Kinetics and Mechanism Of the oxidation Of Alanine by Cerium (IV) in presence of silver (I)

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ABSTRACT:

Kinetics of oxidation of alanine was carried out by using Ag **(I)** as a catalyst. The reaction is first order each with respect to both the reactants, cerium **(IV)** and alanine . The reaction rate increase linearly with Ag **(I)** . the added neutral salts produced retarding effect on the reaction rate while the acid has an accelerating effect , a suitable reaction mechanism has been suggested.

Introduction:

The investigation of amino – acids in the context of non enzymatic oxidation processes constitutes a potential area for intensive experimentation[1-10] . the oxidation of glycine in the presence of some transition metal ions as catalyst has been shown to result in the formation of ammonia , carbon dioxide , and formaldehyde[11] . Khalid[12] studied the kinetics of silver **(I)** catalysed the oxidation of some amino – acids by Ce **(IV)** , the reaction was first order with respect to ce **(IV)** and zero order with respect to amino – acids . the rate constants were increased in the presence of silver . The kinetics of oxidation of glycine by persulphate have been investigated by srivas tava and Chandra[13] **.** The reaction was first order each in persulphate and Ag (I) and independent of alanine .

In this work cerium **(IV)** being a strong oxidant , has been used for investigating the oxidation kinetics of alanine in HNO_3 medium using silver **(I)** as a catalyst.

Experimental:

All the chemicals used were of AR grade and the solutions were prepared in doubly distilled water and standardized by appropriate methods. Shimadz spectrophotometer was used for kinetic experiments. The measurements were performed at $25C^\circ$ The amino acid solution and Ce (IV) solution with known concentrations were mixed in a quartz cell of 1cm optical path, and the absorbance of Ce (IV) at 395 nm vs . time was followed at constant acidity (1M in [H^+] ions) .

Results and Discussion :

The oxidation kinetics of alanine was followed spectrophotometrically at wave length chosen for eliminating spectra intenference , i.e λ = 395 nm   were neither the alanine nor the oxidation product absorb light and the only species responsible for light absorption was Ce (IV) species .

The stoichiometry of the reaction was studied , the results indicate that one mole requires generally 1 mole of Ce (IV) .
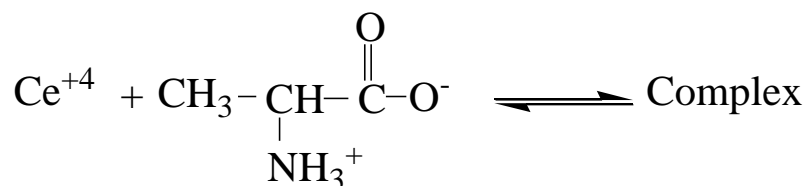
The oxidation products were identified as corresponding aldehyde , ammonia , and carbon dioxide. Carbon dioxide and ammonia were confirmed by usual tests[14-15]. To be identified , the aldehydes were precipitated as hydrazones by the adding 2,4dinitrophenyl hydrazine to reaction product.
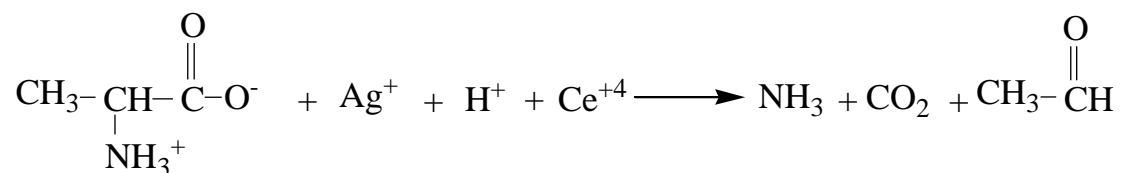
Tollen test was also used for aldehyde identification .

The results show the reaction is first order with respect to[Ce (IV)] and alanine . The rate constants did not vary with initial concentrations of Ce (IV), the variation of first order rate constants with alanine concentration was followed in form of log k_{obs} versus log [alanine] , the values of k_{obs} are given in table I and fig. 1 since it is observed from this table, the rate constants are increasing with increasing substrate concentration .

The same thing occurred with varying concentrations of HNO_3 and AgI as shown in table (1) and figures 2 and 3, salt effect studies employing concentrations of KNO_3 (0.2 – 1.0 M) show the reaction rate decreases with increasing ionic strength.

At the acidity (1M) used in this study the most probable predominant ceric species may be regarded as an hydrolyzed nitrates cationic complex which may however under to dimerization to form a rather less reactive dimeric species , the ceric species may be written in the abbreviated form as $Ce(OH)^{+3}$, the reaction mechanism may be represented as follow .

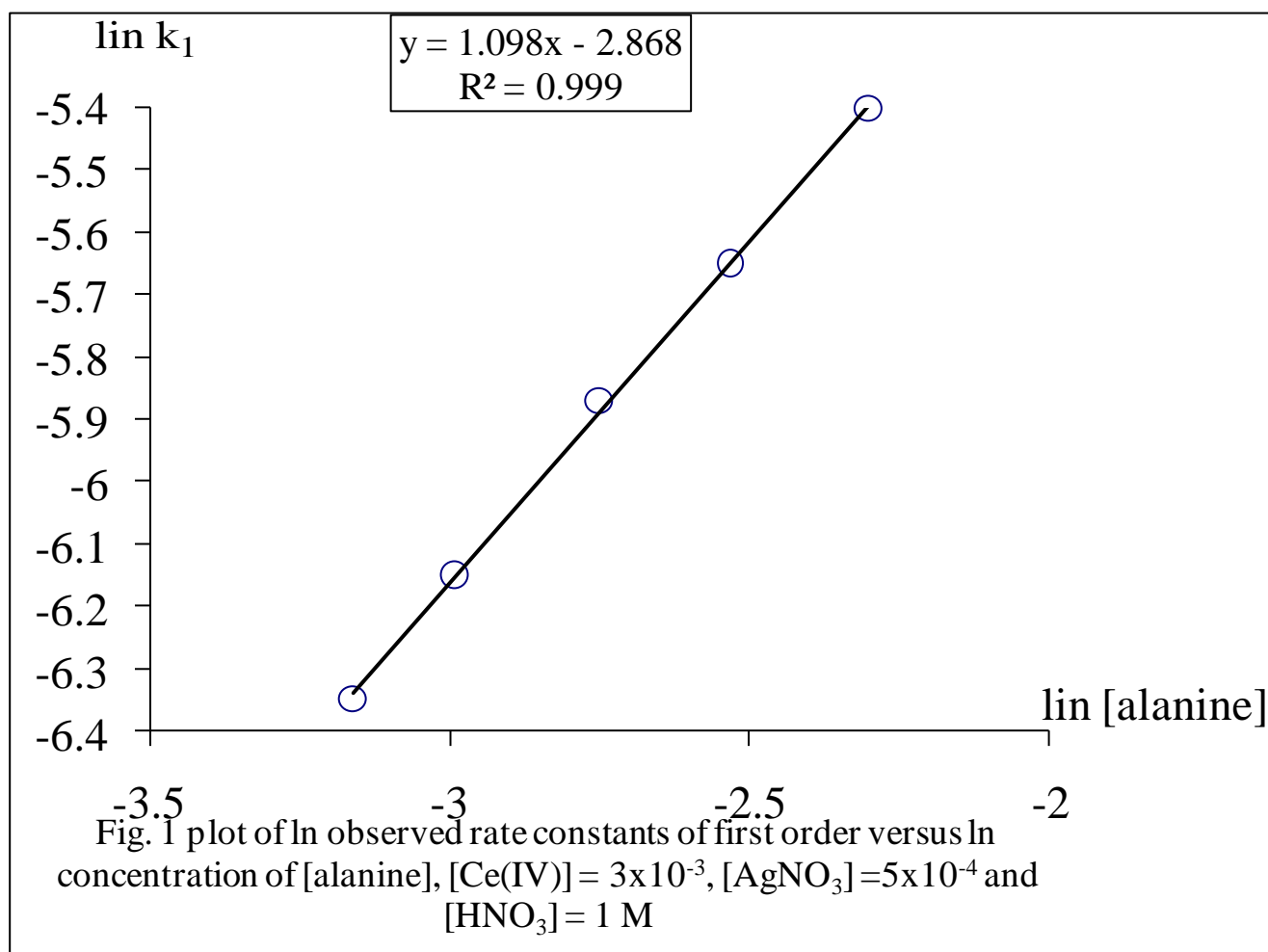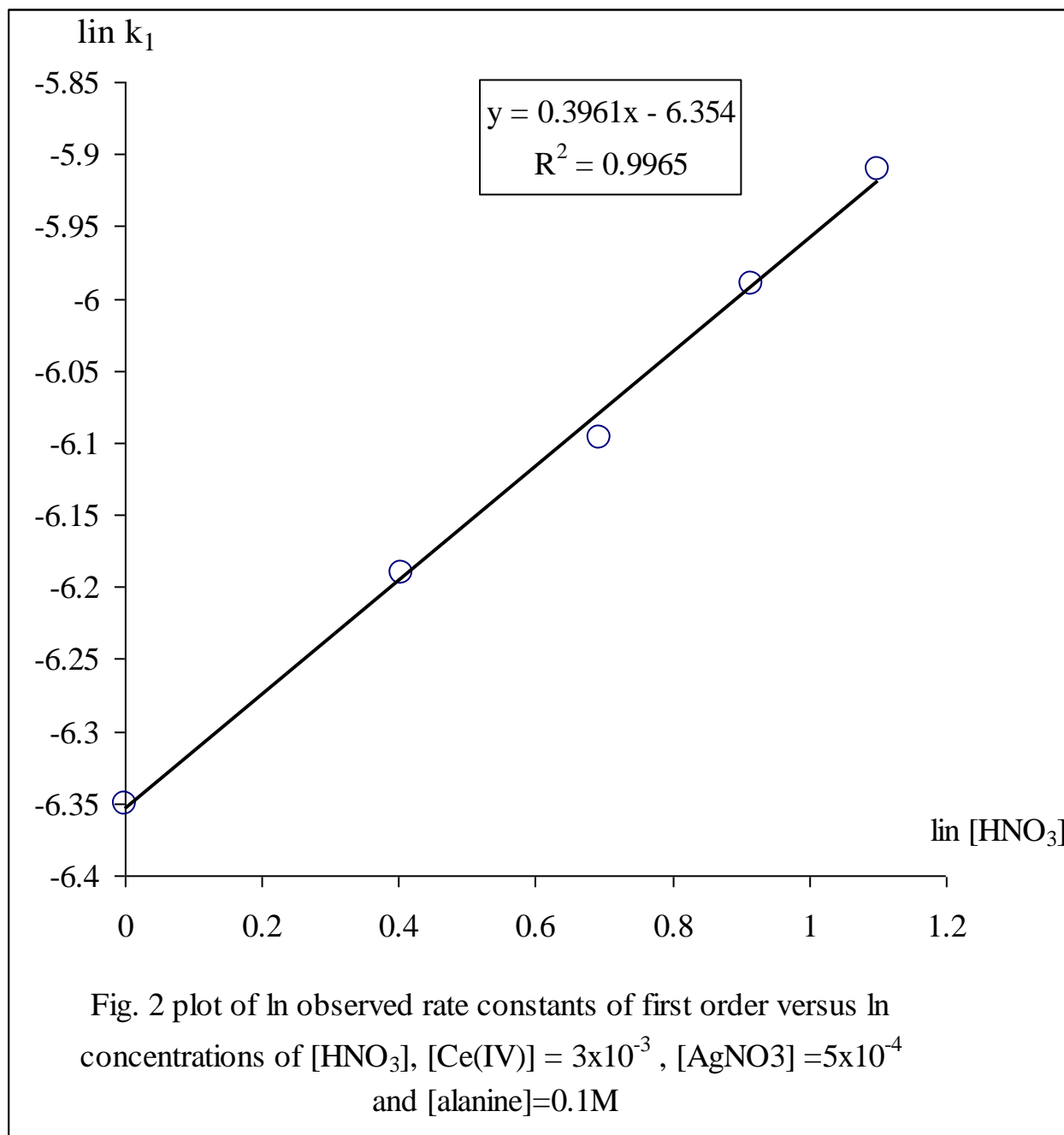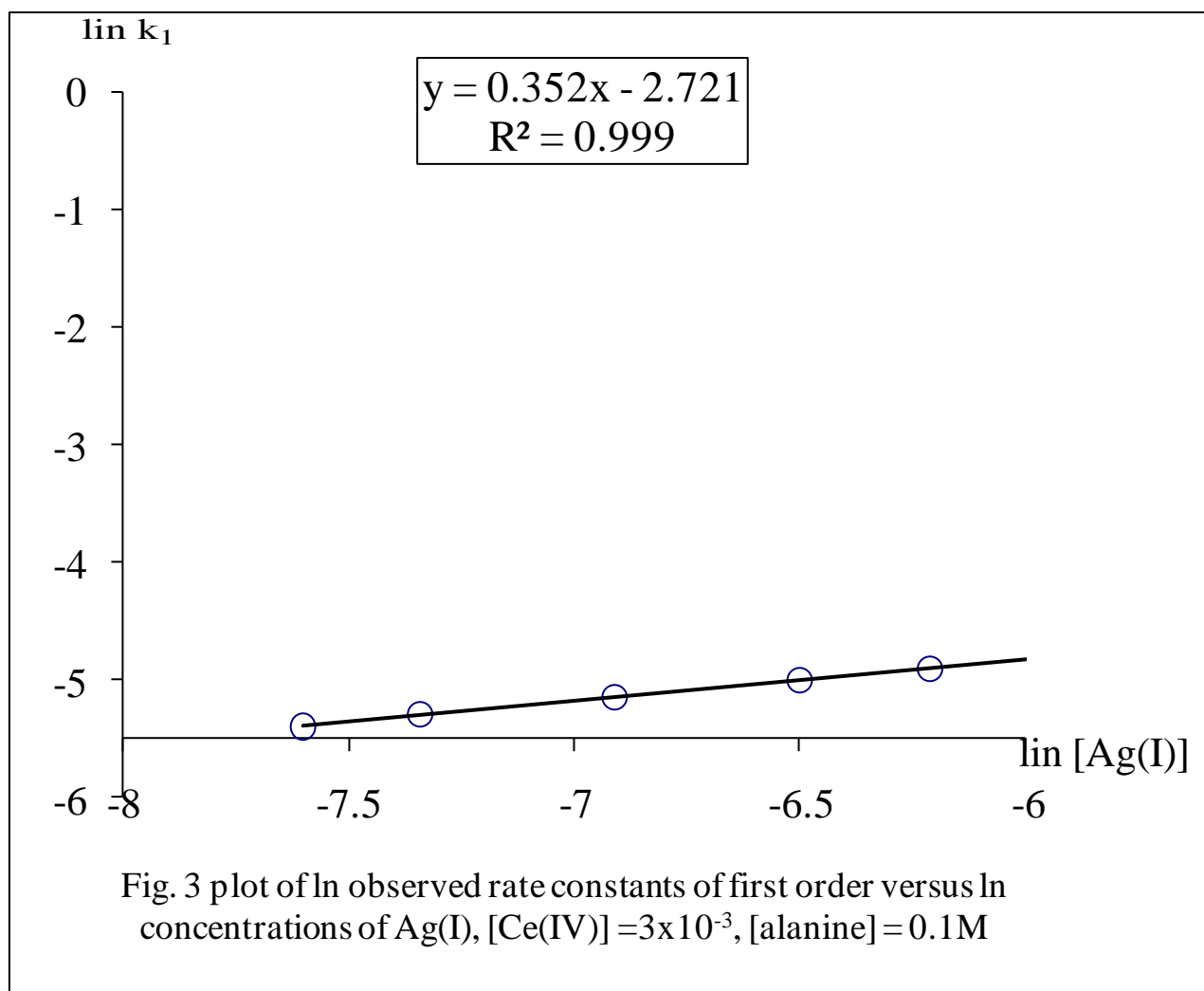$$[Ce(OH)^{+3}] + H^+ \rightleftharpoons H_2O + Ce^{+4}$$

$$Ce^{+4} + CH_3-\underset{\underset{NH_3^+}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O^- \rightleftharpoons Complex$$

$$Complex + Silver(I) \rightleftharpoons Silver(II)-Complex + Ce^{+3}$$

$$CH_3-\underset{\underset{NH_3^+}{|}}{CH}-\overset{\overset{O}{\|}}{C}-O^- \ + \ Ag^+ \ + \ H^+ \ + \ Ce^{+4} \longrightarrow NH_3 \ + CO_2 \ + CH_3-\overset{\overset{O}{\|}}{CH}$$

the rate expression may be represented by

$-d\ [Ce\ (IV)\ ]/\ dt\ = k\ [\ ceric]\ [\ H^+\ ]\ [alanine]\ [Ag^+]$

Table 1, shows the values of rate constants at different concentration of alanine and $[HNO_3] = 1\ M$

[Alanin]x10^{-2} /$_M$	[Ce(IV)]/M	[Ag(I)]/M	[HNO₃]/M	$k_{obs}\times10^{-3}$
4.25	3x10⁻³M	5×10⁻⁴	1.0	1.75
5.00	3x10⁻³M	5×10⁻⁴	1.0	2.5
6.40	3x10⁻³ M	5×10⁻⁴	1.0	3.0
8.00	3x10⁻³ M	5×10⁻⁴	1.0	3.5
10.00	3x10⁻³ M	5×10⁻⁴	1.0	4.5
	3x10⁻³ M	5×10⁻⁴	1.5	1.83
	3x10⁻³ M	5×10⁻⁴	2.0	2.25
	3x10⁻³ M	5×10⁻⁴	2.5	2.5
	3x10⁻³ M	5×10⁻⁴	3.0	2.8
	3x10⁻³ M	6.5×10⁻⁴	1.0	5.00
	3x10⁻³M	10×10⁻⁴	1.0	5.79
	3x10⁻³M	15×10⁻⁴	1.0	6.74
	3x10⁻³M	20×10⁻⁴	1.0	7.40

Fig. 1 plot of ln observed rate constants of first order versus ln concentration of [alanine], $[Ce(IV)] = 3 \times 10^{-3}$, $[AgNO_3] = 5 \times 10^{-4}$ and $[HNO_3] = 1$ M

The plot shows $y = 1.098x - 2.868$, $R^2 = 0.999$, with axes lin k_1 (y-axis) and lin [alanine] (x-axis).

Fig. 2 plot of ln observed rate constants of first order versus ln concentrations of $[HNO_3]$, $[Ce(IV)] = 3x10^{-3}$, $[AgNO3] = 5x10^{-4}$ and $[alanine]=0.1M$

Fig. 3 plot of ln observed rate constants of first order versus ln concentrations of Ag(I), [Ce(IV)] = 3×10^{-3}, [alanine] = 0.1M

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