



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

A kinetic and mechanistic study on the silver (I)-catalyzed oxidation of L-alanine by cerium (IV) in sulfuric acid medium

T. Sumathi ^{a,*}, P. Shanmuga Sundaram ^b, G. Chandramohan ^c

^a Department of Chemistry, B.N.M. Institute of Technology, P.O. Box No. 7087, BSK 2nd Stage, Bangalore 560 070, India

^b TÜV Rheinland (India) Pvt. Ltd., Sigma Tech Park, White Field Main Road, Bangalore 560 066, India

^c P.G. and Research Department of Chemistry, A.V.V.M. Sri Pushpam College, Poondi 613 503, Tamil Nadu, India

Received 7 June 2010; accepted 3 July 2010

Available online 8 July 2010

KEYWORDS

Kinetics;
Oxidation;
L-Alanine;
Ag(I) catalysis;
Ce(IV);
H₂SO₄ medium

Abstract The kinetics and mechanism of Ag(I)-catalyzed oxidation of L-alanine by cerium (IV) in sulfuric acid media have been investigated by titrimetric technique of redox in the temperature range of 298–313 K. It is found that the reaction is of first order with respect to Ce(IV) and L-alanine, and it is of a positive fractional order with respect to Ag(I). It is found that the pseudo first order ([L-alanine] $\gg$ [Ce(IV)] $\gg$ [Ag(I)]) rate constant k' increases with the increase of [H⁺]. The major oxidation product of alanine has been identified as acetaldehyde by an ¹H NMR and IR spectroscopy. Under the experimental conditions, the kinetically active species has been found to be Ce⁴⁺. Under nitrogen atmosphere, the reaction system can initiate the polymerization of acrylonitrile, indicating generation of free radicals. On the basis of the experimental results, a suitable mechanism has been proposed. The rate constants of the rate-determining step together with the activation parameters were evaluated.

© 2010 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +91 80 26711781/82, mobile: +91 9972812978; fax: +91 80 26710881.

E-mail address: pranavsumathi@gmail.com (T. Sumathi).

1878-5352 © 2010 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

Peer-review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2010.07.002



Production and hosting by Elsevier

1. Introduction

The oxidation of amino acids is of utmost important from a chemical point of view of its bearing on the mechanism of amino acid metabolism. Metallic ions play a significant role in the oxidative decarboxylation of amino acids. However, our preliminary observations indicate that the oxidation of some organic compounds by Ce(IV) in aqueous sulfuric acid is kinetically sluggish, the process can be efficiently catalyzed by various metal ions even at trace concentration. Among the different metal ions, Ag(I) has been used as a catalyst here. Kinetics of oxidation of amino acids by a variety of oxidants such as Mn(III) (Beg and Kamaluddin, 1975), Co(III) (Usha

et al., 1977), Os(VIII)-Fe(CN)₆³⁻ (Upadhyay and Agrawal, 1977), Chloramine-T (Mahadevappa et al., 1981), 1-chloro-benzotriazole (Hiremath et al., 1987), *N*-bromosuccinimide (Gopalkrishnan and Hogg, 1985; Schonberg et al., 1951), and Peroxomonosulfate (PMS) (Ramachandran and Vivekanandan, 1984) in acid and alkaline media has been reported. Oxidation of alanine has received much attention because of the involvement in the biological process such as stability of glucose in the system and is associated with chronic fatigue as well as Epstein-Barr virus, when alanine level becomes excessive (Shanmugam, xxxx).

Ce(IV) is a well known oxidant (Thabaj et al., 2006) in acid media having the reduction potential (Day and Selbin, 1964) 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 (Yatsimirskii and Luzan, 1965).

The sluggish reaction of Ce(IV) oxidation of L-alanine 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 (Thabaj et al., 2006; Kharzeeva and Serebrennikov, 1967) of Ce(IV) form exist such as Ce(OH)³⁺, Ce(SO₄)₂²⁺, Ce(SO₄)₂, Ce(SO₄)₂HSO₄⁻, and H₃Ce(SO₄)₄⁻, but their role has not received much attention so far. Thus for example, increase 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-alanine by Ce(IV) has been investigated in order to understand the behavior of active species of oxidant in sulfuric acid media and a suitable mechanism is proposed.

2. Experimental

2.1. Materials

In the present work, double distilled water was used for preparing the solutions. L-alanine (E. Merck) was used as such. A stock solution of L-alanine was prepared by dissolving it in 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 was standardized with iron (II) ammonium sulfate solution (Jeffery and G.H., 1996). Other chemicals and reagents such as sodium sulfate, potassium sulfate, potassium bisulfate, silver nitrate, sulfuric acid, acetonitrile, acetone, hydrated copper sulfate, and aluminum sulfate used were of analytical grade with 99.9% purity.

2.2. Kinetic measurements

Kinetic studies were carried out in a sulfuric acid medium in the temperature range (298–313 K) under pseudo first order conditions with a large excess of L-alanine over Ce(IV). The reaction was followed by estimating the unreacted Ce(IV) as a function of time by titrating against ferrous ammonium sulfate solution employing ferroin as indicator (Walden et al., 1933).

No precautions were taken to exclude the diffused light entering into the reaction mixture (Krishna and B., 1959). The Ce(IV) solution was thermally quite stable (Grant, 1964)

in the visible region and undergoes photochemical decomposition (Heidt and Smith, 1948) only in the UV region. Since, the oxidation of (Kolp and Thomas, 1949) water even at 333 K by Ce(IV) was immeasurably slow and insignificant, no further precautions were taken to account for this.

From the titer values, plots of log [Ce(IV)] vs. time were made and from the slope of such plots, the pseudo first order rate constants k' (s⁻¹) (Table 1) were obtained. To evaluate k' , generally 8–10 values at least up to 80% completion of the reaction were used. Average values of at least two independent determinations of k' were taken for analysis. All the first order plots were linear, with a correlation coefficient of 0.996–0.999. The observed rate constants were reproducible within the experimental error $\pm 5\%$.

3. Results

Factors influencing the rate of oxidation of L-alanine by Ce(IV) such as effects of (i) [L-alanine], (ii) [Ce(IV)], (iii) [H⁺], (iv) ionic strength, (v) dielectric constant, (vi) monovalent (Ag⁺), and (vi) Bivalent (Cu²⁺) and trivalent (Al³⁺) catalysts have been studied. Rate and activation parameters were evaluated.

3.1. Effect of [L-alanine]

At a constant [Ce(IV)] (6 $\times$ 10⁻³ mol dm⁻³), [H⁺] (0.05 mol dm⁻³) [Na₂SO₄] (0.1 mol dm⁻³) and [Ag⁺] (6 $\times$ 10⁻⁶ mol dm⁻³) the kinetic runs were carried out with various initial concentrations of L-alanine, which yielded rate constants whose values depended on [L-alanine]. The pseudo first order rate constants k' (s⁻¹) thus obtained were found to increase with [L-alanine] (Table 1) over a range of [L-alanine] used (2–10 $\times$ 10⁻² mol dm⁻³). This shows that the reaction obeys first order with respect to [L-alanine]. This was confirmed by the linear plots of k' (s⁻¹) vs. [L-alanine] which yielded a straight line passing through the origin. Fig. 1. The plot of 1/ k' vs. 1/[L-alanine] exhibits an excellent linearity (Fig. 2) with a positive slope. Observed reaction order $n_{ap} = 1.01$ ($r = 0.998$). The values of k_2 (mol dm⁻³ s⁻¹) were evaluated from the slope of k' (s⁻¹) vs. [L-alanine] plots (Fig. 1) 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 $k'(\text{s}^{-1})/[\text{L-alanine}]$.

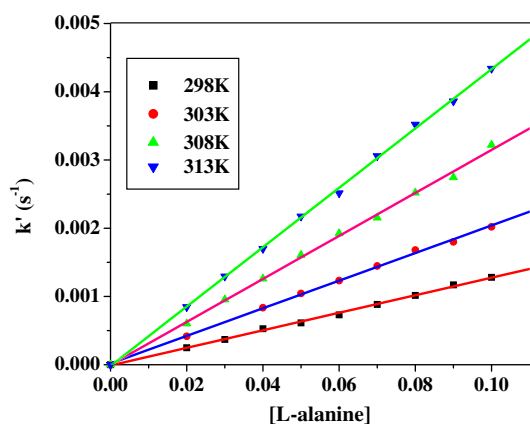
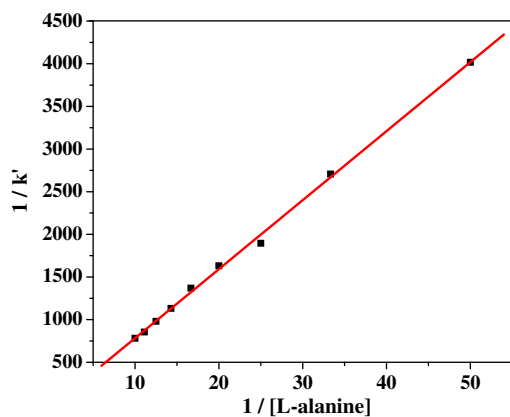
3.2. Effect of [Ce(IV)]

The kinetics of oxidation of L-alanine has been investigated under pseudo first order conditions, keeping the concentrations of L-alanine always in large excess (nearly 10-folds) over that of [Ce(IV)]. When the log [Ce(IV)]_T was plotted against 't', very good straight line plots were obtained indicating that the reaction was of first order with respect to [Ce(IV)] (Table 1). Effect of varying [Ce(IV)] (2–10 $\times$ 10⁻³ mol dm⁻³) on the rate of oxidation has been studied at constant [L-alanine] (6 $\times$ 10⁻² mol dm⁻³), [H⁺] (0.05 mol dm⁻³) [Na₂SO₄] (0.1 mol dm⁻³), and [Ag⁺] (6 $\times$ 10⁻⁶ mol dm⁻³). The pseudo first order rate constants k' were found to be independent of [Ce(IV)], confirming the first order dependence of rate on [Ce(IV)].

Table 1 Effect of concentration of L-alanine and Ce(IV) on the pseudo first order rate constant k' and second order rate constant k_2 .

[L-Alanine] $\times 10^2$ (mol dm ⁻³)	[Ce(IV)] $\times 10^3$ (mol dm ⁻³)	$k' \times 10^5$ s ⁻¹				$k_2 \times 10^3$ (mol dm ⁻³ s ⁻¹)			
		298 K	303 K	308 K	313 K	298 K	303 K	308 K	313 K
2.0	6.0	24.88	41.69	60.16	84.6	12.4	20.8	30.0	42.3
3.0	6.0	36.93	62.90	95.36	129.6	12.3	20.9	31.7	43.2
4.0	6.0	52.75	83.51	125.9	170.0	13.1	20.8	31.4	42.5
5.0	6.0	61.29	104.4	160.5	217.5	12.2	20.8	32.1	43.5
6.0	6.0	74.04	123.2	192.2	251.4	12.3	20.5	32.0	41.9
7.0	6.0	88.35	144.7	215.3	305.9	12.6	20.6	30.7	43.7
8.0	6.0	101.6	168.0	252.0	352.0	12.7	21.0	31.5	44.0
9.0	6.0	117.0	180.0	274.5	386.1	13.0	20.0	30.5	42.9
10.0	6.0	128.0	202.0	322.0	434.0	12.8	20.2	32.2	43.4
6.0	2.0	72.58	—	—	—	—	—	—	—
6.0	3.0	72.73	—	—	—	—	—	—	—
6.0	4.0	73.10	—	—	—	—	—	—	—
6.0	5.0	73.13	—	—	—	—	—	—	—
6.0	6.0	74.04	123.2	192.2	—	12.3	20.5	32.0	41.9
6.0	7.0	73.10	—	—	—	—	—	—	—
6.0	8.0	72.85	—	—	—	—	—	—	—
6.0	9.0	74.32	—	—	—	—	—	—	—
6.0	10.0	73.42	—	—	—	—	—	—	—

$[H^+] = 0.05$ mol dm⁻³, $[Ag^+] = 6.0 \times 10^{-6}$ mol dm⁻³, $[\mu] - [Na_2SO_4] = 0.1$ mol dm⁻³.

**Figure 1** The linear plot of k' (s⁻¹) vs [L-alanine] confirms the first order reaction with respect to [L-alanine].**Figure 2** Excellent linearity with a positive slope confirms the first order reaction with respect to [L-alanine].**Table 2**

Temp (K)	$k_2 \times 10^3$ (mol dm ⁻³ s ⁻¹) graphical	$k_2 \times 10^3$ (mol dm ⁻³ s ⁻¹) observed	R correlation co-efficient
298	12.85	12.60	0.995
303	20.23	20.60	0.997
308	31.50	31.30	0.998
311	43.49	43.04	0.996

3.3. Effect of $[H^+]$

The reaction rates were measured at constant [L-alanine] (6.0×10^{-2} mol dm⁻³), [Ce(IV)] (6.0×10^{-3} mol dm⁻³), $[Na_2SO_4]$ (0.1 mol dm⁻³), and $[Ag^+]$ (6×10^{-6} mol dm⁻³) but with various $[H^+]$ (3.5 – 7.5×10^{-2} mol dm⁻³) (Table 3). $[H^+]$ was calculated ignoring the dissociation of $[HSO_4^-]$ and assuming $[H^+] \approx [HSO_4^-]$. Herein, k' increases with the increase of $[H^+]$. Observed reaction order of n_{ap} of $[H^+]$ is 1.3 obtained from the linear regression ($r = 0.9928$) of $\log k'$ vs. $\log H^+$ indicating that this reaction is of first order with respect to H^+ . The plot of $1/k'$ against $1/[H^+]$ at 298 K was found to be linear ($r = 0.9928$) with a positive slope.

3.4. Effect of [ionic strength]

The reaction rates were measured at constant [L-alanine] (6.0×10^{-2} mol dm⁻³), [Ce(IV)] (6.0×10^{-3} mol dm⁻³) $[H^+]$ (0.05 mol dm⁻³), and $[Ag^+]$ (6×10^{-6} mol dm⁻³) but with various $[Na_2SO_4]$ (0.1–0.8 mol dm⁻³). It was observed that the rate was not influenced by the ionic strength (Table 4).

3.5. Effect of $[HSO_4^-]$ and SO_4^{2-}

$[HSO_4^-]$ (K_2SO_4) and SO_4^{2-} ($KHSO_4$) were varied in the range of (0.1–0.8 mol dm⁻³) at fixed [L-alanine] (6.0×10^{-2}

Table 3 Effect of concentration of H^+ on the pseudo first order rate constant k' .

[L-Alanine] $\times 10^2$ (mol dm $^{-3}$)	[Ce(IV)] $\times 10^3$ (mol dm $^{-3}$)	[H $^+$] (mol dm $^{-3}$)	[Ag $^+$] $\times 10^6$ (mol dm $^{-3}$)	[μ] [Na $_2$ SO $_4$] (mol dm $^{-3}$)	$k' \times 10^5$ s $^{-1}$ 298 K
6.0	6.0	0.035	6.0	0.1	45.258
6.0	6.0	0.040	6.0	0.1	52.165
6.0	6.0	0.045	6.0	0.1	60.125
6.0	6.0	0.050	6.0	0.1	74.040
6.0	6.0	0.055	6.0	0.1	79.876
6.0	6.0	0.060	6.0	0.1	92.066
6.0	6.0	0.065	6.0	0.1	114.23
6.0	6.0	0.070	6.0	0.1	123.35
6.0	6.0	0.075	6.0	0.1	146.55

Table 4 Effect of ionic strength [Na $_2$ SO $_4$] [μ], K $_2$ SO $_4$, and KHSO $_4$ on the pseudo first order rate constant, k' .

[H $^+$] (mol dm $^{-3}$)	[Ag $^+$] $\times 10^6$ (mol dm $^{-3}$)	[μ] [Na $_2$ SO $_4$] (mol dm $^{-3}$)	[K $_2$ SO $_4$] (mol dm $^{-3}$)	[KHSO $_4$] (mol dm $^{-3}$)	$k' \times 10^5$ s $^{-1}$ 298 K
0.05	6.0	0.1	—	—	74.04
0.05	6.0	0.2	—	—	73.64
0.05	6.0	0.3	—	—	73.29
0.05	6.0	0.4	—	—	73.06
0.05	6.0	0.5	—	—	70.00
0.05	6.0	0.6	—	—	71.23
0.05	6.0	0.7	—	—	74.64
0.05	6.0	0.8	—	—	72.32
0.05	6.0	—	0.1	—	69.76
0.05	6.0	—	0.2	—	69.30
0.05	6.0	—	0.3	—	69.55
0.05	6.0	—	0.4	—	67.82
0.05	6.0	—	0.5	—	74.36
0.05	6.0	—	0.6	—	72.45
0.05	6.0	—	0.7	—	69.89
0.05	6.0	—	0.8	—	69.54
0.05	6.0	—	—	0.1	67.84
0.05	6.0	—	—	0.2	69.55
0.05	6.0	—	—	0.3	69.30
0.05	6.0	—	—	0.4	69.76
0.05	6.0	—	—	0.5	75.46
0.05	6.0	—	—	0.6	74.64
0.05	6.0	—	—	0.7	75.64
0.05	6.0	—	—	0.8	69.45

[L-Alanine] = 6.0×10^{-2} mol dm $^{-3}$, [Ce(IV)] = 6.0×10^{-3} mol dm $^{-3}$.

mol dm $^{-3}$), [Ce(IV)] (6.0×10^{-3} mol dm $^{-3}$) [H $^+$] (0.05 mol dm $^{-3}$), and [Ag $^+$] (6×10^{-6} mol dm $^{-3}$). It was observed that the rate was not influenced by the increasing concentration of SO $_4^{2-}$ and HSO $_4^-$ (Table 4) confirming that the reaction occurs between an ion Ce $^{4+}$ and a neutral molecule [L-alanine] (Laidler, 1965).

3.6. [Ag $^+$] dependence

The reaction rates were measured at constant [L-alanine] (6.0×10^{-2} mol dm $^{-3}$), [Ce(IV)] (6.0×10^{-3} mol dm $^{-3}$), [Na $_2$ SO $_4$] (0.1 mol dm $^{-3}$), and [H $^+$] (5.0×10^{-2} mol dm $^{-3}$) but with various [Ag $^+$] (6 – 1.5×10^{-5} mol dm $^{-3}$) (Table 5). A plot of rate constant k' (s $^{-1}$) against [Ag $^+$] yields a straight line with a non zero intercept (Indu Sharma et al., 1995) (Fig. 3). Observed reaction order of Ag(I) can be obtained from linear

regression of log k' vs. log Ag(I) (order ~ 0.374) at 298 K. This indicates that the reaction is of fractional order with respect to Ag(I). The plot of $1/k'$ vs. $1/[Ag^+]$ exhibits excellent linearity ($r = 0.998$) with a positive slope and positive intercept.

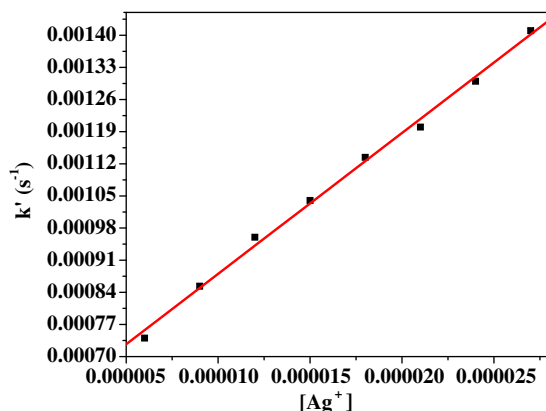
3.7. Effect of bivalent (Cu $^{2+}$) and trivalent (Al $^{3+}$) catalyst

The reaction rates were measured at constant [L-alanine] (6.0×10^{-2} mol dm $^{-3}$), [Ce(IV)] (6.0×10^{-3} mol dm $^{-3}$), [Na $_2$ SO $_4$] (0.1 mol dm $^{-3}$), and [H $^+$] (5.0×10^{-2} mol dm $^{-3}$) but with various [Cu $^{2+}$] and [Al $^{3+}$] (6 – 2.7×10^{-5} mol dm $^{-3}$) (Table 5). The rate of the reaction has not affected much with [Cu $^{2+}$]. [Ag $^+$] can alone show the catalytic activity, but [Cu $^{2+}$] cannot show any catalytic activity in this reaction. The same type of results has been reported for the oxidation of organic carboxylic acids by Ce(IV) in aqueous sulfuric acid (Rao

Table 5 Effect of concentration of Ag^+ , Cu^{2+} , and Al^{3+} on the pseudo first order rate constant k' .

$[\text{H}^+]$ (mol dm $^{-3}$)	$[\mu]$ $[\text{Na}_2\text{SO}_4]$ (mol dm $^{-3}$)	$[\text{Ag}^+] \times 10^6$ (mol dm $^{-3}$)	$[\text{Cu}^{2+}] \times 10^6$ (mol dm $^{-3}$)	$[\text{Al}^{3+}] \times 10^6$ (mol dm $^{-3}$)	$k' \times 10^5 \text{ s}^{-1}$ 298 K
0.05	0.1	6.00	—	—	74.04
0.05	0.1	9.00	—	—	85.36
0.05	0.1	12.0	—	—	96.22
0.05	0.1	15.0	—	—	103.5
0.05	0.1	18.0	—	—	113.0
0.05	0.1	21.0	—	—	120.0
0.05	0.1	24.0	—	—	130.0
0.05	0.1	27.0	—	—	141.0
0.05	0.1	—	6.00	—	67.84
0.05	0.1	—	9.00	—	63.48
0.05	0.1	—	12.0	—	66.84
0.05	0.1	—	15.0	—	64.81
0.05	0.1	—	18.0	—	69.32
0.05	0.1	—	21.0	—	68.93
0.05	0.1	—	24.0	—	74.04
0.05	0.1	—	27.0	—	72.34
0.05	0.1	—	—	6.00	80.00
0.05	0.1	—	—	9.00	94.36
0.05	0.1	—	—	12.0	136.3
0.05	0.1	—	—	15.0	144.7
0.05	0.1	—	—	18.0	173.4
0.05	0.1	—	—	21.0	192.3
0.05	0.1	—	—	24.0	223.4
0.05	0.1	—	—	27.0	253.2

$[\text{L-Alanine}] = 6.0 \times 10^2 \text{ mol dm}^{-3}$, $[\text{Ce(IV)}] = 6.0 \times 10^3 \text{ mol dm}^{-3}$.

**Figure 3** The linear plot of rate constant k' (s^{-1}) vs $[\text{Ag}^+]$ with non zero intercept confirms that the reaction is fractional order with respect to $[\text{Ag}^+]$.

et al., 1978; Asim and Das., 2001). The rate of the reaction increases with increase in $[\text{Al}^{3+}]$. It is observed that the catalytic efficiency of Al^{3+} was higher than Ag^+ .

3.8. Effect of dielectric constant

In order to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of L-alanine by Ce(IV) was studied in acetonitrile as well as acetone mixtures of various compositions (Table 6). The data clearly reveal that the rate decreased with increase in acetonitrile and acetone content of solvent. The rate of the reaction decreased with increase in

the percentage of solvents such as acetonitrile and acetone. This indicates that there is a charge development in the transition state involving a more polar activated complex than the reactants (Indu Sharma et al., 1995). The reaction is between a neutral molecule (alanine) and an ion (Ce^{4+}) and absence of ion-ion or dipole-dipole type mechanism which is also supported by the negative $\Delta S^\ddagger$ values obtained in this work.

3.9. Test for free radical intermediates

When acrylonitrile solution (40% V/V) was added to the reaction mixture under the protection of nitrogen gas, a white deposition could be found, indicating that the reaction system can initiate polymerization of acrylonitrile and proving free radicals are formed in the reaction.

3.10. Rate and activation parameters

The effect of temperature on $k'(\text{s}^{-1})$ was studied in the range (298–313 K) and the results were shown in Table 7. From Arrhenius plot (Fig. 4), the value of energy of activation (E_a) was calculated. Hence, the values of $\Delta S^\ddagger$, $\Delta H^\ddagger$, and $\Delta G^\ddagger$ were computed from the Eyring's plot (Fig. 5). The obtained large negative value of entropy of activation ($\Delta S^\ddagger$) is attributed to the severe restriction of solvent molecules (electrostriction) around the transition state (Anis, 1992) and it indicates that the complex is more ordered than the reactants (Hiremath et al., 2007).

3.11. Stoichiometry and product analysis

Different reaction mixtures with different sets of concentration of reactants, where $[\text{Ce(IV)}]$ was in excess over $[\text{L-alanine}]$ at

Table 6 Effect of dielectric constant on the pseudo first order rate constant k' .

$[H^+]$ (mol dm ⁻³)	$[Ag^+] \times 10^6$ (mol dm ⁻³)	$[\mu] [Na_2SO_4]$ (mol dm ⁻³)	Acetonitrile (%)	Acetone (%)	$k' \times 10^4 \text{ s}^{-1}$ 298 K
0.05	6.0	0.1	35	—	19.23
0.05	6.0	0.1	40	—	15.40
0.05	6.0	0.1	45	—	12.34
0.05	6.0	0.1	50	—	11.53
0.05	6.0	0.1	—	35	25.00
0.05	6.0	0.1	—	40	21.20
0.05	6.0	0.1	—	45	15.90
0.05	6.0	0.1	—	50	14.20

$[L\text{-Alanine}] = 6.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[Ce(IV)] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$.

Table 7 Effect of temperature variation on pseudo first order rate constant k' and second order rate constant k_2 .

$[L\text{-Alanine}] \times 10^2$ (mol dm ⁻³)	$k' \times 10^5 \text{ s}^{-1}$				$k_2 \times 10^3 \text{ (mol dm}^{-3} \text{ s}^{-1})$			
	298 K	303 K	308 K	313 K	298 K	303 K	308 K	313 K
2.0	24.88	41.69	60.16	84.6	12.4	20.8	30.0	42.3
3.0	36.93	62.90	95.36	129.6	12.3	20.9	31.7	43.2
4.0	52.75	83.51	125.9	170.0	13.1	20.8	31.4	42.5
5.0	61.29	104.4	160.5	217.5	12.2	20.8	32.1	43.5
6.0	74.04	123.2	192.2	251.4	12.3	20.5	32.0	41.9
7.0	88.35	144.7	215.3	305.9	12.6	20.6	30.7	43.7
8.0	101.6	168.0	252.0	352.0	12.7	21.0	31.5	44.0
9.0	117.0	180.0	274.5	386.1	13.0	20.0	30.5	42.9
10.0	128.0	202.0	322.0	434.0	12.8	20.2	32.2	43.4

$[H^+] = 0.05 \text{ mol dm}^{-3}$, $[Ag^+] = 6.0 \times 10^{-6} \text{ mol dm}^{-3}$, $[\mu] - [Na_2SO_4] = 0.1 \text{ mol dm}^{-3}$, $[Ce(IV)] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$.
 $E_a = 63.856 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 61.379 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -75.068 \text{ kJ mol}^{-1}$, $\Delta G^\ddagger = 86.226 \text{ kJ mol}^{-1}$.

constant ionic strength, acidity, and at constant concentration of catalyst were kept for 24 h at 298 K in an inert atmosphere. The unreacted Ce(IV) was titrated against standard ferrous ammonium sulfate by using ferroin as an indicator. The main reaction products are Ce(III), aldehyde, ammonia, and CO₂ (Baryta water test).

Acetaldehyde was confirmed with an ¹H NMR and IR spectroscopy. The IR value for C=O group stretching is 1745 cm⁻¹ and for the two C-H stretchings: one at 2820 cm

⁻¹ and the other at 2720 cm⁻¹. The NMR values are one –CH₃ doublet at 2.2 ppm and one quartet for –CHO proton at 9.85 ppm. Further, an aldehyde group was confirmed with qualitative test such as Tollen's reagent (Chimatadar Shivamurti et al., 2007) and Schiff's reagent. Nitrile test was negative, and the product is usually reported in the oxidation of amino acids. Ammonia was confirmed with Nessler's test. Therefore, the stoichiometry of the reaction with a positive test of an

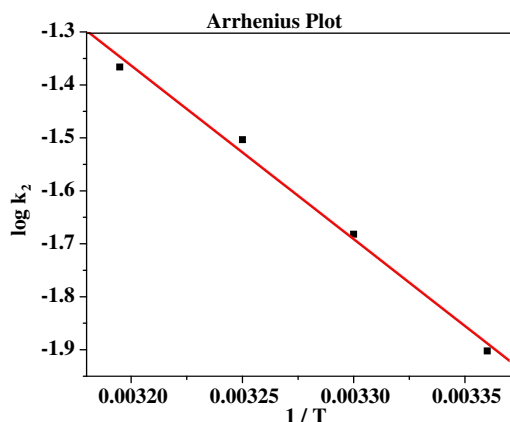


Figure 4 Arrhenius plot shows the linear plot of $\log k_2$ vs $1/T$. From Arrhenius plot, energy of activation (E_a) is calculated.

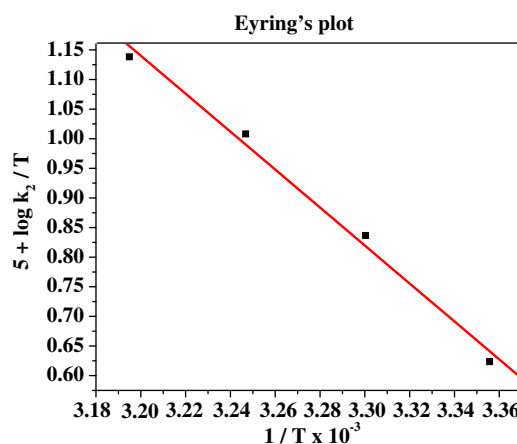
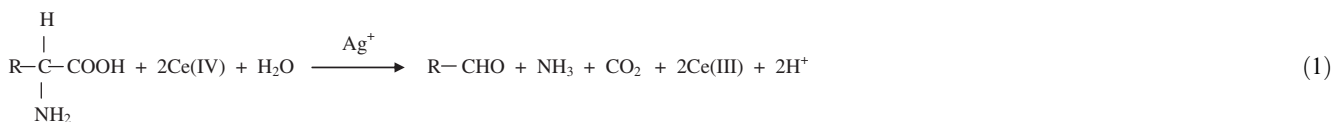


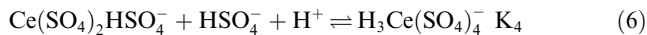
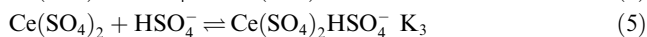
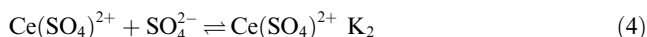
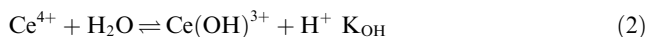
Figure 5 Eyring's plot shows the linear plot of $5 + \log k_2 / T$ vs $1/T \times 10^{-3}$. From Eyring's plot the value of $\Delta S^\ddagger$, $\Delta H^\ddagger$, $\Delta G^\ddagger$ is computed.



aldehyde can be represented by the Eq. (1). Further work on other related amino acids with Ce(IV) is in progress.

4. Discussion

Ce(IV) is known to form several complexes in sulfuric acid–sulfate media such as $\text{Ce}(\text{SO}_4)_4^{2+}$, $\text{Ce}(\text{SO}_4)_2$, $\text{Ce}(\text{SO}_4)_2\text{HSO}_4^-$, and $\text{H}_3\text{Ce}(\text{SO}_4)_4^-$ as shown in equilibria (2)–(6) (Chimatadar Shivamurti et al., 2007; Hardwick and Robertson, 1951; Duke and Parchen, 1956; Hintz and Johnson, 1967; Dayal and Bakore, 1972; Hanna and Sarac, 1977).



The $\text{Ce}(\text{OH})^{3+}$ species may also be present in these solutions and their concentrations varied with acidity. The total Ce(IV) concentration is the sum of different Ce(IV) species concentrations, $[\text{Ce}^{4+}]$, $[\text{Ce}(\text{OH})^{3+}]$, $[\text{Ce}(\text{SO}_4)^{2+}]$, $[\text{Ce}(\text{SO}_4)_2^{2+}]$, $[\text{Ce}(\text{SO}_4)_2\text{HSO}_4^-]$, and $[\text{H}_3\text{Ce}(\text{SO}_4)_4^-]$, the complexes having the cumulative equilibrium constants, K_{OH} , β_1 , β_2 , β_3 , and β_4 as shown in Eq. (7):

$$\begin{aligned} [\text{Ce}^{4+}]_{\text{T}} = [\text{Ce}^{4+}]_{\text{F}} & \left\{ 1 + \frac{K_{\text{OH}}}{[\text{H}^+]} + \beta_1 [\text{SO}_4^{2-}] + \beta_2 [\text{SO}_4^{2-}]^2 \right. \\ & \left. + \beta_3 [\text{SO}_4^{2-}]^2 [\text{HSO}_4^-] + \beta_4 [\text{SO}_4^{2-}]^2 [\text{HSO}_4^-] + [\text{H}^+] \right\} \quad (7) \end{aligned}$$

where, $K_{\text{OH}} = 15$, $\beta_1 = K_1 = 3.85 \times 10^2$, $\beta_2 = K_1 K_2 = 1.69 \times 10^2$, $\beta_3 = K_1 K_2 K_3 = 1.01 \times 10^2$, and $\beta_4 = K_1 K_2 K_3 K_4 = 2.03 \times 10^2$. The approximate concentrations of cerium sulfate complexes can be calculated from the concentrations of dissolved Ce^{4+} , H^+ , HSO_4^- , and SO_4^{2-} from the equilibria and their constants (Usha et al., 1977; Gopalkrishnan and Hogg, 1985). The formation of $\text{Ce}(\text{OH})^{3+}$ occurs at a much smaller extent in comparison with the others and is therefore neglected. The results of such calculation show that there is no such involvement of sulfato–Ce(IV) complexes. This has been further confirmed by studying the effects of SO_4^{2-} and HSO_4^- (Table 4). The negligible effects of SO_4^{2-} and HSO_4^- indicate the absence of the involvement of sulfato–Ce(IV) complexes as the reactive species. Since the rate increases with increasing hydrogen ion concentration (Table 3), Ce^{4+} should be more reactive species than sulfato–Ce(IV) complexes form (Laidler, 1965; Indu Sharma et al., 1995; Hardwick and Robertson, 1951). In the range of $[\text{H}^+]$ (0.05 mol dm^{-3}) used in this work, Ce^{4+} predominated whereas sulfato–Ce(IV) complexes are negligible. Further (Laidler, 1965; Indu Sharma et al., 1995; Rao et al., 1978; Asim and Das., 2001; Anis, 1992; Hiremath et al., 2007; Chimatadar Shivamurti et al.,

2007; Hardwick and Robertson, 1951), the rate increases with increase in $[\text{H}^+]$ (Table 3) and this confirms that the reactive Ce(IV) species in this reaction is Ce^{4+} (Laidler, 1965; Hardwick and Robertson, 1951). If the concentration of the monomeric cerium (IV) species is calculated only by employing dimerization constant negating the presence of polymeric forms, a quantitative approach to analyze the kinetic data is more successful. Since the dimerization constant is known (Lowrier and Steemers, 1976), the same can be employed to calculate the concentration of monomeric cerium (IV) species.

Even though, 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 (Arun Prakash et al., 1988), in this paper it is considered as a neutral molecule. This was confirmed by the negligible influence of ionic strength on the reaction rate and also the rate of the reaction decreases with decrease in dielectric constant of the medium which indicates that the transition state involves a more polar activated complex than the reactants.

Since it is well established that Ag^+ forms adducts (Usha et al., 1977) with the oxygen containing compounds with the lone pair of electrons on the oxygen atom (Chimatador et al., 2002; Pullin and Pollock, 1958), the probability of formation of an adduct between Ag^+ and alanine in a fast equilibrium preceded by the rate-limiting interaction of adduct with cerium (IV) can be assumed. Such an interaction in the rate-limiting step yields Ag^+ –alanine adduct as it is confirmed spectrophotometrically by the addition of 2,2'-bipyridyl in the reaction mixture that yielded a brown orange colored Ag^+ –bipyridyl complex with its characteristic absorption maximum at 454 nm (Miller, 1978). Thus considering the first order with respect to cerium (IV) and alanine for each, the following reaction mechanism consisting of steps (8)–(13) can be proposed. Plot of $1/k'$ vs. $1/[\text{L-alanine}]$ was linear (Fig. 6) with a non zero

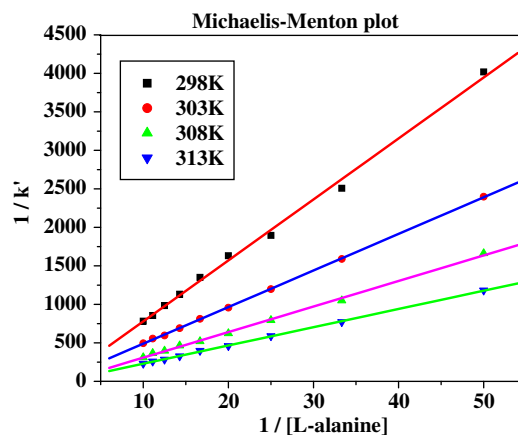


Figure 6 The linear plot of $1/k'$ Vs $1/[\text{L-alanine}]$ with non zero intercept confirms the complex between $\text{Ag}(\text{I})$ and L-alanine in a first step. This shows Michaelis–Menton type of relationship.

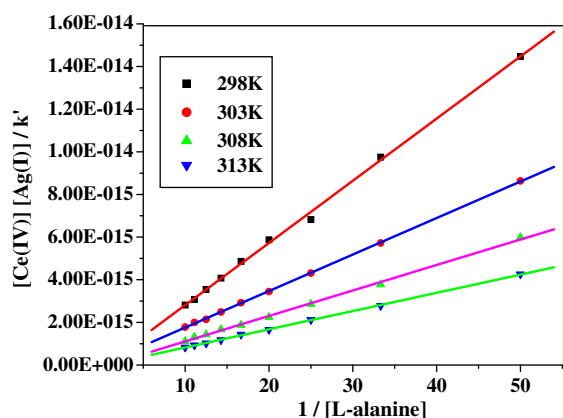


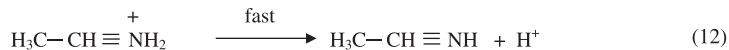
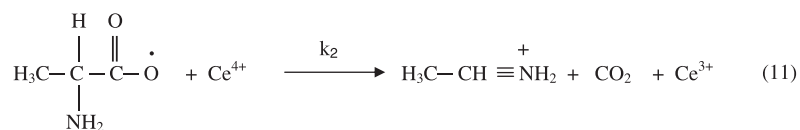
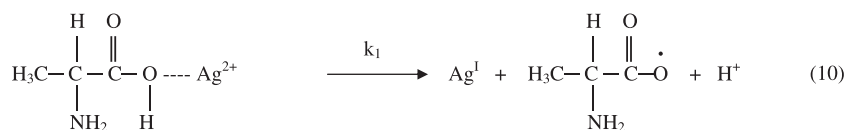
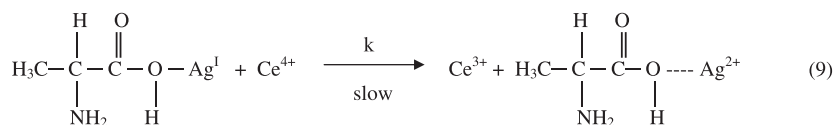
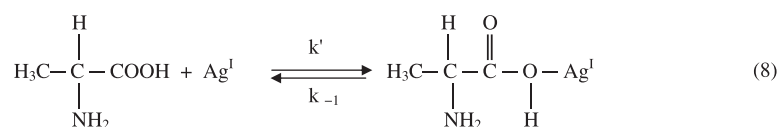
Figure 7 The linear plot of $[Ce(IV)][Ag(I)]/k'$ vs $1/[L\text{-alanine}]$ with non-zero intercept confirms the formation of the complex between $Ag(I)$ and $L\text{-alanine}$ in a first step.

intercept confirms the complex between $Ag(I)$ and $L\text{-alanine}$ in first step. This shows Michaelis–Menton type of relationship. The formation of the complex was also proved kinetically by a non zero intercept of the plot of $[Ce(IV)][Ag(I)]/k'$ vs. $1/[L\text{-alanine}]$ (Fig. 7). Such a complex formation has been observed already in the literature (Usha et al., 1977; Hiremath et al., 2007; Hintz and Johnson, 1967). The rate constant, k of the slow step of Scheme 1 was obtained from (intercept)/(slope) of the plot of $[Ce(IV)][Ag(I)]/k'$ vs. $1/[L\text{-alanine}]$ at four different temperatures. The energy of activation was obtained by the plot of $\log k_2$ vs. $1/T$ Arrhenius plot (Fig. 4) from which the activation parameters were calculated (Table 7). The thermodynamic quantities were calculated by using Eyring's plot (Fig. 5) and are given in (Table 7).

Considering these facts along with the experimental results and the complex hydrogen ion dependence, a reaction mechanism consisting of steps (8)–(13) can be proposed.

Based on the kinetic data a probable mechanism may be suggested as in Scheme 1.

So far as the transfer of electron from the substrate to the oxidant is concerned, the detailed analytical mode of the reaction events can be given as in Scheme 1. Since the pK' s of amino acids generally vary from 2.1 ± 0.3 to 9.6 ± 0.7 , the presence of alkyl group at the α -carbon hardly influences either amino or carboxyl groups. The hydrocarbon portion of the amino acid does not undergo any chemical reaction obviously owing to the highly reactive functional groups. The imine intermediate involves the cleavage of the bond between the α -carbon and the carboxylic carbon. However, there are two distinct possibilities of the intermediate imine undergoing reactions to the final products, either by reacting with water or by an interaction of imine with the oxidizing species taking place. Of these, the reaction with water is an acid-catalyzed reaction. Since the acid catalysis has been observed in the title reaction, the hydrolysis of imine appears to be the most predominant path. Imines of the type $RCH=NH$ with hydrogen attached to the nitrogen have been identified spectrophotometrically (McLeod and Crowell, 1961); these cannot be isolated owing to their fast decomposition (Sachs and Steinert, 1964). Moreover, the reaction has been carried out in sufficiently high hydrogen ion concentrations, the interaction of electron deficient metal ion with the protonated amino group cannot be considered to be a sound proposition. Hence $Ce(IV)$ attacks carboxyl group instead of amino group. The color reaction (Soloway and Lipschitz, 1952) for the presence of nitrile in the reaction mixture was done by adding hydroxylamine and ferric chloride; this test, however, confirmed its absence and ruled out any further interaction of the imine $R-CH=NH$



Scheme 1

with cerium (IV). Thus the hydrolytic decomposition of imine rather than interaction of cerium (IV) becomes important reaction events yielding aldehyde to be the oxidation product of the amino acid.

The rate expression may thus be represented by Eq. (15).

$$\frac{d\Sigma[\text{Ce(IV)}]}{dt} = \frac{k'kk_1k_2[\text{Ce(IV)}][\text{alanine}][\text{H}^+][\text{Ag}^+]}{k_{-1} + k_2} \quad (14)$$

If $k_2 \gg k_{-1}$, then

$$\text{Rate} = K[\text{Ce(IV)}][\text{alanine}][\text{H}^+][\text{Ag}^+] \quad (15)$$

where, $K = k'kk_1$

The rate expression is quite consistent with kinetic results, which are discussed above. The plausible scheme of electron transfer reactions may be represented as Scheme 1. A similar mechanism has been already reported in the literature (McLeod and Crowell, 1961; Devra, 2005).

5. Conclusion

The reaction between cerium (IV) and L-alanine is sluggish in sulfuric acid medium at 298 K. The reaction occurs with a measurable velocity in the presence of a small amount of (10^{-6} mol dm $^{-3}$) of silver. The main active species of cerium (IV) is considered as Ce^{4+} , although other species might be active to a much lesser extent. The role of hydrogen ions is crucial to the reaction. The description of the mechanism is consistent with all experimental evidences.

References

- Anis, S.S., 1992. J. Chim. Phy. Phys.-Chim. Biol. 89, 659.
- Arun Prakash, Dwivedi, P., Srivastava, M.N., Saxena, B.B.L., 1988. Nat. Acad. Sci. Letters II(4), 109.
- Asim, K. Das., Coord. Chem. Rev. 213(1) (2001) 307, 310.
- Beg, Kamaluddin, M.A., 1975. Indian J. Chem. 13, 1167.
- Bugaenko, L.T., Huang, K.L., 1963. Russ. J. Inorg. Chem. 8, 1299.
- Chappelle, E.W., Luck, J.M., 1957. Biol. Chem. 171, 229.
- Chimatadar, S.A., Koujalagi, S.B., Nandibewoor, S.T., 2001. Trans. Met. Chem. 26, 241.
- Chimatadar, S.A., Basavaraj, T., Nandibewoor, S.T., 2002. Inorg. React. Mech. 4, 209.
- Shivamurti, A. Chimatadar, Shankar, V. Madawale, Sharanappa, T. Nandibewoor, 2007. Trans. Met. Chem., 634–641.
- Chimatador, S.A., Basavaraj, T., Nandibewoor, S.T., 2002. Inorg. React. Mech. 4, 209.
- Chitamatador, S.A., Koujalagi, S.B., Nandibewoor, S.T., 2001. Trans. Met. Chem. 26, 662.
- Day, M.C., Selbin, J., 1964. Theoretical Inorganic Chemistry. Reinhold Publishing Corporation, New York, p. 226.
- Dayal, R., Bakore, G.V., 1972. Indian J. Chem. 10, 1165.
- Devra, Vijay, 2005. J. Indian Chem. Soc. 82, 290–294.
- Duke, F.R., Parchen, F.R., 1956. J. Am. Chem. Soc. 78, 1540.
- Gopalkrishnan, G., Hogg, J.L., 1985. J. Org. Chem. 50, 1206.
- Grant, D., 1964. J. Inorg. Nucl. Chem. 26, 337.
- Guilbault, G.G., McCurdy Jr., W.H., 1963. J. Phys. Chem. 67, 283.
- Hanna, S.B., Sarac, S.A., 1977. Inorg. Chem. 42, 2063.
- Hardwick, T.J., Robertson, E., 1951. Can. J. Chem. 29, 828.
- Heidt, L.J., Smith, M.E., 1948. J. Am. Chem. Soc. 70, 2476.
- Hintz, H.L., Johnson, D.C., 1967. J. Org. Chem. 32, 556.
- Hiremath, R.C., Mayanna, S.M., Venkatasubramanian, N., 1987. J. Chem. Soc., Perkin Trans. II, 1569.
- Hiremath, C.V., Kiran, T.S., Nandibewoor, S.T., 2006. J. Mol. Catal. A: Chem. 248, 163.
- Hiremath, D.C., Kiran, T.S., Nandibewoor, S.T., 2007. Int. J. Chem. Kinet. 39, 1.
- Jeffery, G.H., Bassett, J., Mendham, J., Denney, R.C., 1996. Vogel's Text book of Quantitative Chemical Analysis, fifth ed., ELBS, Longman, Essex, England, pp. 381, 195.
- Kharzeeva, S.E., Serebrennikov, V.V., 1967. Russ. J. Inorg. Chem. 12, 1601.
- Kolp, D., Thomas, H.C., 1949. J. Am. Chem. Soc. 71, 3047.
- Konigsberg, N., Stevenson, G.W., Luck, J.M., 1961. J. Biol. Chem. 236, 715.
- Krishna, B., Sinha, B.P., 1959. J. Phys. Chem. 212, 149, 155.
- Laidler, K.J., 1965. Chemical Kinetics. Tata-McGraw Hill, New Delhi, p. 229.
- Lowrier, K.P., Steemers, T., 1976. Inorg. Nucl. Chem. Lett. 12, 185.
- Mahadevappa, D.S., Rangappa, K.S., Gowda, N.M.M., 1981. J. Phys. Chem. 85, 3651.
- McLeod, R.K., Crowell, T.I., 1961. J. Org. Chem. 26, 1094.
- Miller, J.D., 1978. J. Chem. Soc. (A), 1968.
- Pullin, A.D.E., Pollock, J.M.C., 1958. Trans. Faraday Soc. 54, 11.
- Ramachandran, M.S., Vivekanandan, T.S., 1984. J. Chem. Soc., Perkin Trans. 2, 1341.
- Rao, M.A., Adinarayana, M., Sethuram, B., Rao, T.N., 1978. Indian J. Chem., Sect A 16, 440.
- Sachs, F., Steinert, P., 1964. Chem. Ber. 37, 1733.
- Schonberg, A., Maubasher, R., Bardkat, M.Z., 1951. J. Chem. Soc., 1529.
- Ambika Shanmugam, Fundamentals of Biochemistry for Medical students, seventh ed., Madras 600 035.
- Indu Sharma, Vijai, Devra, Divya, Gupta, Gangwas, C.M., Sharma, P.D., 1995. Int. J. Chem. Kinet. 27, 311–319.
- Soloway, S., Lipschitz, A., 1952. Anal. Chem. 24, 898.
- Thabaj, K.A., Chimatadar, S.A., Nandibewoor, S.T., 2006. Trans. Met. Chem. 31, 186.
- Upadhyay, S.K., Agrawal, M.C., 1977. Indian J. Chem. 15 (A), 416.
- Usha, A.V., Sethuram, B., Rao, T.N., 1977. Indian J. Chem. 15 (A), 528.
- Walden Jr., G.H., Hammett, L.P., Chapman, R.P., 1933. J. Am. Chem. Soc. 55, 2649.
- Yatsimirskii, K.B., Luzan, A.A., 1965. Zh. Neorg. Khim. 10, 2268.