

Kinetics and mechanism of oxidation of tyrosine by vanadium(V) in aqueous hydrochloric and ethanoic acid medium

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Vanadium(V) and tyrosine does not react in sulphuric acid or perchloric acid media at 25 °C. However, in aqueous hydrochloric and ethanoic acid media vanadium(V) is reduced to vanadium(IV) and tyrosine oxidized to 4-hydroxyphenyl acetaldehyde. In this reaction, two moles of vanadium(V) consume one mole of tyrosine. The reaction is first order with respect to vanadium(V) and less than unit order with respect to tyrosine concentrations. Increase in hydrochloric acid concentration increases the rate. The order with respect to acid concentration is found to be less than unity. The effect of ionic strength and dielectric constant of the medium have been studied and a suitable mechanism is proposed. The activation parameters and frequency factor have been determined on the basis of the rate law:

$$\text{Rate} = -d[\text{VO}_2^+]/dt = \frac{k K_1 K_2 [\text{VO}_2^+] [\text{tyrosine}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{tyrosine}] [\text{H}^+]}$$

Amino acids act not only as the building block in protein synthesis but also play a significant role in metabolism and have been oxidized by a variety of oxidizing agents^{1,2}. The study of the oxidation of amino acids is of interest because of their biological significance and selectivity towards oxidant to yield different products^{3,4}. Tyrosine is an essential amino acid, used for the treatment of tuberculosis, myelitis, encephalitis, thyroid bacteria infections and as a nutritional supplement.

Vanadium(V) is an efficient oxidant in acid medium⁵. The oxidation of organic^{5,6} and inorganic^{5,7} compounds have been studied by using vanadium(V) as an oxidant. The reaction between vanadium(V) and tyrosine does not occur in perchloric acid or sulphuric acid media. The redox potential⁸ of the couple $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ in aqueous acid is 1.0 V. However, vanadium(V) is very sensitive to solvent and acidity. Increasing the

amounts of ethanoic acid and hydrochloric acid increases the redox potential⁹ of the couple $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ and vanadium(V) can oxidise tyrosine. The mechanism of oxidation may be quite complicated due to the presence of high content hydrochloric acid and ethanoic acid content, and also due to the formation of different species of vanadium(V) in such media¹⁰. The literature survey reveals that there are no reports on the kinetics of oxidation of tyrosine by vanadium(V). Hence, we have investigated the kinetics of oxidation of tyrosine by vanadium(V) in the presence of hydrochloric acid and ethanoic acid in order to understand the behaviour of the active species of vanadium(V) in such media and to arrive at a suitable mechanism.

Experimental

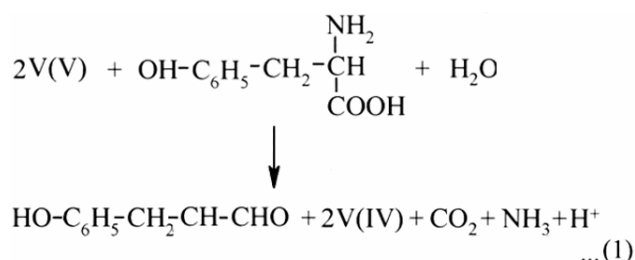
The solutions were prepared with reagent grade chemicals in water, which had been twice distilled in an all-glass unit in the presence of potassium permanganate. The stock solution of the oxidant, vanadium(V), was obtained by dissolving a known weight of ammonium metavanadate in 0.50 mol dm⁻³ hydrochloric acid and standardized with ferrous ammonium sulphate solution using barium diphenylamine sulphonate as an indicator¹¹. Stock solution of tyrosine was prepared by dissolving tyrosine in 1.0 mol dm⁻³ hydrochloric acid. Ethanoic acid and hydrochloric acid were obtained from Glaxo Excelar. The former was purified by refluxing with potassium permanganate for 5-6 h and then distilled. Further distillation yielded the fraction at 118 °C which was used further. Vanadium(IV) solution was prepared by dissolving vanadyl sulphate solution in water, and standardized with cerium(IV) sulphate solution using methyl orange as an indicator¹². Sodium perchlorate and hydrochloric acid were used to provide required ionic strength and acidity respectively. Sodium perchlorate was prepared by mixing equal volumes of sodium hydroxide and perchloric acid and neutralized to pH = 7.0.

All kinetic runs were carried out under the condition where tyrosine concentration was excess over vanadium(V) concentration at a constant temperature of 25±0.1 °C. The thermally equilibrated solution of vanadium(V) and tyrosine also containing the required quantities of hydrochloric

acid, ethanoic acid and sodium perchlorate were used. The progress of the reaction was followed by monitoring the decrease in the absorbance of vanadium(V) as the function of time at 310 nm in 1 cm cell placed in the thermostatted compartment of Varian Cary 50 Bio UV-vis spectrophotometer. The application of Beer's law under the reaction conditions was verified in the concentration range 1.0×10^{-4} to 1.0×10^{-3} mol dm⁻³ of vanadium(V) at 310 nm in 3.0 mol dm⁻³ hydrochloric acid and 40 % ethanoic acid. The molar absorptivity index of vanadium(V) at 310 nm was found to be $\epsilon = 575 \pm 5$ dm³ mol⁻¹ cm⁻¹. The spectral changes during the chemical reaction for the standard condition at 25 °C are shown in Fig. 1. The reaction was followed for more than 80 % completion of the reaction. The first order rate constants, k_{obs} was obtained from the slope of the plot of $\log [V(V)]$ versus time. The first order plots were linear over 75 % completion of the reaction (Fig. 2). The rate constants k_{obs} were reproducible within ± 5 % and are the average of at least four independent kinetic runs.

Results and discussion

With V(V) in excess, five different sets of concentration of reactants were mixed at constant acid concentration in the presence of 40 % of ethanoic acid and kept in a closed container under nitrogen atmosphere at 25 °C. After 4 h, the unused [V(V)] was assayed by measuring the absorbance at 310 nm. Vanadium(IV) concentration was measured at 745 nm. The results indicate that two moles of vanadium(V) reacted with one mole of tyrosine as shown in Eq. (1).



4-Hydroxyphenyl acetaldehyde among the products was identified by LC-ESI-MS and IR spectra. LC-ESI-MS analysis of 4-hydroxyphenyl acetaldehyde was carried out using reverse phase high performance liquid chromatography (HPLC) with a phenomenes C-18 column, UV/visible detector and series mass analyzer. The acidified reaction mixture (12 μ L) was injected, while the mobile phase

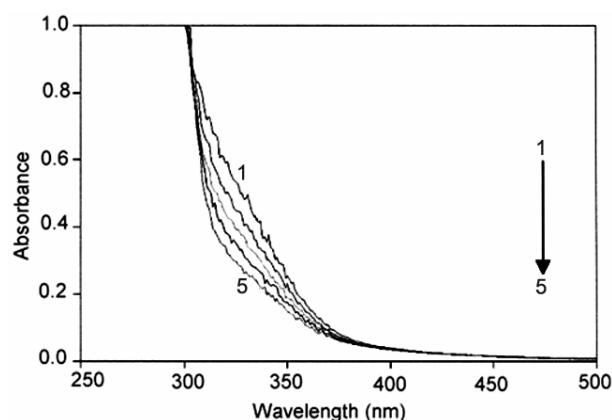


Fig. 1—UV-vis spectral change during the oxidation of tyrosine by vanadium(V) in aqueous hydrochloric acid and ethanoic acid-water media at 25 °C. {[V(V)] = 1.5×10^{-3} ; [tyrosine] = 2.0×10^{-2} ; [HCl] = 3.0; $I = 3.10$ mol dm⁻³; scanning time interval 2 min}.

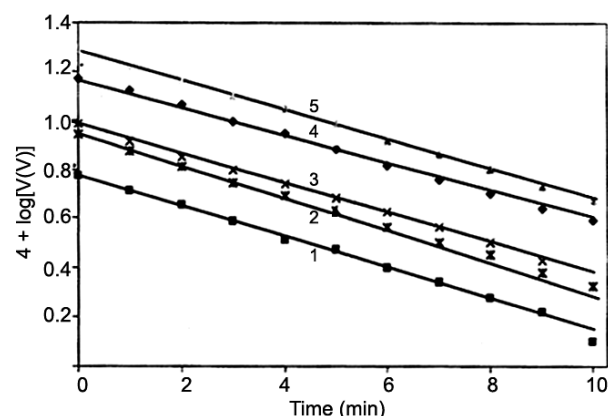


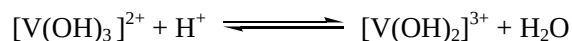
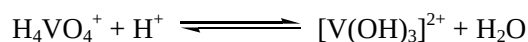
Fig. 2—First order plots of the oxidation of tyrosine by vanadium(V) in aqueous hydrochloric acid and ethanoic acid-water (40 : 60 v/v) media at 25 °C. {[tyrosine] = 2.0×10^{-2} ; [HCl] = 3.0; $I = 3.10$ mol dm⁻³; [V(V)] $\times 10^3$ (mol dm⁻³) = 1, 0.5; 2, 0.8; 3, 1.0; 4, 1.5; 5, 2.0}.

consisted of acetonitrile (eluent A) and methanol (containing 0.1 % CH₃COOH) at a flow rate of 1 mL/min. Gradient elution was run to separate the substrate and reaction products (Gradient: 0 min/ 95 % A; 15 min/ 35 % A; 25 min/ 35 % A; 30 min/ 95 % A; 35 min/ 35 % A). LC-ESI-MS analysis of tyrosine reaction indicated the presence of product with molecular ion of m/z 136 (yield 90 %). The molecular ion of tyrosine is m/z 182, the m/z 136 corresponding to 4-hydroxyphenyl acetaldehyde (Supplementary Data, Fig. S1). The part of the reaction mixture, where [vanadium(V)] > [tyrosine], was extracted with ether and evaporated. The solid, 4-hydroxyphenyl acetaldehyde product was subjected to IR spectra by KBr pellet method (Supplementary Data Fig. S2).

The IR spectrum shows characteristic high intensity band at 1763 cm^{-1} attributed to $\nu(\text{C}=\text{O})$ of aldehyde group. The broad band around 3430 cm^{-1} and a strong band at 1385 cm^{-1} are assigned to $-\text{OH}$ and phenolic $\nu(\text{C}-\text{O})$ vibration respectively. The other products were identified as ammonia (Nessler reagent test) and carbon dioxide, qualitatively detected^{13,14} by passing the liberated gas through a tube containing limewater.

The order with respect each of the oxidant, reductant and acid was determined by the slopes of $\log k_{\text{obs}}$ versus $\log (\text{conc.})$ plots by varying the concentration of substrate and acid in turn, while keeping the concentration of the others constant. At constant concentration of tyrosine, $2.0 \times 10^{-2}\text{ mol dm}^{-3}$, hydrochloric acid, 3.0 mol dm^{-3} , 40 % ethanoic acid-water (v/v) and at constant ionic strength, $I = 3.10\text{ mol dm}^{-3}$, the vanadium(V) concentration was varied (Table 1). The order with respect to vanadium(V) in the $0.2 \times 10^{-3} - 2.0 \times 10^{-3}\text{ mol/dm}^3$ concentration range was unity, since the rate constant k_{obs} , were almost constant at different vanadium(V) concentrations (Table 1). The first order plots under these conditions were almost parallel and linear (Fig. 2) over 75 % completion of the reaction at varying initial concentrations of vanadium(V) which also confirms the unit order in vanadium(V) concentration. The substrate, tyrosine, concentration was varied in the concentration range

5.0×10^{-3} to $5.0 \times 10^{-2}\text{ mol dm}^{-3}$ at $25\text{ }^{\circ}\text{C}$, keeping all other conditions constant. The rate constant, k_{obs} increased with increase in the concentration of tyrosine (Table 1). The order with respect to tyrosine concentration was found to be less than unity (0.71). At constant ionic strength, $I = 3.10\text{ mol dm}^{-3}$ and with other conditions remaining constant, the rate was found to increase with increasing hydrochloric acid concentration (Table 1). The order with respect to acid concentration was determined from the log-log plots of k_{obs} versus acid concentration and was found to be less than unity (0.69) in the $0.50-3.0\text{ mol dm}^{-3}$ range of acid. Vanadium(V) is known to form protonated species in acid medium¹⁰. In higher acid concentration, VO_3^- ion is completely converted into tetrahydroxovanadium (V) ion, H_4VO_4^+ , which on protonation forms mono and diprotonated oxidant species as given below:



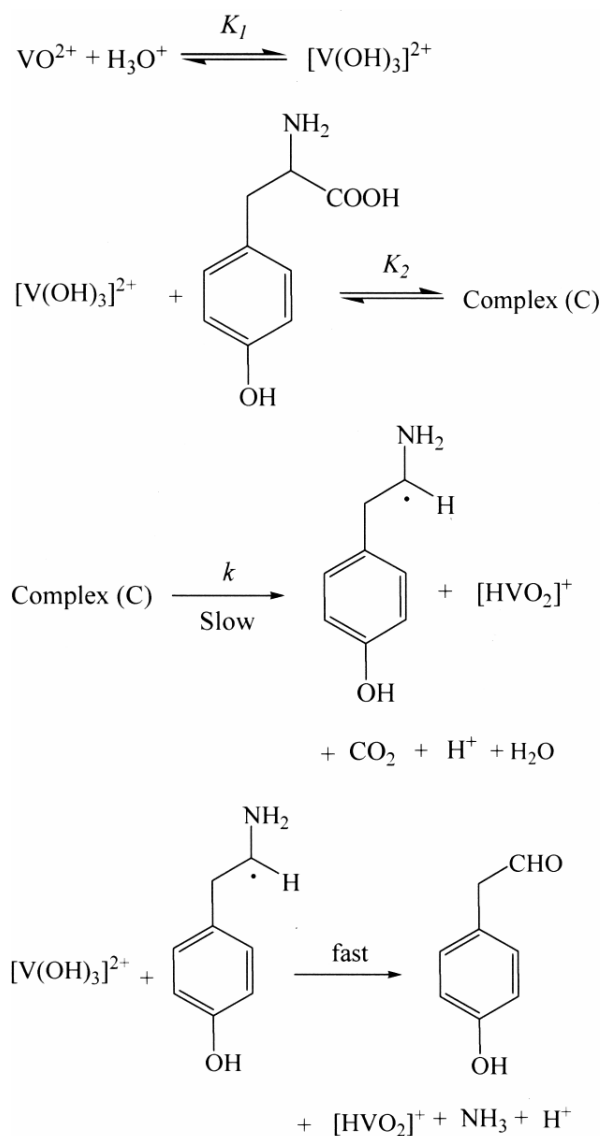
Since the order with respect to acid concentration was less than unity, the monoprotonated species of vanadium(V), i.e., $[\text{V}(\text{OH})_3]^{2+}$ is considered to be the kinetically active species. With the concentration of

Table 1—Effect of variation of vanadium(V), tyrosine and hydrochloric acid concentrations on the oxidation of tyrosine by vanadium(V) in aqueous hydrochloric acid and ethanoic acid–water (40 %) medium at $I = 3.10\text{ mol dm}^{-3}$ and at $25\text{ }^{\circ}\text{C}$

$[\text{V}^{\text{V}}] \times 10^3$ (mol dm^{-3})	$[\text{tyrosine}] \times 10^2$ (mol dm^{-3})	$[\text{HCl}]$ (mol dm^{-3})	$k_{\text{obs}} \times 10^3$ (s^{-1})	$k_{\text{cal}} \times 10^3$ (s^{-1})
0.2	2.0	3.0	0.63	0.69
0.5	2.0	3.0	0.61	0.69
0.8	2.0	3.0	0.61	0.69
1.0	2.0	3.0	0.62	0.69
1.5	2.0	3.0	0.69	0.69
2.0	2.0	3.0	0.62	0.69
1.5	0.5	3.0	0.25	0.23
1.5	0.8	3.0	0.32	0.31
1.5	1.0	3.0	0.45	0.43
1.5	2.0	3.0	0.69	0.62
1.5	3.0	3.0	0.71	0.77
1.5	4.0	3.0	0.79	0.80
1.5	5.0	3.0	0.90	0.91
1.5	2.0	0.5	0.20	0.27
1.5	2.0	1.0	0.30	0.33
1.5	2.0	1.5	0.39	0.40
1.5	2.0	2.0	0.48	0.50
1.5	2.0	2.5	0.59	0.57
1.5	2.0	3.0	0.69	0.61

the reactants and other conditions kept constant, ionic strength was varied from 2.6–4.2 mol dm⁻³; the rate was found to increase with increasing ionic strength. A plot of log k_{obs} versus $\sqrt{I}$ was linear with a positive slope. The effect of dielectric constant was studied by varying the ethanoic acid–water concentration in the reaction mixture with all other conditions being maintained constant. It was found that the rate constant increased with decreasing dielectric constant of the medium. It was also verified and found that there is no appreciable reaction between solvent mixture and oxidant under the present experimental conditions. A plot of log k_{obs} versus $1/D$ was linear with positive slope. The effect of initially added product, vanadium(IV), was studied in the 5.0×10^{-5} to 5.0×10^{-4} mol dm⁻³ concentration range, keeping the ionic strength, reactant concentrations and other conditions constant. It was found that vanadium(IV) did not have any significant effect on the rate of reaction. The intervention of free radicals was also examined. The reaction mixture, to which a known quantity of acrylonitrile had been added initially, was kept in an inert atmosphere for 2 h at room temperature. Precipitate was formed when the reaction mixture was diluted with methanol, suggesting that free radical is formed in the reaction.

The rate of reaction was measured at four different temperatures, 20, 25, 30 and 35 °C under varying acid and tyrosine concentrations. The rate was found to increase with increasing temperature (Table 2). The rate constant (k) of the slow step, K_1 the value of first equilibrium step and K_2 the value of second equilibrium step of the Scheme 1 were obtained from the slopes and intercepts of plots of $1/k_{\text{obs}}$ versus $1/[\text{tyrosine}]$ and $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ at four different temperatures. The values of k , K_1 and K_2 are given in Tables 2 and 3. From the Arrhenius plot, log k versus



Scheme 1

Table 2—Effect of temperature on the oxidation of tyrosine by vanadium(V) in hydrochloric acid and ethanoic acid–water (40:60 v/v) medium and activation parameters with respect to slow step of Scheme 1

Temp. (K)	$k \times 10^3 \text{ (s}^{-1}\text{)}$
293	4.31
298	5.99
303	8.0
308	10.1
$E_a \text{ (kJ mol}^{-1}\text{)}$	33 ± 2
$\Delta H^\ddagger \text{ (kJ mol}^{-1}\text{)}$	32 ± 2
$\Delta S^\ddagger \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$	-180 ± 3
$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)}$	55 ± 3
log A	3.5 ± 0.01

Table 3—Equilibrium constants and thermodynamic quantities at different temperatures for the oxidation of tyrosine by vanadium(V) in hydrochloric acid and ethanoic acid–water (40:60 v/v) medium

Temp.(K)	$K_1 \text{ (dm}^3 \text{ mol}^{-1}\text{)}$	$K_2 \text{ (dm}^3 \text{ mol}^{-1}\text{)}$
293	0.98	4.56
298	1.11	6.38
303	1.19	7.32
308	1.31	8.22
$\Delta H \text{ (kJ mol}^{-1}\text{)}$	14 ± 0.3	28 ± 1
$\Delta S \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$	48 ± 2	130 ± 4
$\Delta G \text{ (kJ mol}^{-1}\text{)}$	-0.34 ± 0.01	-11 ± 0.3

$1/T$, the energy of activation was calculated and from which the remaining activation parameters were calculated (Table 2). A van't Hoff plot was drawn for the variation of K_1 and K_2 with temperature i.e., ($\log K_1$ versus $1/T$) and ($\log K_2$ versus $1/T$). Comparison of the values of enthalpy of reaction ΔH , entropy of reaction ΔS and free energy of reaction ΔG , (Table 3) with those obtained for the slow step shows that the reaction before the rate-determining step is fairly slow and involves high activation energy. All these experimental results can be accommodated in the Scheme 1.

It is well known that in acid solution vanadium(V) exists⁷ mainly as $[V(OH)_3]^{2+}$. The monoprotonated species of vanadium(V) combines with one mole of tyrosine to form a complex. In the rate determining step, the complex is decomposed to liberate carbon dioxide and form the free radical and vanadium(IV). In the next fast step, the free radical reacts with one more molecule of protonated species of vanadium(V) to give the products, 4-hydroxyphenyl acetaldehyde, vanadium(IV) and ammonia. Formation of a complex between tyrosine and vanadium(V) was indicated by the non-zero intercept of the Michaelis-Menten plot (Fig. 3). Complex formation was also indicated by a hypsochromic shift from 555 nm to 550 nm and hyperchromicity at 550 nm on mixing the oxidant with the substrate. The complex formation between oxidant and substrate is also reported in literature¹⁵.

From Scheme 1, the rate law can be derived as follows:

$$\begin{aligned} \text{Rate} &= -d[V(V)]/dt = k [\text{Complex (C)}] \quad \dots(2) \\ [\text{Complex (C)}] &= K_2 [V(OH)_3]^{2+} [\text{tyrosine}] \\ [V(OH)_3]^{2+} &= K_1 [VO_2^+] [H_3O^+] \end{aligned}$$

Therefore,

$$[\text{Complex (C)}] = K_1 K_2 [\text{tyrosine}]_f [V(V)]_f [H_3O^+]_f \quad \dots(3)$$

Substituting Eq. (3) in Eq. (2) we get,

$$\begin{aligned} \text{Rate} &= -d[V(V)]/dt \\ &= k K_1 K_2 [\text{tyrosine}]_f [V(V)]_f [H_3O^+]_f \quad \dots(4) \end{aligned}$$

The total concentration of vanadium(V) is given by

$$\begin{aligned} [V(V)]_t &= [VO_2^+]_t \\ &= [VO_2^+]_f + [V(OH)_3]^{2+} + [\text{Complex (C)}] \\ &= [VO_2^+]_f + K_1 [VO_2^+]_f [H_3O^+] \\ &\quad + K_1 K_2 [VO_2^+]_f [H_3O^+] [\text{tyrosine}] \\ &= [VO_2^+]_f \{1 + K_1 [H_3O^+] \\ &\quad + K_1 K_2 [\text{tyrosine}] [H_3O^+]\} \end{aligned}$$

Therefore,

$$[V(V)]_f = [V(V)]_t / \{1 + K_1 [H_3O^+] + K_1 K_2 [\text{tyrosine}] [H_3O^+]\} \quad \dots(5)$$

where 't' and 'f' stands for total and free.

Similarly,

$$\begin{aligned} [\text{tyrosine}]_t &= [\text{tyrosine}]_f + [\text{Complex (C)}] \\ &= [\text{tyrosine}]_f + K_1 K_2 [VO_2^+]_f [\text{tyrosine}]_f [H_3O^+] \\ &= [\text{tyrosine}]_f \{1 + K_1 K_2 [VO_2^+]_f [H_3O^+]\} \\ [\text{tyrosine}]_f &= [\text{tyrosine}]_t / \{1 + K_1 K_2 [VO_2^+]_f [H_3O^+]\} \quad \dots(6) \end{aligned}$$

In view of the low concentration of vanadium(V) used in the present studies, in Eq. (6), the term $K_1 K_2 [VO_2^+]_f [H_3O^+]$ can be neglected in comparison with unity.

$$\text{Hence, } [\text{tyrosine}]_t = [\text{tyrosine}]_f \quad \dots(7)$$

In the same way, total H^+ ion concentration can be written as

$$\begin{aligned} [H_3O^+]_t &= [H_3O^+]_f + [V(OH)_3] + [\text{Complex (C)}] \\ &= [H_3O^+]_f + K_1 [VO_2^+]_f [H_3O^+] \\ &\quad + K_2 [V(OH)_3] [\text{tyrosine}] \\ &= [H_3O^+]_f + K_1 [VO_2^+]_f [H_3O^+] \\ &\quad + K_1 K_2 [\text{tyrosine}] [VO_2^+]_f [H_3O^+] \\ &= [H_3O^+]_f \{1 + K_1 [VO_2^+]_f + K_1 K_2 [\text{tyrosine}] [VO_2^+]_f\} \end{aligned}$$

Therefore,

$$[H_3O^+]_f = [H_3O^+]_t / \{1 + K_1 [VO_2^+] + K_1 K_2 [\text{tyrosine}] [VO_2^+]\} \quad \dots(8)$$

In view of the low concentrations of vanadium(V) and tyrosine used herein, in Eq. (8), the term $K_1 [VO_2^+]_f + K_1 K_2 [\text{tyrosine}] [VO_2^+]_f$ is neglected in comparison with unity.

$$\text{Hence, } [H^+]_t = [H^+]_f \quad \dots(9)$$

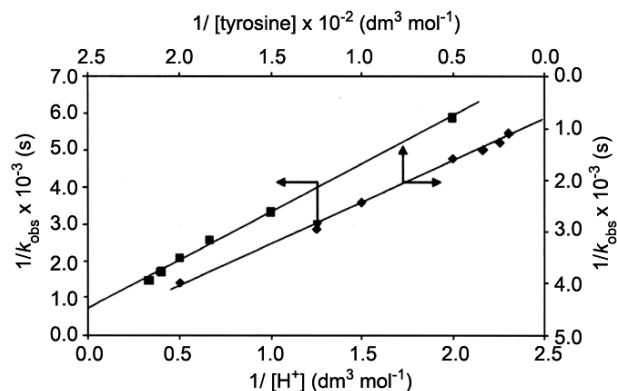


Fig. 3—Verification of rate law (10) in the form of (11) for the oxidation of tyrosine by vanadium(V) in aqueous hydrochloric acid and ethanoic acid-water (40:60 v/v) media at 25 °C.

Substituting Eqs (5), (7) and (9) in Eq. (4), and omitting subscripts we get Eq. (10), which explains all the experimentally observed orders with respect to different species of reaction.

$$\frac{\text{Rate}}{[\text{V(V)}]} = k_{\text{obs}} = \frac{k K_1 K_2 [\text{tyrosine}] [\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{tyrosine}] [\text{H}^+]} \quad \dots(10)$$

Rate law (10) can be rearranged to the form of Eq. (11), which is suitable for verification.

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [\text{tyrosine}] [\text{H}^+]} + \frac{1}{k K_2 [\text{tyrosine}]} + \frac{1}{k} \quad \dots(11)$$

From Eq. (11) it is evident that the plots of $1/k_{\text{obs}}$ versus $1/[\text{H}^+]$ and $1/k_{\text{obs}}$ versus $1/[\text{tyrosine}]$ are expected to be linear, and are found to be so (Fig. 3). The slopes and intercepts of such plots lead to the values of k , K_1 and K_2 (Tables 2 and 3).

Similarly, the values of k , K_1 and K_2 were calculated at 20, 30 and 35 °C and are given in Tables 2 and 3. The values of k , K_1 and K_2 at 25 °C were utilized to calculate the rate constants. The experimental and the calculated values of rate constants reasonably agreed (Table 1).

The moderate values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are both favorable for electron transfer processes. The negative value of $\Delta S^\ddagger$ indicates that the complex (C) is more ordered than the reactants¹⁶. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an innersphere mechanism. This conclusion is also supported by literature^{17,18}. The effect of ionic strength on the rate of the reaction is contrary to that expected, in view of the high

ionic strength ($I = 3.10 \text{ mol dm}^{-3}$) used in the experiments. During the study on the effect of dielectric constant, it was found that the rate of oxidation increases with lowering the dielectric constant of the reaction medium. These results may be expected in the case of a reaction between ion and a dipole as shown in Scheme 1.

Supplementary Data

Supplementary Data associated with this article, i.e., LC-ESI-MS and IR spectral data of 4-hydroxyphenyl acetaldehyde (Figs S1 and S2), are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_51A\(11\)1574-1579_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_51A(11)1574-1579_SupplData.pdf).

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