.5	5.0	2.5	0.0
$k_{obs} \times 10^5 / \text{s}^{-1}$	15.23 ± 0.61	13.97 ± 0.67	12.27 ± 0.72	11.602 ± 0.39

**Table 2: Effect of ionic strength on the rate of reaction and values of thermodynamic parameters and catalytic ratios**

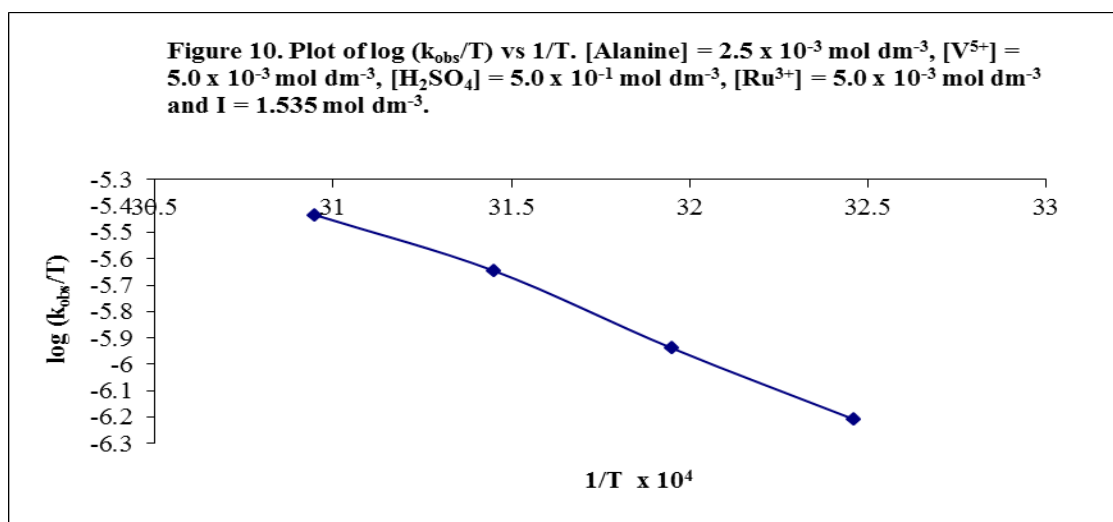
[Alanine] = $2.5 \times 10^{-3}$ mol dm <sup>-3</sup> , [V <sup>5+</sup> ] = $5.0 \times 10^{-3}$ mol dm <sup>-3</sup> , [Ru <sup>3+</sup> ] = $5.0 \times 10^{-3}$ mol dm <sup>-3</sup> , Temperature = 313 K, [H <sub>2</sub> SO <sub>4</sub> ] = $5.0 \times 10^{-1}$ mol dm <sup>-3</sup>					
[NaClO <sub>4</sub> ] × 10 <sup>3</sup> /mol dm <sup>-3</sup>	5.0	10.0	15.0	20.0	
I/mol dm <sup>-3</sup>	1.54	1.545	1.55	1.555	
k <sub>obs</sub> × 10 <sup>5</sup> /s <sup>-1</sup>	20.64 ± 0.72	21.43 ± 0.43	20.53 ± 0.47	20.99 ± 0.83	
Thermodynamic parameters	ΔH <sup>#</sup> /kJ mol <sup>-1</sup>	E <sub>a</sub> /kJ mol <sup>-1</sup>	ΔS <sup>#</sup> /JK <sup>-1</sup> mol <sup>-1</sup>	ΔG <sup>#</sup> /kJ mol <sup>-1</sup>	
	92.671 ± 0.0065	125.067 ± 0.083	-15.136 ± 0.34	97.332 ± 0.11	
I = 1.568 mol dm <sup>-3</sup>					
[Ru <sup>3+</sup> ] × 10 <sup>3</sup> /mol dm <sup>-3</sup>	0.0	2.5	5.0	7.5	10.5
k <sub>obs</sub> × 10 <sup>5</sup> /s <sup>-1</sup>	5.928	11.465	11.957	12.307	12.713
k <sub>cat</sub> /k <sub>o</sub>	.....	1.933	2.0169	2.076	2.1445











## REFERENCES

- Nelson DL and Cox MM. Principles of Biochemistry. W. H. Freeman, New York. 2005;684-685.
- Sah MP. Ag<sup>I</sup>-catalysed oxidation of D-galactose by vanadium(v) in aqueous sulphuric acid solution: A kinetic and mechanistic study. J Indian Chem Soc. 2006;574-576.
- Rai SK, Shivakumar K and Sherigara BS. Polymerization of acrylonitrile initiated by the vanadium(v)-potassium thiocyanate redox system: a kinetic study. J Indian Chem Soc. 2002;79:252-255.
- Rizvi AH and Singh SP. Oxidation of some monosaccharides with vanadium(v). J Indian Chem Soc. 1990;67:23-28.
- Nath RV, Sundar BS and Radhakrishnamurti PS. Kinetics of oxidation of iodine by vanadium(v). J Indian Chem Soc. 1999;76: 5-78.
- Cotton FA, Wilkinson G, Murillo CA and Bochmann M. Advanced Inorganic Chemistry. 6<sup>th</sup> edition, John Wiley & Sons, Inc, New York. 1999;715-722.
- Crans DC, Gottlieb MS, Tawara J, Bunch RL and Theisen LA. A kinetic method for determination of free vanadium(IV) and vanadium(v) at trace level concentrations. Anal Biochem. 1990;188:53-64.
- Melwanki MB, Seetharamappa J and Masti SP. Spectrophotometric determination of vanadium(v) in minerals, steels, soil and biological samples using phenothiazine derivatives. Anal Sci. 2001;17:979-982.
- Vogel AI. A Text Book of Quantitative Inorganic Analysis. 4<sup>th</sup> edition, Longman, London. 1978; 730.
- Vogel AI. A Text Book of Practical Organic Chemistry. 4<sup>th</sup> edition, Longman, London. 1978;1072.
- Zucker L and Hammett LP. Kinetics of Iodination of Acetophenone in Sulphuric Acid and Perchloric Acid Solutions. J Am Chem Soc. 1939;61(10):2791-2798.
- Bunnett JF. Kinetics of Reactions in Moderately Concentrated Aqueous Acids. J Am Chem Soc. 1961;83:4956-4983.
- Long FA and Paul MA. Application of The H<sub>0</sub> Acidity Function To Kinetics And Mechanism of Acid Catalysis. 1957;57(5):935-1010.
- Singh B and Sahai S. Mechanism of Ruthenium(III) Catalysis in Oxidation of Levulinic Acid by N-Bromoacetamide in Perchloric Acid. J Indian Chem Soc. 1991;68:208-209.
- Laidler KJ. Chemical Kinetics. 3<sup>rd</sup> edition, Pearson Education Pte. Ltd. New Delhi. 2004;195-197.
- Mahadevappa DS, Anand S, Nadegowda MB and Rangappa KS. Oxidation of aminoacids with sodium N-bromo-p-toluene sulphonamide: A kinetic study. 1984;61:323-328.