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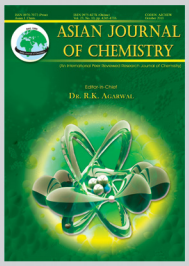

Silver(I)-Catalyzed Oxidation of L-Tyrosine and N-Acetyl L-Tyrosine by Cerium(IV) in Sulfuric Acid Medium (Stopped Flow Fluorimetric Technique)-A Kinetic and Mechanistic Study

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The kinetics of the oxidation of silver(I) catalyzed oxidation of L-tyrosine, N-acetyl L-tyrosine (L-tyr & N-A-tyr) by Ce(IV) in sulfuric acid medium at a constant ionic strength of 0.1 mol dm^{-3} was studied spectrophotometrically (stopped flow fluorimetry). The reaction between L-tyrosine, N-acetyl L-tyrosine and Ce(IV) in sulfuric acid medium in presence of [Ag(I)] exhibits 1:2 stoichiometry. The reaction was first order with respect to L-tyrosine, N-acetyl L-tyrosine, inverse order with respect to Ce(IV) and a positive fractional order with respect to Ag(I). Intervention of free radicals was observed in the reaction. The oxidation reaction in sulfuric acid medium has been shown to proceed *via* a Ag(I)-L-tyr and N-A-tyr complex, which reacts with Ce(IV) to decompose in a rate determining step followed by other fast steps to give the products. The main products were identified by LC-ESI-MS and IR spectra. Probable mechanism is proposed and discussed. The activation parameters with respect to the slow step of the mechanism were computed and discussed and thermodynamic quantities were also calculated. The active species of oxidant has been identified as $Ce(SO_4)_2$.

Key Words: Kinetics, Oxidation, L-Tyrosine, N-Acetyl-L-tyrosine, Ag(I) Catalyst, Ce(IV), H_2SO_4 medium.

INTRODUCTION

In aqueous H_2SO_4 media, Ce(IV) is both thermodynamically and kinetically weaker as an oxidizing agent compared to Ce(IV) in aqueous $HClO_4$ media (cf. E_0 = 1.7 V in 1.0 mol dm^{-3} $HClO_4$; E_0 = 1.4 V in 1.0 mol dm^{-3} H_2SO_4). However, Ce(IV) in aqueous H_2SO_4 media is highly stable[1] and does not require any special precautions to prevent its photochemical decomposition[2] which occurs spontaneously in aqueous $HClO_4$ media. This is why Ce(IV) in aqueous H_2SO_4 media is very often used in analytical chemistry, specially in cerate oxidimetry[3]. On the other hand, Ce(IV) oxidation of different substances in aqueous H_2SO_4 media is in many cases kinetically highly sluggish and needs some metal ion catalysts[4,5]. Some metal ions (*e.g.*, Ru(III), Ir(III),Ag(I)) even at ultra trace concentration can potentially catalyze the Ce(IV) oxidation reactions in many cases and such reactions can be utilized for catalytic kinetic methods of estimation[4-7]. Thus the use of suitable catalysts in Ce(IV) oxidation reaction in aqueous H_2SO_4 media is of much importance in cerate oxidimetry[4] as well as in catalytic kinetic methods of analysis[4-7]. Among the different metal ions, Ag(I) has been used as a catalyst here. Ce(IV) is a well known oxidant in acid media having the reduction potential[8] of the couple Ce(IV)/Ce(III):1.70 V. The oxidation of organic compounds by Ce(IV) in general seems to proceed *via* the formation of an intermediate complex[9].

The study of the oxidation of amino acids is of interest because of their biological significance and selectivity towards the oxidants to yield different products[10-14]. Tyrosine (Tyr) is an essential amino acid and has been used in nutritional supplements, on medicine for the treatment of tuberculosis, myelitis, encephalitis and thyroid bacterial infections.

The sluggish reaction of Ce(IV) oxidation of L-tyrosine and N-acetyl L-tyrosine is catalyzed by a small amount of Ag^+ (10^{-6} mol dm^{-3}) in aqueous sulfuric acid medium. In sulfuric acid and sulfate media, several sulfate complexes[15,16] of Ce(IV) form exists such as $Ce(OH)^{3+}$, $Ce(SO)_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^-$ and $H_3Ce(SO_4)_4^-$, but their role has not received much attention so far. Thus for example, decrease in the rate of reaction with increasing sulfuric acid concentration has not been understood. The mechanism may be quite complicated due to the formation of different Ce(IV) complexes in the form of active species. Hence, Ag(I) catalyzed oxidation of L-tyrosine and N-acetyl L-tyrosine by Ce(IV) has been investigated in order to understand the behaviour of active species of oxidant in sulfuric acid media and a suitable mechanism is proposed.

EXPERIMENTAL

In the present work, double distilled water was used for preparing the solutions. L-Tyrosine and N-acetyl L-tyrosine (E. Merck) was used as such. A stock solution of L-tyrosine and N-acetyl L-tyrosine was prepared by dissolving it in 0.98 mol dm^{-3} sulfuric acid and made it up to the mark by distilled water. The Ce(IV) stock solution was obtained by dissolving cerium(IV) ammonium sulfate (E. Merck) in 0.98 mol dm^{-3} sulfuric acid and standardized with iron(II) ammonium sulfate solution[17]. Other chemicals and reagents such as sodium sulfate, silver nitrate, sulfuric acid, acetonitrile, acetone, hydrated copper sulfate and aluminum sulfate used were of analytical grade with 99.9 % purity.

Kinetic measurements: The kinetics was followed under pseudo first-order condition where [tyr and N-acetyl tyr] > [Ce(IV)] at 293 ± 0.1 K, unless specified. The reaction was initiated by mixing the Ce(IV) to [tyr and N-acetyl tyr] solution which also contained required concentrations of Ag(I), H_2SO_4, Na_2SO_4 and H_2O the progress of the reaction was followed spectrophotometrically at 590 nm by monitoring the emission spectra by using MOS-200/M spectrometer (I.I.Sc., Bangalore) in SFM-300/S advanced mode and the mixing ratio of S1:5, S2:4, S3:1. Since the amino acid tyrosine and N-acetyl tyrosine is fluorescent, the emission mode of the spectrophotometer has been used for the kinetic study at excitation wavelength of 320 nm. At this excitation wavelength, the kinetic curves of tyrosine and N-acetyl tyrosine *i.e.*, fluorimetric intensity in volt *versus* time (Fig. 1a-b) were obtained. The rate constant of the reaction were obtained from this curve directly by using the software which is inbuilt in spectrophotometer.

Procedure: One-drive syringe was filled with a solution containing N-acetyl tyrosine, 0.05M H^+, 0.1M Na_2SO_4 and water The other syringe was filled with a solution containing 8×10^{-3} mol dm^{-3} cerium(IV) and the other syringe was filled with 2×10^{-6} mol dm^{-3} Ag^+ solution. The stopped flow reactor was prepared for the acquisition of the kinetic curve. The instrument was set up as follows: λ_{exc} = 260 nm and λ_{em} = 320 nm (bandpass 4 nm), detector voltage 580 V. The kinetic curve was scanned up to 60 s, with a resolution of 30 ms. Three replicates were registered for each concentration.

RESULTS AND DISCUSSION

Effect of [L-tyrosine and N-acetyl L-tyrosine]: The kinetic runs were carried out with various (4×10^{-2}-8×10^{-2} mol dm^{-3}) concentrations of L-tyrosine and N-acetyl L-tyrosine

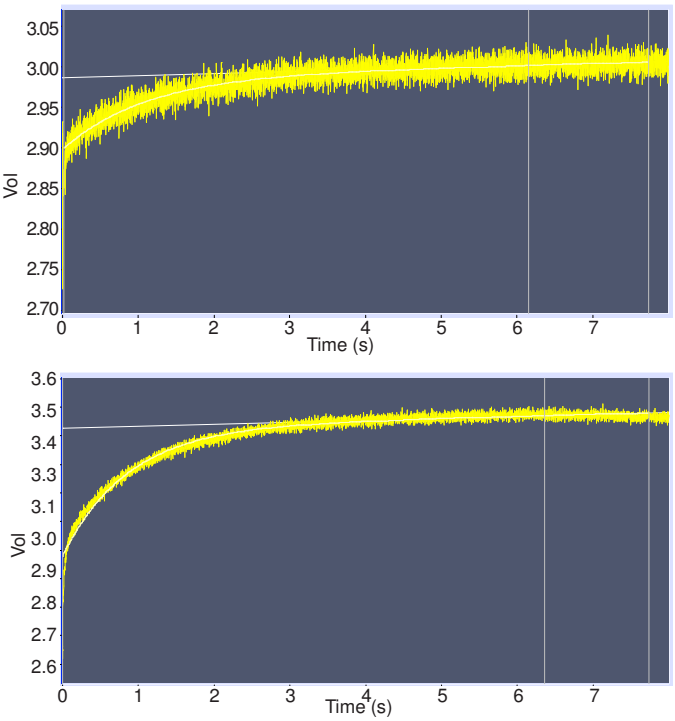


Fig. 1. (a-b) Shows the plot of fluorimetric intensity in volt *versus* time (s)

at [Ce(IV)] (8×10^{-3} mol dm^{-3}), [H^+] (0.05 mol dm^{-3}), [Na_2SO_4] (0.1 mol dm^{-3}) and [Ag(I)] (2×10^{-6} mol dm^{-3}), which yielded rate constants whose values depended on [L-tyrosine and N-acetyl L-tyrosine]. The pseudo first order rate constants k' (s^{-1}) thus obtained were found to increase with [L-tyrosine and N-acetyl L-tyrosine] (Table-1) This shows that the reaction obeys first order with respect to [L-tyrosine and N-acetyl L-tyrosine]. This was confirmed by the linear plots of k' (s^{-1}) *versus* [L-tyrosine and N-acetyl L-tyrosine] yielded a straight line (Fig. 2a-b). The plot of 1/ k' *versus* 1/ [L-tyrosine and N-acetyl L-tyrosine] exhibits excellent linearity (Fig. 3a-b) with a positive slope. Observed reaction order n_{ap} = 1.0015 (r = 0.996). The values of k_2 (mol dm^{-3} s^{-1}) was evaluated from the slope of k' (s^{-1}) *versus* L-tyrosine and N-acetyl L-tyrosine] plots (Fig. 2a-b). The k_2 (mol dm^{-3} s^{-1}) values thus obtained from such plots (Table-2) were in agreement with the corresponding values calculated from the factor k' (s^{-1})/[L-L-tyrosine and N-acetyl L-tyrosine].

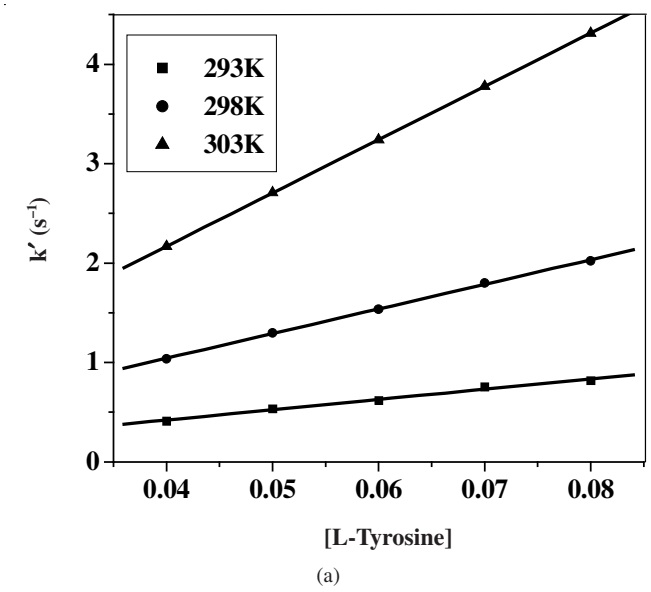
Effect of [Ce(IV)]: The concentration of cerium(IV) was varied from 4×10^{-3}-8×10^{-3} mol dm^{-3} at [L-tyrosine and N-acetyl L-tyrosine] 6×10^{-2} mol dm^{-3}, [H^+] (5×10^{-2} mol dm^{-3}), [Na_2SO_4] (1×10^{-1} mol dm^{-3}) and [Ag(I)] 2×10^{-6} mol dm^{-3}. The rate of the reaction was decreased with increase in [Ce(IV)]

TABLE-1
EFFECT OF CONCENTRATION OF L-TYROSINE AND N-ACETYL L-TYROSINE AND Ce(IV) ON THE PSEUDO FIRST ORDER RATE CONSTANT K'AND SECOND ORDER RATE CONSTANT k_2 Ce(IV)] = 8×10^{-3} mol dm^{-3}
[H^+] = 5×10^{-2} mol dm^{-3}, [Ag^+] = 2.0×10^{-6} mol dm^{-3}, [Na_2SO_4] = 10×10^{-2} mol dm^{-3}

[Substrates] × 10^2 (mol dm^{-3})	L-Tyr k' s^{-1}			L-Tyr k_2 (mol dm^{-3} s^{-1})			N-A-L-Tyr k' s^{-1}			N-A-L-Tyr k_2 (mol dm^{-3} s^{-1})		
	293 K	298 K	303 K	293 K	298 K	303 K	293 K	298 K	303 K	293 K	298 K	303 K
4.0	0.412	1.037	2.167	10.30	25.92	54.175	0.924	1.48	2.561	23.09	37	64.02
5.0	0.537	1.298	2.707	10.75	25.96	54.14	1.168	1.852	3.24	23.36	37.04	64.80
6.0	0.62	1.536	3.240	10.33	25.6	54.00	1.411	2.232	3.842	23.51	37.2	64.03
7.0	0.756	1.8	3.776	10.80	25.71	53.942	1.677	2.644	4.459	23.95	37.77	63.7
8.0	0.819	2.023	4.313	10.24	25.28	53.912	1.852	2.975	5.146	23.15	37.18	64.32

TABLE-2
COMPARISON OF GRAPHICAL AND CALCULATED VALUES OF k_2

Temp. K L-Tyr	k_2 (mol dm^{-3} s^{-1}) graphical	k_2 (mol dm^{-3} s^{-1}) calcd.	Temp. K N-A-L-Tyr	k_2 (mol dm^{-3} s^{-1}) graphical	k_2 (mol dm^{-3} s^{-1}) calcd.
293	10.444	10.484	293	23.4925	23.412
298	25.420	25.694	298	37.4125	37.238
303	53.910	54.033	303	64.0925	64.174



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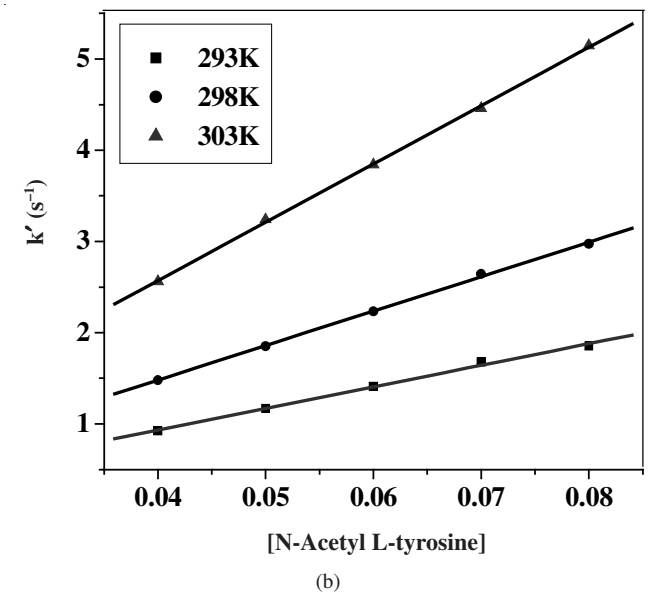
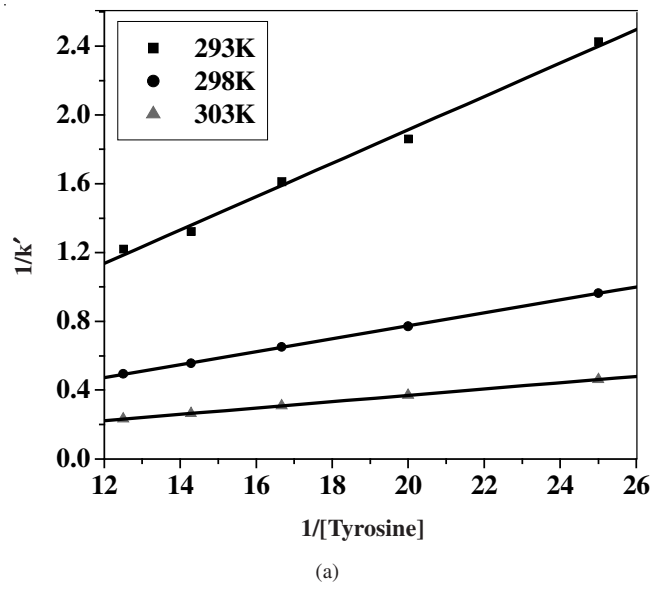


(b)

Fig. 2. (a-b) Shows excellent linearity with a positive slope confirms the first order reaction with respect to [L-tyrosine and N-acetyl tyrosine]



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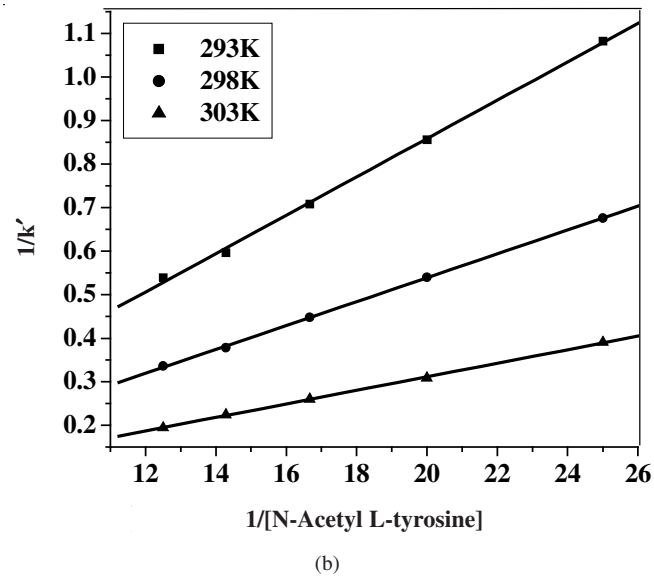


(b)

Fig. 3. (a-b) Shows the linear plot of 1/k' *versus* 1/[L-tyrosine and N-acetyl tyrosine]

indicates that the order with respect to [Ce(IV)] was negative (-3.921) as found from a plot of log k' *versus* log [Ce(IV)]. (Fig. 4a-b and Table-3). The rate constants were decreased with increase in [Ce(IV)], possibly due to the formation of some less reactive polymeric Ce(IV) species at higher [Ce(IV)][18,19]. It is supported by a linear plot of k' *versus* 1/[Ce(IV)].

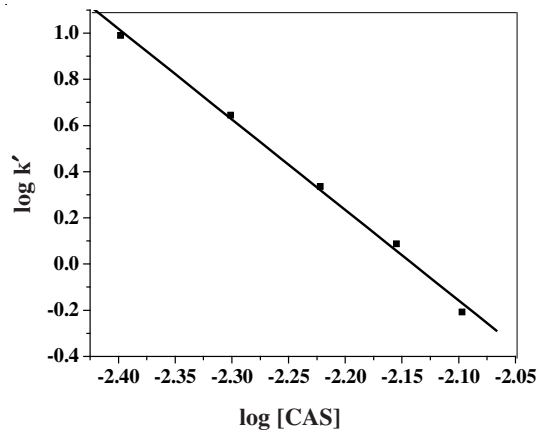
Effect of [H$^+$]: Hydrogen ion concentration was varied from 2.5×10^{-2} to 1.25×10^{-2} mol dm^{-3} at [L-tyrosine and N-acetyl L-tyrosine] (6.0×10^{-2} mol dm^{-3}), [Ce(IV)] (8.0×10^{-3} mol dm^{-3}), [Na_2SO_4] (1×10^{-1} mol dm^{-3}) and [Ag(I)] (2×10^{-6} mol dm^{-3}). The rate of the reaction was decreased with increase in hydrogen ion concentration (Table-4). The order with respect to [H$^+$] was negative (-1.2763 and -1.034) as found from a plot of log k' *versus* log [H$^+$]. (Fig. 5a-b).

TABLE-3
OXIDANT VARIATION [Ag^+] = 2.0×10^{-6} mol dm^{-3} [H^+] = 5×10^{-2} mol dm^{-3}, [Sub] = 6×10^{-2} mol dm^{-3}, [μ] - [Na_2SO_4] = 1×10^{-1} mol dm^{-3}

[Ce(IV)] $\times 10^3$ (mol dm^{-3})	L-Tyr (k s^{-1}) 293 K	N-A-L-Tyr (k s^{-1}) 293 K
4.0	9.751	2.847
5.0	4.412	2.300
6.0	2.166	1.852
7.0	1.223	1.570
8.0	0.620	1.411

TABLE-4
EFFECT OF CONCENTRATION OF H^+ ON THE PSEUDO FIRST ORDER RATE CONSTANT k^1 [Tyr and N-Acetyl Tyr] 6×10^{-2} mol dm^{-3}, [Ce(IV)] = 8×10^{-3} mol dm^{-3}, [Ag^+] = 2.0×10^{-6} mol dm^{-3}, [Na_2SO_4] = 1×10^{-1} mol dm^{-3}

$[H^+] \times 10^2$ (mol dm^{-3})	L-Tyr ($k' s^{-1}$) 293 K	N-A-L-Tyr ($k' s^{-1}$) 293 K
4	1.5700	2.9750
5	0.6200	1.4110
6	0.3751	0.9238
7	0.2169	0.7561
8	0.2000	0.5376



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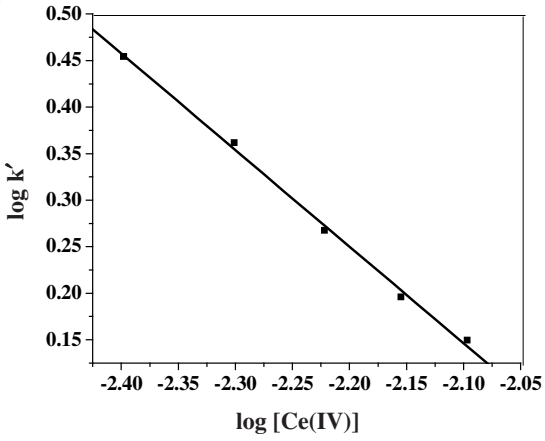
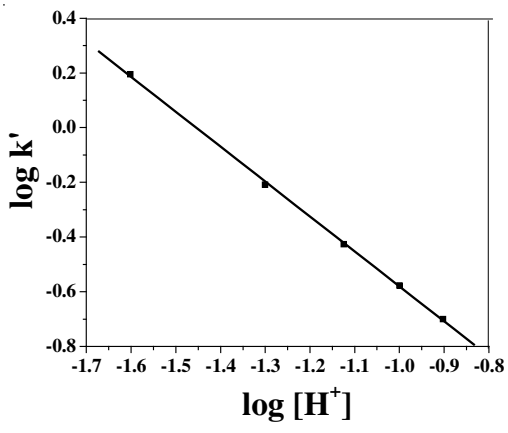


(b)

Fig. 4. (a-b) Shows the linear plot of log k' *versus* log [Ce(IV)] confirms that the reactions are negative order with respect to [Ce(IV)]



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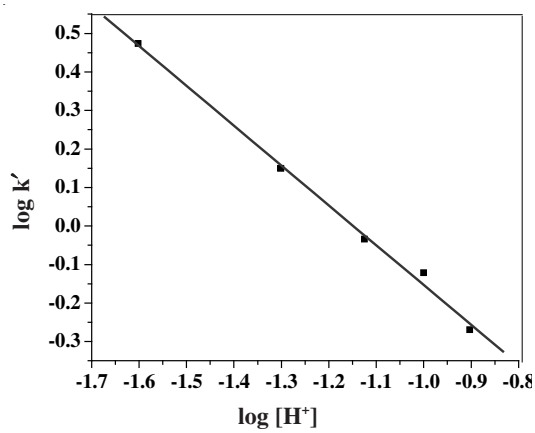


(b)

Fig. 5. (a-b) Shows the linear plot of log k' *versus* log [H^+] confirms that the reactions are negative order with respect to [H^+]

Effect of [ionic strength]: The effect of ionic strength was studied by varying the concentration of sodium sulfate from 5.0×10^{-2} to 25×10^{-2} mol dm^{-3} at [L-tyrosine and N-acetyl L-tyrosine] (6.0×10^{-2} mol dm^{-3}), [Ce(IV)] (8.0×10^{-3} mol dm^{-3}), [H^+] (5×10^{-2} mol dm^{-3}) and [Ag(I)] (2×10^{-6} mol dm^{-3}). The rate of the reaction was decreased with increase in [μ]. (Table-4). The effect of sulfate ions may be explained as due to the removal of the reactive species[20] as $Ce(SO_4)_3^{2-}$.

$$Ce(SO_4)_2 + SO_4^{2-} \rightleftharpoons Ce(SO_4)_3^{2-}$$

Effect of [HSO_4^-]: The effect of HSO_4^- was studied by varying the concentration of HSO_4^- from 5×10^{-2} to 50×10^{-2} mol dm^{-3} at [L-tyrosine and N-acetyl L-tyrosine] 6×10^{-2} mol dm^{-3}, [Ce(IV)] (8×10^{-3}) mol dm^{-3} [H^+] (5×10^{-2} mol dm^{-3}) and [Ag(I)] (2×10^{-6} mol dm^{-3}). The rate of the reaction was decreased with increase in [HSO_4^-] indicates that the order with respect to [HSO_4^-] was negative (-3.0). This is confirmed by the linear plot of 1/ k' *versus* [HSO_4^-]. Therefore HSO_4^- shows rate retarding effect. The plot of 1/ k' *versus* [HSO_4^-] was found to be linear with positive slope. Thus the hydrogen sulfate dependence can be represented as eqn. 1:

$$k' = \frac{a}{b + c[HSO_4^-]} \quad (1)$$

where, a, b and c are constants under experimental conditions.

Effect of dielectric constant: In order to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of [L-tyrosine and N-acetyl L-tyrosine] by Ce(IV) was studied in acetonitrile as well as acetone mixtures of various compositions (Table-5). The data clearly reveals that the rate decreased with increase in acetonitrile and acetone content of solvent. *i.e*., with decrease in dielectric constant of the solvent mixture. This indicates that there is a charge development in the transition state involving a more polar activated complex than the reactants[21]. The reaction is between a neutral molecule and an ion and absence of ion-ion or dipole-dipole type mechanism which is also supported by the negative $\Delta S^{\#}$ values obtained in this work.

[Ag(I)] dependence: The concentration of silver(I) was varied from 1×10^{-6} to 4×10^{-6} mol dm^{-3} at [L-tyrosine and N-acetyl L-tyrosine] (6.0×10^{-2} mol dm^{-3}), [Ce(IV)] (8.0×10^{-3}

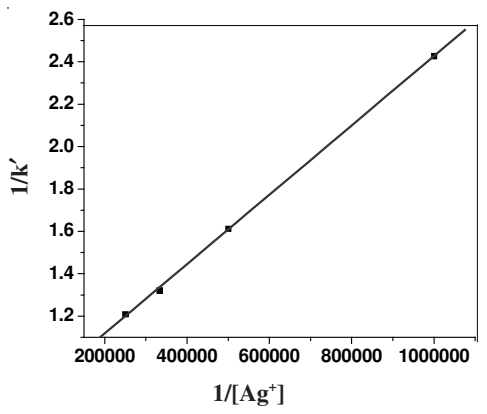
TABLE-5
EFFECT OF IONIC STRENGTH, μ AND $[HSO_4^-]$ ON THE PSEUDO FIRST ORDER RATE CONSTANT, k^1 [Ce(IV)] = 8×10^{-3} mol dm^{-3}, $[H^+]$ = 5.0×10^{-2} mol dm^{-3}, $[Ag^+] = 2.0 \times 10^{-6}$ mol dm^{-3}

$[L\text{-Tyr}] \times 10^2$ (mol dm^{-3})	$[Na_2SO_4] \times 10^2$ (mol dm^{-3})	$[HSO_4^-] \times 10^2$ (mol dm^{-3})	$k' s^{-1}$ 293K	$k' s^{-1}$ 293K	[N-Acetyl L-Tyr] $\times 10^2$ (mol dm^{-3})	$[Na_2SO_4] \times 10^2$ (mol dm^{-3})	$[HSO_4^-] \times 10^2$ (mol dm^{-3})	$k' s^{-1}$ 293K	$k' s^{-1}$ 293K
6.0	5	5	1.0370	2.0230	6.0	5	5	2.300	5.146
6.0	10	10	0.6200	1.5360	6.0	10	10	1.411	4.504
6.0	15	15	0.5376	1.2300	6.0	15	15	0.923	4.078
6.0	20	20	0.3751	1.0370	6.0	20	20	0.537	3.750
6.0	25	25	0.2038	0.9192	6.0	25	25	0.016	3.323

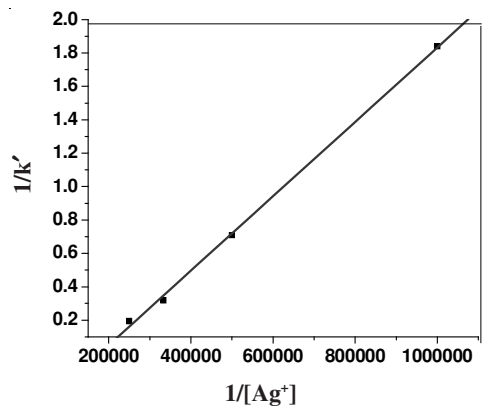
mol dm^{-3}), $[Na_2SO_4]$ (0.1 mol dm^{-3}) and $[H^+]$ (5.0×10^{-2} mol dm^{-3}). The rate of the reaction was increased with increase in $[Ag^+]$. (Table-6). The order with respect to $[Ag^+]$ was n_{ap} = 1.63×10^{-6} as found from a plot of log k' *versus* log $[Ag^+]$. A plot of 1/ k' *versus* 1/$[Ag^+]$ at constant $[H^+]$ and [tyrosine and N-acetyl tyrosine] yielded a good linear plot through origin as shown in (Fig. 6) passing nearly through origin[22].

TABLE-6
EFFECT OF DIELECTRIC CONSTANT ON THE PSEUDO FIRST ORDER RATE CONSTANT k' [Tyr and N-Acetyl Tyr] 6×10^{-2} mol dm^{-3}, [Ce(IV)] 8×10^{-3} mol dm^{-3}, $[Na_2SO_4] = 10 \times 10^{-2}$ mol dm^{-3}

Acetone (%) (V/V)	k' s^{-1} 293 K	
	L-Tyr	N-Acetyl Tyr
35.00	4.384	4.645
37.50	1.570	4.392
38.75	7.561	3.997
40.00	3.751	3.750



(a)



(b)

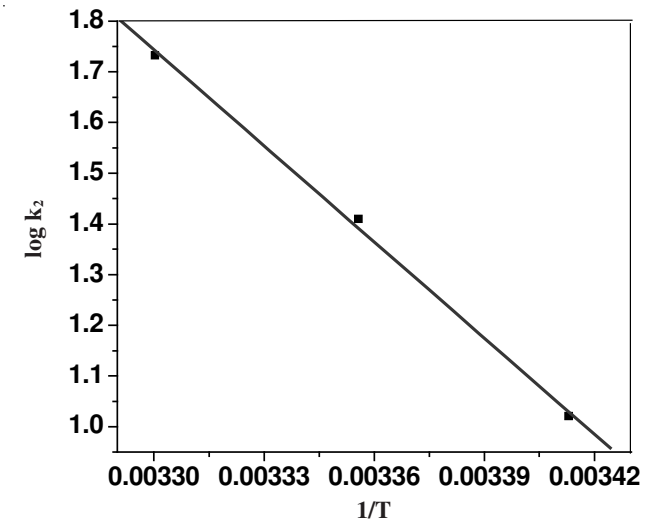
Fig. 6. (a-b) Shows the linear plot of rate constant k' (s^{-1}) *versus* $[Ag^+]$ with non zero intercept confirms that the reaction is fractional order with respect to $[Ag^+]$

Test for free radical intermediates: The intervention of free radicals was examined as follows; the reaction mixture, to which a known quantity of acrylonitrile monomer had been added initially was kept in an inert atmosphere for 2 h. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the intervention of free radicals in the reaction. The blank experiments of either Ce(IV) or [L-tyrosine and N-acetyl L-tyrosine] alone with acrylonitrile did not induce any polymerization under the same conditions as those induced for reaction mixture. Initially, added acrylonitrile decreased the rate of reaction indicating free radical intervention as reported earlier[14,23].

TABLE-7
EFFECT OF CONCENTRATION OF Ag^+ ON THE PSEUDO FIRST ORDER RATE CONSTANT k' [Tyr and N-Acetyl Tyr] 6×10^{-2} mol dm^{-3}, [Ce(IV)] 8×10^{-3} mol dm^{-3}, $[Na_2SO_4] = 10 \times 10^{-2}$ mol dm^{-3}

$[Ag^+] \times 10^6$ (mol dm^{-3})	k' s^{-1} 293 K	
	L-Tyr	N-Acetyl Tyr
1.0	0.4120	0.5435
2.0	0.6200	1.4110
3.0	0.7561	3.1390
4.0	0.8192	5.1410

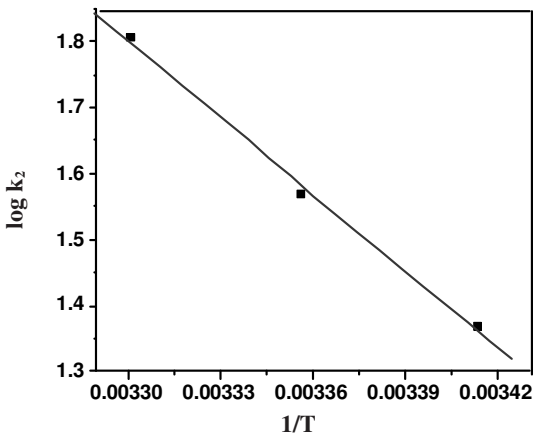
Rate and activation parameters: The reaction was studied at different temperatures (293-303 K) (Table-8) and the activation parameters were computed from Arrhenius (Fig. 7a-b) and Eyring's plots (Fig. 8a-b).



(a)

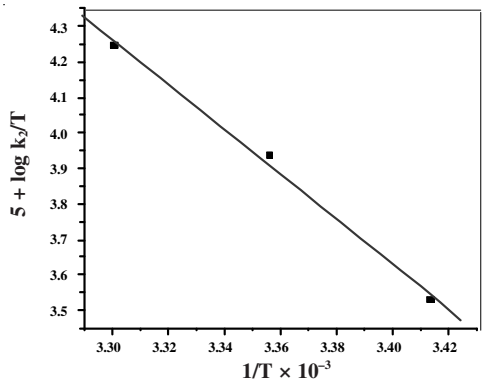
TABLE-8
EFFECT OF TEMPERATURE VARIATION ON PSEUDO FIRST ORDER RATE CONSTANT k' AND SECOND ORDER RATE CONSTANT k_2 [Ce(IV)] = 8×10^{-3} mol dm^{-3} $[H^+] = 5 \times 10^{-2}$ mol dm^{-3}, $[Ag^+] = 2.0 \times 10^{-6}$ mol dm^{-3}, $[Na_2SO_4]$ = 10×10^{-2} mol dm^{-3} substrates = L-Tyr and N-A-L-Tyr E_a = 125.081 and 74.6078 KJ mol^{-1}, $\Delta H^{\#}$ = 122.068 and 72.171 KJ mol^{-1}, $\Delta S^{\#}$ = -177.2734 and -185.819 KJ mol^{-1}, $\Delta G^{\#}$ = 81.875 and 126.616 KJ mol^{-1}

[Substrates] × 10^2 (mol dm^{-3})	L-Tyr k' s^{-1}			L-Tyr k_2 (mol $dm^{-3}s^{-1}$)			N-A-L-Tyr k' s^{-1}			N-A-L-Tyr k_2 (mol $dm^{-3}s^{-1}$)		
	293 K	298K	303K	293K	298K	303K	293K	298K	303K	293K	298K	303K
4.0	0.412	1.037	2.167	10.30	25.92	54.175	0.924	1.48	2.561	23.09	37	64.02
5.0	0.537	1.298	2.707	10.75	25.96	54.14	1.168	1.852	3.24	23.36	37.04	64.80
6.0	0.62	1.536	3.240	10.33	25.6	54.00	1.411	2.232	3.842	23.51	37.2	64.03
7.0	0.756	1.8	3.776	10.80	25.71	53.942	1.677	2.644	4.459	23.95	37.77	63.7
8.0	0.819	2.023	4.313	10.24	25.28	53.912	1.852	2.975	5.146	23.15	37.18	64.32

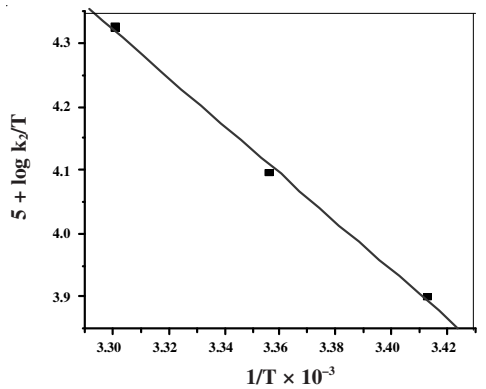


(b)

Fig. 7. (a-b) (Arrhenius plot) shows the linear plot of log k_2 *versus* 1/T. From Arrhenius plot, energy of activation (Ea) is calculated



(a)



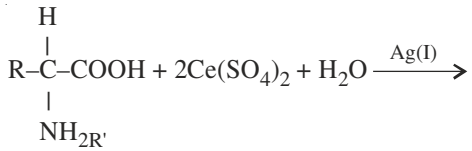
(b)

Fig. 8. (a-b) (Eyring's plot) shows the linear plot of 5 + log k_2/T *versus* 1/ T × 10^{-3}. From Eyring's plot the value of $\Delta S^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$ is computed

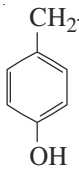
Stoichiometry and product analysis: Different sets of reaction mixtures containing varying ratios of Ce(IV) to L-tyrosine and N-acetyl L-tyrosine in presence constant amounts of [Ag(I)], $[H^+]$ and $[Na_2SO_4]$ were kept for 6 h in closed vessel under inert atmosphere. The remaining Ce(IV) concentration was estimated by spectrophotometrically at 620 nm. The results indicate a 1:2 stoichiometry as given in **Scheme-I**. The main product, 4-hydroxy phenylacetaldehyde was confirmed by LC-ESI-MS and IR spectra.

LC-ESI-MS analysis of 4-hydroxy phenyl acetaldehyde was carried out using reverse phase high performance liquid chromatography (HPLC) system with a phenomenes C_{18} column, UV/visible detector and series mass analyzer. 12 µL of acidified mixture was injected. The mobile phase consisted of acetonitrile (eluent A) and methanol (containing 0.1 % CH_3COOH) at a flow rate of 1 mL/ min. Gradient elution was run to separate 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 corresponds to 4-hydroxy phenylacetaldehyde[24]. In the IR spectrum, the characteristic high intensity band at 1763 cm^{-1}, is attributed to ν(C=O) of aldehyde group. The broad band around 3430 cm^{-1} and a strong band at 1385 cm^{-1}, are assigned to -OH and phenolic ν(C-O) vibration, respectively[24]. The byproducts were identified as ammonia by Nessler's reagent[17] and the CO_2 by Baryta water test.

Further work on other related amino acids with Ce(IV) is in progress.



$$RCHO + NH_3R' + CO_2 + 2Ce(III) + 4SO_4^{2-} + 2H^+ \quad (2)$$

where R =  R' = H, $-COCH_3$.

Based on the foregoing observations such as first order dependence of rate on [Amino acid], negative order dependence on [ceric ammonium sulfate], negative order dependence

on [H$^+$], negative order dependence on (μ), the stoichiometry, the active species of cerium as $Ce(SO_4)_2$ and confirmation for the complex between gly and Ag(I), the following rate expression may thus be represented by eqn. 3. AA = tyrosine or N-acetyl tyrosine

$$k' = \frac{kfK[AA][Ag^+]}{K[Ce(IV)][H^+][AA]+1} \quad (3)$$

The rate law (3) may be rearranged to eqn. 4 which is suitable for verification

$$\frac{1}{k'} = \frac{[Ce(IV)][H^+]}{kf[Ag^+]} + \frac{1}{kfK[AA][Ag^+]} \quad (4)$$

$$\frac{1}{k'} = \frac{[Ce(IV)][H^+]}{kf[Ag^+]} + \frac{1}{kfK[Ag^+]} \cdot \frac{1}{[AA]} \quad (5)$$

$$\frac{1}{k'} = \frac{[Ce(IV)][H^+]}{kf[Ag^+]} + \frac{1}{kfK[AA]} \cdot \frac{1}{[Ag^+]} \quad (6)$$

Eqn. 3 suggests that $n_{ap} \approx 1.0$, $0 < n_{ap}[AA]$ which is consistent with the results of our experiments. Eqn. 5 suggests that 1/k' *versus* 1/[AA] at constant [H$^+$] and [Ag$^+$] should be linear plots with positive intercept as shown in (Fig. 3). Eqn. 6 suggests that 1/k' *versus* 1/[Ag$^+$] at constant [H$^+$] and [AA] should yield good linear plots nearly through origin as shown in (Fig. 5).

Kinetically active cerium species: Under the experimental conditions in aqueous sulfuric acid medium, the important Ce(IV)-sulfato complexes are $Ce(SO)_4^{2+}$, $Ce(SO_4)^2$, $HCe(SO_4)^{3-}$ and the relevant equilibria are[25].

$$Ce^{4+} + HSO_4^- \rightleftharpoons Ce(SO_4)^{2+} + H^+ \qquad \beta_1 = 3500 \quad (7)$$

$$Ce(SO_4)^{2+} + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^+ \qquad \beta_2 = 200 \quad (8)$$

$$Ce(SO_4)_2 + HSO_4^- \rightleftharpoons HCe(SO_4)_3^- \qquad \beta_3 = 3.4 \quad (9)$$

Among the different sulfato species, the kinetically active species should be inferred on the basis of kinetic data, not according to the magnitude of concentration[26]. From the relationship between hydrogen sulfate and k', $Ce(SO_4)_2$ has been found as the kinetically active species in the present study. The concentration of $Ce(SO_4)_2$ can be approximately obtained. According to the mass balance eqn. 10 is obtained.

$$[Ce(IV)]_T = [Ce^{4+}] + [Ce(SO_4)^{2+}] + [Ce(SO_4)_2] + [HCe(SO_4)_3^-] \quad (10)$$

From eqns. 7-9, the following eqs can be derived:

$$[Ce^{4+}] = \frac{[Ce(SO_4)^{2+}][H^+]}{\beta_1[HSO_4^-]}$$

$$[Ce(SO_4)^{2+}] = \frac{[Ce(SO_4)_2][H^+]}{\beta_2[HSO_4^-]}$$

$$[HCe(SO_4)_3^-] = \beta_3[HSO_4^-][Ce(SO_4)_2]$$

Substituting the above equations into eqn. 10, we get:

$$[Ce(IV)_T] = \frac{[Ce(SO_4)_2][H^+]}{\beta_1[HSO_4^-]} + \frac{[Ce(SO_4)_2][H^+]}{\beta_2[HSO_4^-]} + [Ce(SO_4)_2] + \beta_3[HSO_4^-][Ce(SO_4)_2] \quad (11)$$

By considering the relative magnitudes of the successive formation equilibrium constants which are in the order: $\beta_1 >> \beta_2 >> \beta_3$, the value of $\frac{[Ce(SO_4)_2][H^+]}{\beta_1[HSO_4^-]}$ and $\frac{[Ce(SO_4)_2][H^+]}{\beta_2[HSO_4^-]}$ are much less than the other two terms. Therefore, we get eqn. 12 from eqn. 11.

$$[Ce(IV)]_T = [Ce(SO_4)_2] + \beta_3[HSO_4^-][Ce(SO_4)_2] = [Ce(SO_4)_2]\ (1 + \beta_3[HSO_4^-]) \quad (12)$$

so, $$[Ce(SO_4)_2] = \frac{[Ce(IV)_T]}{1 + \beta_3[HSO_4^-]} = f[Ce(IV)]_T$$

$$f = \frac{1}{1 + \beta_3[HSO_4^-]} \quad (13)$$

Substituting eqn. 13 into eqn. 3 we get,

$$k' = \frac{kK[AA][Ag^+]}{K[CeSO_4)_2](1+\beta_3[HSO_4^-])([H^+][AA]+1)} \quad (14)$$

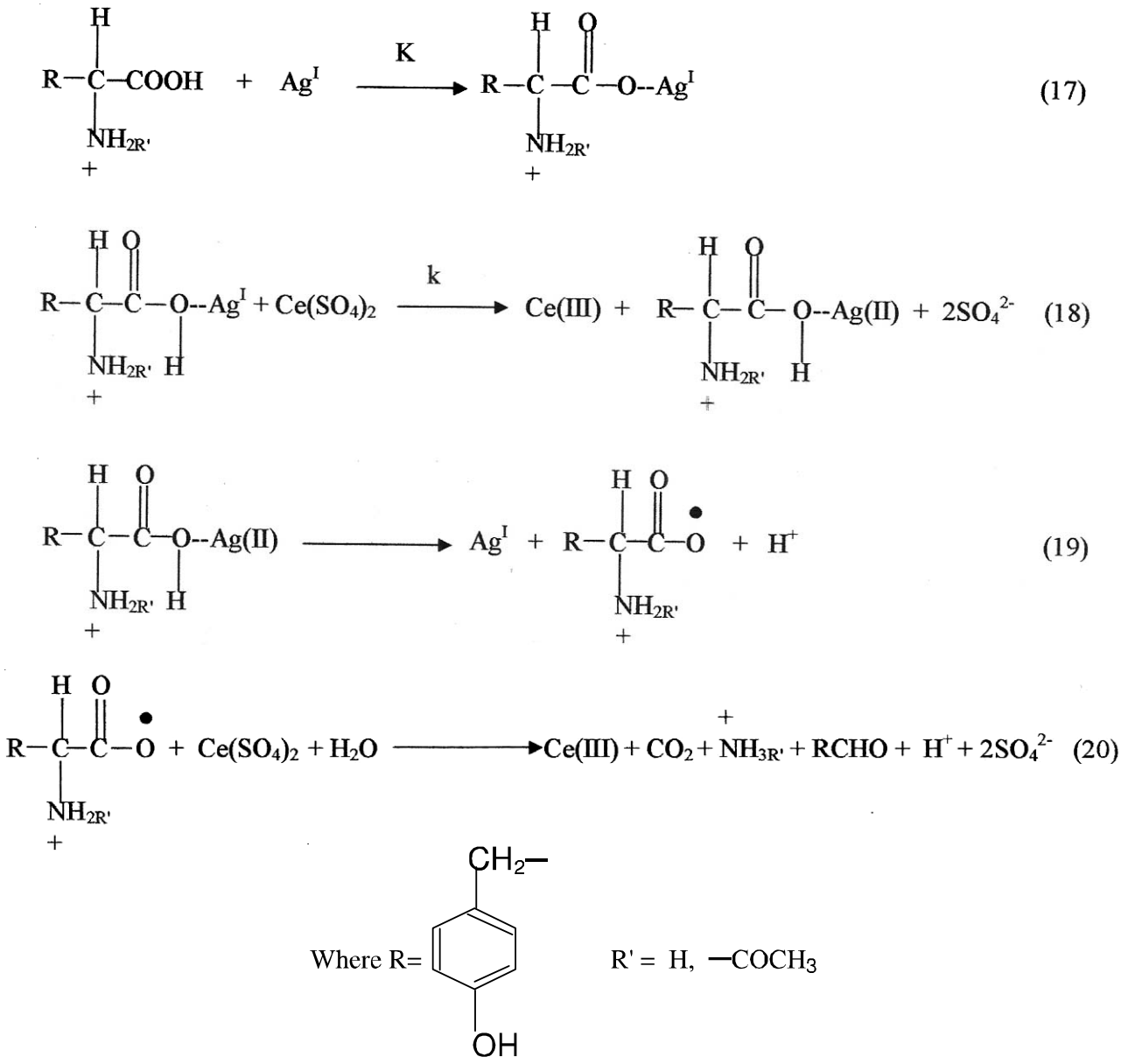
Assuming that $m = \frac{kK[AA][Ag^+]}{K[CeSO_4)_2][H^+][AA]+1}$

Eqn. 14 may be written as

$$k' = \frac{m}{(1 + \beta_3[HSO_4^-])} \quad (15)$$

or $$\frac{1}{k'} = \frac{1}{m} + \frac{\beta_3}{m}[HSO_4] \quad (16)$$

Eqn. 16 is same as eqn. 1 which can explain well the negative order dependence on [HSO_4^-]. Eqn. 16 suggests that 1/ k' *versus* [HSO_4^-] should be linear and agrees with the experimental data. All the above result shows that $Ce(SO_4)_2$ is the kinetically active species. Furthermore, the rate constants were decreased with increase in [H$^+$]. (Table-3). This is due to the formation[25,26] of an active inhibitor $H_2Ce(SO_4)_2^{2-}$. The order with [H$^+$] was negative. As the sulfuric acid concentration increased in the reaction mixture, the [H$^+$] increased, but there is also a corresponding increase in [HSO_4^-]. If the rate is inversely dependent on the [HSO_4^-] to a great extent the overall effect of adding sulfuric acid would lower the rate (Table-3). Similar behaviour has been reported in the oxidation of antimony(III)[24] mandelic acid[24-27] malic acid[28] fructose[29] by cerium(IV). The observation that SO_4^{2-} ions retard the rate of oxidation coupled with the observation that increase in [H$^+$] decreased the rate, point to the fact that the neutral covalently bound $Ce(SO_4)_2$ is the active species of oxidant[19]. In the oxidation of glutamic acid[24], lactic acid[30] and mandelic acid[25, 26,31] by cerium(IV) in sulfuric acid-sulfate media, $Ce(SO_4)_2$, had been identified as the active species, which supports the present work. Furthermore, the ionic strength has little effect on k'. According to the principle of salt effect, there must be a neutral



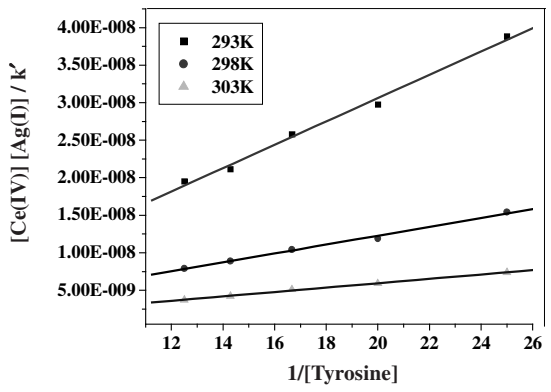
Scheme-I

molecule in the rate determining step, which confirms $Ce(SO_4)_2$ as the kinetically active species in the present study.

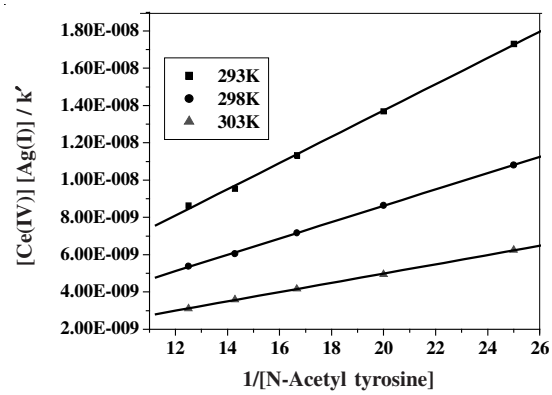
The amino acids are known to exist in Zwitter-ionic form in equilibrium with anionic and cationic forms depending upon the pH of the solution[21,32-35]. The pKa values for the amino acids used[36] in this study are 2.05-2.38. The pH of the reaction was maintained *ca.* 1.3 and the influence of $[H^+]$ ion was studied starting from pH 1.1. The concentration of hydrogen ion employed in these reactions is sufficiently high, amino acids in view of its pKa, should be exclusively be in the cationic form.

$$R\text{–}CHNH_3^+COOH \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} R\text{–}CHNH_3^+COO^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} R\text{–}CHNH_2COO^-$$

Amino acids are reported to form an adduct with Ag(I) owing to availability of electron pair on nitrogen atom. Therefore, an adduct between Ag(I) and corresponding amino acid is initially formed that on further interaction with Ce(IV) yields another adduct of higher valent silver. A plot of $1/k_1$ *versus* 1/[AA] (Fig. 2) is linear with nonzero intercept showing Michaelis-Menton type of relationship. Thus providing the evidence for complex between Ag(I) and amino acid in a first step. The formation of the complex was also proved kinetically by a non zero intercept of the plot of [Ce(IV)][Ag(I)]/rate *versus* 1/[AA] (Fig. 9a-b). Such complex formation has been observed already in the literature[23,27,37]. The results suggest that amino acid combines with catalyst Ag(I) to form a complex, which then reacts in a slow step with one mole of $Ce(SO_4)_2$ to give the product cerium(III), complex, H^+ and $2SO_4^{2-}$ with regenerating the catalyst Ag(I). The complex reacts with another mole of $Ce(SO_4)_2$ in a further fast step to give the products cerium(III), 4-hydroxy phenylacetaldehyde, carbon dioxide and ammonia. The results are accommodated in **Scheme-I**.



(a)



(b)

Fig. 9. (a-b) Are the linear plot of [Ce(IV)][Ag(I)]/ k' *versus* 1/[tyrosine and N-acetyl tyrosine] with non-zero intercept confirms the formation of the complex between Ag(I) and L-tyrosine and N-acetyl tyrosine in a first step

Conclusion

The Ag(I) catalyzed oxidation of tyrosine and N-acetyl tyrosine by Ce(IV)in sulfuric acid medium was studied. Oxidation products were identified. Among various species of Ce(IV) in sulfuric acid medium, $Ce(SO_4)_2$ is considered to be the active species for the title reaction. Activation parameters were evaluated. Catalytic constants and the activation parameters with reference to the catalyst were also computed.

REFERENCES

1. D. Grant, *J. Inorg. Nucl. Chem*., **26**, 337 (1964); (b) D. Grant and D.S. Payne, *Anal. Chim. Acta*, **25**, 422 (1961).
2. L.J. Heidt and M.E. Smith, *J. Am. Chem. Soc*., **70**, 2476 (1948).
3. G.F. Smith, Cerate Oxidimetry Chemical Co., Columbus, OH (1942); I.M. Kolthoff and R. Belcher, Volumetric Analysis, Interscience, New York, Vol. 3, p. 121 (1957).
4. A.R. Day and A.L. Underwood, Quantitative Analysis, Prentice-Hall, New Delhi, edn. 5, p. 326 (1988).
5. A.K. Das, S.S. Mahapatra, P.N. Saha and M. Das, *Indian J. Chem*., **35A**, 623 (1996).
6. A.K. Das and M. Das, *J. Indian Chem. Soc*., **73**, 373 (1996) and the references cited therein.
7. A.K. Das, *Coord. Chem. Rev*., **213**, 307 (2001).
8. A. Schonberg, R. Maubasher and M.Z. Bardkat, *J. Chem. Soc*., 1529 (1951); E.W. Chappelle and J.M. Luck, *Biol. Chem*., **171**, 229 (1957); N. Konigsberg, G.W. Stevenson and J.M. Luck, *J. Biol. Chem*., **715**, 236 (1961).
9. M.S. Ramachandran and T.S. Vivekanandan, *J. Chem. Soc. Perkin Trans. II*, 1341 (1984).
10. D.S. Mahadevappa, K.S. Rangappa, N.N.M. Gowda and B. Thimmegowda, *Int. J. Chem. Kinet*., **14**, 1183 (1982).
11. M.K. Mahanti and D. Laloo, *J. Chem. Soc. Dalton Trans*., 311 (1990).
12. R.M. Kulkarni, D.C. Bilehal and S.T. Nandibewoor, *Transition Met. Chem*., **28**, 199 (2003).
13. K.K. Adari, A. Nowduri and V. Parvataneni, *Acta Chim. Slov*., **55**, 425 (2008).
14. N.P. Shetti, R.R. Hosamani and S.T. Nandibewoor, *Open Catal. J*., **2**, 130 (2009).
15 K.A. Thabaj, S.A. Chimatadar and S.T. Nandibewoor, *Transition Met. Chem*., **31**, 186 (2006); S.A. Chimatadar, T. Basavaraj and S.T. Nandibewoor, *Inorg. React. Mech*., **4**, 209 (2002); S.A. Chimatadar, S.B. Koujalagi and S.T. Nandibewoor, *Transition Met. Chem*., **26**, 241 (2001).
16. S.E. Kharzeeva and V.V. Serebrennikov, *Russ. J. Inorg. Chem*., **12**, 1601 (1967); L.T. Bugaenko and K.L. Huang, *Russ. J. Inorg. Chem*., **8**, 1299 (1963).
17. G.H. Jeffery, J. Bassett, J. Mendham and R.C. Denney, Vogel's Text Book of Quantitative Chemical Analysis, ELBS, Longman, Essex, England, edn. 5, pp. 381, 195 and 455 (1996).
18. B.D. Blaustein and J.W. Gryder, *J. Am. Chem. Soc*., **79**, 540 (1957).
19. Arun Prakash, P. Dwivedi, M.N. Srivastava and B.B.L. Saxena, *Indian J. Chem*., **26**, 960 (1987).
20. Y.R. Sarma and P.K. Saiprakash, *Indian J. Chem*., **19A**, 1175 (1980).
21. K.J. Laidler, Chemical Kinetics, Tata-McGraw Hill, New Delhi, p. 229 (1965).
22. I. Sharma, V. Devra, D. Gupta, C.M. Gangwas and P.D. Sharma, *Int. J. Chem. Kinet*., **27**, 311 (1995).
23. R.V. Jagdeesh and Puttaswamy, *J. Phy. Org. Chem*., **21**, 844 (2008).
24. R.K.Patil, R.H. Patil, S.T. Nandibewoor and S.A. Chimatadar, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem*., **39**, 637 (2009).
25. S.K. Mishra and Y.K. Gupta, *J. Chem. Soc. A*, 2918 (1970).
26. A.C. Shivamurti, V.M. Shankar and S.T. Nandibewoor, *Transition Met. Chem*., 634 (2007).
27. B. Krishna and K.C. Tiwari, *J. Chem. Soc*., 3097 (1961).
28. S.K. Mishra and Y.K. Gupta, *J. Chem. Soc. A*, 2918 (1970).
29. B. Krishna and K.C. Tiwari, *J. Chem. Soc*., 3097 (1961).
30. A. McAuley and C.H. Brubakar, *J. Chem. Soc*., 960 (1966).
31. K.K. Sengupta, *J. Indian Chem. Soc*., **42**, 725 (1965).
32. H.D. Jakubke and H. Jesehein, Amino Acids, Peptides and Proteins, Wiley, New York (1977); H.C. Freeman, *Adv. Protein Chem*., **22**, 258 (1967).
33. A.V. Usha and B. Sethuram, *Indian J. Chem*., **13**, 1167 (1975).
34. R.C. Hiremath and J.M. Mayanna, *J. Chem. Soc. Perkin Trans. II*, 1569 (1987).
35. D. Laloo and M.K. Madhani, *J. Chem. Soc. Dalton Trans*., 311 (1990).
36. J.A. Dean, Lange's Handbook of Chemistry; McGraw-Hill: New York, Sec. 5, p. 17 (1979).
37. A.V. Usha, B. Sethuram and T.N. Rao, *Indian J. Chem*., **15A**, 528 (1977).