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A kinetic and mechanistic study on the oxidation of L-methionine and N-acetyl L-methionine by cerium(IV) in sulfuric acid medium



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KEYWORDS

Kinetics; Oxidation; L-Met; L-Acetyl L-met; Ce(IV); H₂SO₄ medium **Abstract** The kinetics of oxidation of L-methionine and N-acetyl L-methionine by Ce(IV) in sulfuric acid–sulfate media in the range of 288.1–298.1 K has been investigated. The major oxidation products of methionine and N-acetyl L-methionine have been identified as methionine sulfoxide and N-acetyl methionine sulfoxide. The major oxidation products have been confirmed by qualitative analysis and boiling point. The reaction was first order with respect to L-methionine, N-acetyl L-methionine and Ce(IV). Increase in [H⁺], ionic strength and HSO₄⁻ did not affect the reaction rate. Under the experimental conditions, Ce⁴⁺ was the effective oxidizing species of cerium. Increase in dielectric constant of the medium decreased the reaction rate. Under nitrogen atmosphere, the reaction system can initiate polymerization of acrylonitrile, indicating the generation of free radicals. Activation parameters associated with the overall reaction have been calculated. (© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).

1. Introduction

The oxidation of amino acids is of utmost importance from a chemical point of view due to its bearing on the mechanism of

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amino acid metabolism. 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)₆^{3–} (Upadhyay and Agrawal, 1977), chloramine-T (Mahadevappa et al., 1981), 1-chlorobenzotriazole (Hiremath et al., 1987), and *N*-bromosuccinimide (Gopalkrishnan and Hogg, 1985; Schonberg et al., 1951; Chappelle and Luck, 1957; Konigsberg et al., 1961) in acid and alkaline media has been reported. The oxidation of biologically important amino acid methionine and *N*-acetyl L-methionine is very important because it may reveal the mechanism of amino acid metabolism. This oxidation has received much attention because it helps the body process and eliminate fat and is required to produce cysteine

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and taurine, which help eliminate toxins and build strong, healthy tissues, including muscle tissues. It also promotes cardiovascular health. The body uses methionine and *N*-acetyl L-methionine to manufacture creatine and use the sulfur in methionine and *N*-acetyl L-methionine for normal metabolism and growth (Ambika Shanmugam, 1996). Many amino acid residues of proteins are susceptible to oxidation by various forms of reactive oxygen species (ROS), and that oxidatively modified proteins accumulate during aging, oxidative stress, and in a number of age-related diseases. Methionine residues and cysteine residues of proteins are particularly sensitive to oxidation by ROS (Stadtman et al., 2005).

Ce(IV) is a well known oxidant (Thabaj et al., 2006; Chimatadar et al., 2002, 2001) 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 compound by Ce(IV) in general seems to proceed via the formation of intermediate complexes (Yatsimiraskii and Luzan, 1965; Guilbault and McCurdy, 1963).

In sulfuric acid and sulfate media, several sulfate complexes (Thabaj et al., 2006; Chimatadar et al., 2002, 2001; Kharzeeva and Serebrennikov, 1967; Bugaenko and Huang, 1963) of Ce(IV) exist such as $Ce(OH)^{3+}$, $Ce(SO)^{2+}_4$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^-$ and $H_3Ce(SO_4)_4^-$, but their roles have not received much attention so far. The mechanism may be quite complicated due to the formation of different Ce(IV) complexes in the form of active species. Hence, the present investigation, the oxidation of L-methionine and *N*-acetyl L-methionine by Ce(IV), 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

Double distilled water was used for preparing the solutions. L-methionine and N-acetyl L-methionine (SRL) were used as such. Stock aqueous solutions of L-methionine and N-acetyl L-methionine were 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 standardized with iron(II) ammonium sulfate solution (Jeffery et al., 1996). Other chemicals and reagents, such as sodium sulfate, 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 sulfuric acid medium in the temperature range (288.1-298.1 K) under pseudo first order conditions with a large excess of L-methionine and *N*-acetyl L-methionine 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 an indicator (Walden et al., 1933).

No precautions were taken to exclude the diffused light entering into the reaction mixture (Krishna and Sinha, 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 titration values, plots of log [Ce(IV)] vs. time were made and from the slope of such plots, the pseudo first order rate constants k^1 (s⁻¹) were obtained. All the first order plots were linear, with a correlation coefficient of 0.996–0.999. The results were reproducible within an accuracy of $\pm 5\%$

3. Results

3.1. Effect of [L-methionine] and N-acetyl L-methionine

At a constant [Ce(IV)] $(8 \times 10^{-3} \text{ mol dm}^{-3})$, [H⁺] $(5 \times 10^{-2} \text{ mol dm}^{-3})$ and [Na₂SO₄] $(1 \times 10^{-1} \text{ mol dm}^{-3})$ the kinetic runs were carried out with various $(1-10 \times 10^{-2} \text{ mol dm}^{-3})$ concentrations of L-methionine and N-acetyl L-methionine which yielded rate constants whose values depended on [L-methionine] and [N-acetyl L-methionine]. The pseudo first order rate constants k^1 (s⁻¹) thus obtained were found to

Table 1 Effect of concentration of L-methionine and N-Acetyl L-methionine and Ce(IV) on the pseudo-first-rate constant k^1 and second order rate constant k_2 .

[Substrates]	L-Met $k^1 \times 10^3 \text{ s}^{-1}$		L-Met $k_2 \times 10^1 \pmod{\mathrm{dm}^{-3} \mathrm{s}^{-1}}$		<i>N</i> -A-L-Met $k^1 \times 10^3 \text{ s}^{-1}$		<i>N</i> -A-L-Met $k_2 \times 10^1 \pmod{\text{dm}^{-3} \text{s}^{-1}}$					
$ \times 10^{2} $ (mol dm ⁻³)	288.1 K	293.1 K	298.1 K	288.1 K	293.1 K	298.1 K	277.7 K	282.7 K	287.7 K	277.7 K	282.7 K	287.7 K
1	1.022	1.656	2.479	1.022	1.656	2.479	0.909	1.584	2.499	0.9090	1.584	2.499
2	2.049	3.296	4.956	1.024	1.646	2.478	1.827	3.170	5.000	0.9137	1.585	2.500
3	3.039	4.928	7.467	1.013	1.642	2.489	2.739	4.755	7.499	0.9132	1.585	2.499
4	4.044	6.632	9.840	1.011	1.658	2.460	3.693	6.337	10.10	0.9234	1.584	2.500
5	5.100	8.138	12.37	1.020	1.662	2.475	4.578	7.917	12.56	0.9156	1.583	2.512
6	6.100	10.96	15.00	1.017	1.715	2.501	5.373	9.323	15.26	0.8955	1.553	2.543
7	7.044	12.00	17.66	1.000	1.714	2.522	6.526	11.20	17.19	0.9322	1.600	2.456
8	8.094	13.00	19.96	1.011	1.625	2.495	7.230	12.76	20.44	0.9037	1.595	2.555
9	9.022	14.85	22.90	1.024	1.654	2.544	8.307	14.39	22.09	0.9230	1.599	2.454
10	10.20	16.52	24.54	1.020	1.652	2.454	9.302	15.85	25.10	0.9302	1.585	2.510

Effect of concentration of L-methionine, N-acetyl L-methionine and Ce(IV) on the pseudo first order rate constant k^1 and second order rate constant k_2 substrates = L-met and N-A-L-Met [H⁺] = 5×10^{-2} mol dm⁻³, [Ce(IV)] = 8×10^{-3} mol dm⁻³, [μ] - [Na₂SO₄] = 1×10^{-1} mol dm⁻³.

increase with [L-methionine] and [N-acetyl L-methionine] (Table 1). This shows that the reaction obeys first order with respect to [L-methionine] and [N-acetyl L-methionine]. This was confirmed by the linear plots of k^1 (s⁻¹) vs. [L-methionine] Fig. 1a and [N-acetyl L-methionine] Fig. 1b.

The values of $k_2 \pmod{\text{dm}^{-3} \text{s}^{-1}}$ was evaluated from the slope of $k^1 \pmod{\text{s}^{-1}}$ vs. [L-methionine] (Fig. 1a) and [N-acetyl L-methionine] plots (Fig. 1b) The $k_2 \pmod{\text{dm}^{-3} \text{s}^{-1}}$ values thus obtained from such plots were in agreement with the



Figure 1a Shows the linear plot of k' (s⁻¹) vs. [L-methionine] confirms the first order reaction with respect to [L-methionine].



Figure 1b Shows the linear plot of k' (s⁻¹) vs. [*N*-acetyl L-methionine] confirms the first order reaction with respect to [*N*-acetyl L-methionine].

corresponding values calculated from the factor $k^1 (s^{-1})/[L-methionine]$ and [N-acetyl L-methionine] (Table 2).

3.2. Effect of [Ce(IV)]

The reaction rate was measured at constant [L-methionine] and [N-acetyl L-methionine] (Table 3). $2 \times 10^{-2} \text{ mol dm}^{-3}$, [H⁺] $5 \times 10^{-2} \text{ mol dm}^{-3}$ and $\text{Na}_2\text{SO}_4 \ 1 \times 10^{-1} \text{ mol dm}^{-3}$ but with various [Ce(IV)] (5–14×10⁻³ mol dm⁻³). The pseudo first order rate constants k^1 were found to be independent of [Ce(IV)], confirmed the first order dependence of rate on [Ce(IV)]. The log[Ce(IV)]_T was plotted against 't', very good straight line plots were obtained indicating that the reaction was first order with respect to [Ce(IV)].

3.3. Effect of $[H^+]$

The reaction rates were measured at constant [L-methionine] and [N-acetyl L-methionine] $(2.0 \times 10^{-2} \text{ mol } \text{dm}^{-3})$, [Ce(IV)] $(8.0 \times 10^{-3} \text{ mol } \text{dm}^{-3})$ and $[Na_2SO_4]$ $(1 \times 10^{-1} \text{ mol } \text{dm}^{-3})$ but with various [H⁺] (4–11.0 × 10⁻² mol dm⁻³) (Table 4). The insignificant rate variations with [H⁺] shows the absence of Ce(SO₄)₂HSO₄⁻ and H₃Ce(SO₄)₄⁻.

3.4. Effect of [ionic strength]

The influence of ionic strength on the reaction rate was maintained by the addition of sodium sulfate on the reaction rate. It was observed that the rate was not influenced by the ionic strength (Table 5).

Table 3	Effect of concentration of Ce(IV) on the pseudo-first-
rate cons	tant k^1 .

$[Ce(IV)] \times 10^{3}$ (mol dm ⁻³)	L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 293.1 K	<i>N</i> -A-L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 282.7 K
5	3.3854	3.1623
6	3.5696	3.1723
7	3.6848	3.1712
8	3.2960	3.1708
9	3.2856	3.2222
10	3.6926	3.1234
11	3.7829	3.2132
12	3.8234	3.1623
13	3.2354	3.2856
14	3.3150	3.2823
Oxidant v strates $l = 2 \times 1$	ariation $[H^+] = 5 \times 0^{-2} \text{ mol dm}^{-3} [\mu] - [Nas]$	$10^{-2} \text{ mol dm}^{-3}$, [sub- SQ ₄] = 1 × 10 ⁻¹ mol dm ⁻³

Table 2 Comparison of graphically calculated value of k_2 and experimentally calculated value of k_2 .

Temp. K L-met	$k_2 \times 10^1 \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ Graphical	$k_2 \times 10^1 \pmod{\mathrm{dm}^{-3} \mathrm{s}^{-1}}$ Calculated	Temp. K N-A-L-Met	$k_2 \times 10^1 \pmod{\mathrm{dm}^{-3} \mathrm{s}^{-1}}$ Graphical	$k_2 \times 10^1 \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$ Calculated
288.1	1.0109	1.0162	277.7	0.9233	0.9159
293.1	1.6633	1.6624	282.7	1.5920	1.5853
298.1	2.4995	2.4897	287.7	2.4975	2.5028

Table 4 Effect of concentration of H^+ on the pseudo first order rate constant k^1 .

L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 293.1 K	<i>N</i> -A-L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 282.7 K
3.6848	3.1687
3.2960	3.1708
3.5235	3.1578
3.5697	3.1632
3.5780	3.1723
3.5696	3.2222
3.6927	3.1712
3.5234	3.1708
3.2354	3.2856
	L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 293.1 K 3.6848 3.2960 3.5235 3.5697 3.5780 3.5696 3.6927 3.5234 3.2354

[Substrates] = 2×10^{-2} mol dm⁻³, [Ce(IV)] = 8×10^{-3} mol dm⁻³, [Na₂SO₄] = 1×10^{-1} mol dm⁻³.

Table 5 Effect of ionic strength, μ on the pseudo first order rate constant k^1 .

[Na ₂ SO ₄], [K ₂ SO ₄], [HSO ₄ ⁻] × 10 ¹ (mol dm ⁻³)	L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 293.1 K	N-A-L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 282.7 K
1	3.2960	3.1708
2	3.6848	3.1082
3	3.2523	3.1257
4	3.5703	3.1326
5	3.5870	3.1237
6	3.5962	3.2222
7	3.6297	3.1171
8	3.5324	3.1087
9	3.2345	3.2568
10	3.3215	3.2832
[Substrates] = 2×10^{-2} m [H ⁺] = 5×10^{-2} mol dm	n^{-3} , [Ce(IV)] = n^{-3} .	$8 \times 10^{-3} \text{ mol dm}^{-3}$,

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

Concentration of $[\text{HSO}_4^-]$ (KHSO₄) and SO₄⁻² (K₂SO₄) were varied in the range of $(1-8 \times 10^{-1} \ 0.8 \ \text{mol} \ \text{dm}^{-3})$ at fixed [substrate] $(2.0 \times 10^{-2} \ \text{mol} \ \text{dm}^{-3})$, [Ce(IV)] $(8.0 \times 10^{-3} \ \text{mol} \ \text{dm}^{-3})$ and $[\text{H}^+]$ ($5 \times 10^{-2} \ 0.05 \ \text{mol} \ \text{dm}^{-3}$). It was observed that the rate was not influenced by the increasing concentration of SO₄⁻² and HSO₄⁻ (Table 5) confirming that the reaction occurs between an ion Ce⁴⁺ and a neutral molecule (substrate) (Laidler, 1965).

3.6. Effect of dielectric constant

In order to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of substrates by Ce(IV) was studied in acetonitrile as well as acetone mixtures of various compositions (Table 6). The data clearly reveals that the rate decreased with an increase in acetonitrile and acetone contents 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 (Sharma et al., 1995). The reaction is between a neutral molecule (substrate) and an ion (Ce⁴⁺) and the absence of ion–ion or dipole–dipole type mechanism which is also supported by the negative $\Delta S^{\#}$ values obtained in this work.

Table 6	Effect of dielectric constant on the pseudo first o	rder
rate cons	ant k^1	

Aceto nitrile (%) (V/V)	Acetone (%) (<i>V</i> / <i>V</i>)	L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 293.1 K	N-A-L-Met $(k^1 \times 10^3 \text{ s}^{-1})$ 282.7 K
35	-	2.6945	4.8593
40	-	2.4642	4.1684
45	-	1.4076	3.8690
50	-	1.1380	3.1781
_	35	2.5794	4.3757
-	40	1.9950	3.8690
-	45	1.8923	3.2933
-	50	1.6059	2.8327
$[Substrates] = [H^+] = 5 \times 10^{-1}$	$2 \times 10^{-2} \text{ mol dm}^{-2}$ mol dm ⁻³ , [Na	$^{-3}$, [Ce(IV)] = 8 × a_2 SO ₄] = 1×10 ⁻¹ m	$10^{-3} \text{ mol dm}^{-3},$ ol dm $^{-3}$.

3.7. Test for free radical intermediates

The intervention of free radicals was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 2 h. Upon diluting the reaction mixture with methanol, white precipitate has been formed, indicating the presence of free radical intervention in the reaction.

3.8. Rate and activation parameters

The effect of temperature on k^1 (s⁻¹) was studied in the range (288.1–298.1 K) for L-methionine and (277.7–287.7 K) for *N*-acetyl L-methionine, (Table 1) and the results were shown in Table 7. From Arrhenius plot, for L-methionine (Fig. 2(a)) and *N*-acetyl L-methionine, (Fig. 2(b)) the value of energy of activation (Ea) was calculated. Hence, the values of $\Delta S^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$ (Table 7) were computed from the Eyring's plot for L-methionine (Fig. 3(a)) and *N*-acetyl L-methionine, (Fig. 3(b)). The large negative value of entropy of activation ($\Delta S^{\#}$) obtained 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).

3.9. Stoichiometry and product analysis

Different reaction mixtures with different sets of concentration of reactants, where [Ce(IV)] was in excess over [substrate] at constant ionic strength and acidity were kept for 24 h at 293 K in an inert atmosphere. The unreacted Ce(IV) was titrated against standard ferrous ammonium sulfate by using ferroin as an indicator. The results indicated that 2 mol of Ce(IV) was consumed by 1 mol of substrate, (i.e. 2:1) according to Eq. (1).

The main reaction products are Ce(III) and methionine sulfoxide, *N*-acetyl methionine sulfoxide. Sulfoxides of the

Table 7 Act	ivation para	meters.		
Substrate	<i>E</i> a (KJ mol ⁻¹)	$\frac{\Delta H^{\#}}{(\text{KJ mol}^{-1})}$	$\frac{\Delta S^{\#}}{(\text{KJ mol}^{-1})}$	$\Delta G^{\#}$ (KJ mol ⁻¹)
L-Methionine N-Acetyl L-methionine	61.0845 66.8568	63.5213 64.5065	-51.556 -31.875	76.195 73.517



Figure 2 (a) Arrhenius plot for L-methionine). (b) Arrhenius plot for *N*-Acetyl L-methionine shows the linear plot of log k_2 vs. 1/T. From Arrhenius plot, energy of activation (*Ea*) is calculated.

substrates were confirmed by the following reactions. The reaction mixtures were allowed to stand for a few hours. Then, sodium bicarbonate was added and stirred vigorously, followed by a dropwise addition of benzoyl chloride solution. The precipitate *N*-benzoyl methionine sulfoxide was confirmed by its m.p. 183 °C (Goswami et al., 1981; Meenakshisundaram and Vinothini, 2003). The procedure is similar to the one employed in the oxidation of L-methionine by aqueous Cr(VI) (Olatunji and Ayoko, 1988). Further this has been confirmed by the acetone–ethanol mixture resulted in the precipitate of methionine sulfoxide, which was identified by its m.p. 238 °C.

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

MeSR + 2Ce(IV) + H₂O
$$\longrightarrow$$
 MeSR + 2Ce(III) + 2H⁺

$$\begin{array}{ccc} & & & & \\ & & & \\ & & & \\ H^{2} & & & \\ & & & \\ & & & \\ \end{array}$$
Where R=-CH₂-CH₂-CH-COOH, -CH₂-CH₂-CH-COOH (1)



Figure 3 (a) Eyring's plot for L-methionine) and (b) Eyring's plot for *N*-acetyl L-methionine shows the linear plot of $5 + \log k_2/T$ vs. $1/T \times 10^{-3}$. From Eyring's plot the value of $\Delta S\#$, $\Delta H\#$, $\Delta G\#$ is computed.

4. Discussion

Ce(IV) is known to form several complexes in sulfuric acid–sulfate media such as $Ce(SO)_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_2HSO_4^{-}$ and $H_3Ce(SO_4)_4^{-}$ as shown in Eqs. (2)–(6).(Chimatadar et al., 2007; Hardwick and Robertson, 1951; Duke and Parchen, 1956; Hintz and Johnson, 1967; Dayal and Bakore, 1972; Hanna and Sarac, 1977)

$Ce^{4+} + H_2O \rightleftharpoons Ce(OH)^{3+} + H^+$	$K_{\rm OH}$	(2))
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$$\operatorname{Ce}^{4+} + \operatorname{SO}_4^{2-} \rightleftharpoons \operatorname{Ce}(\operatorname{SO})_4^{2+} \qquad K_1 \qquad (3)$$

$$\operatorname{Ce}(\operatorname{SO}_4)^{2+} + \operatorname{SO}_4^{2-} \rightleftharpoons \operatorname{Ce}(\operatorname{SO}_4)_2 \qquad K_2 \qquad (4)$$

$$\operatorname{Ce}(\operatorname{SO}_4)_2 + \operatorname{HSO}_4^- \rightleftharpoons \operatorname{Ce}(\operatorname{SO}_4)_2 \operatorname{HSO}_4^- \qquad K_3 \qquad (5)$$

$$\operatorname{Ce}(\operatorname{SO}_4)_2\operatorname{HSO}_4^- + \operatorname{HSO}_4^- + \operatorname{H}^+ \rightleftharpoons \operatorname{H}_3\operatorname{Ce}(\operatorname{SO}_4)_4^- \quad K_4 \tag{6}$$

The Ce(OH)³⁺ species may also be present in these solutions and its concentrations varied with acidity. The total Ce(IV) concentration is the sum of different Ce(IV) species concentrations, $[Ce^{4+}]$, $[Ce(OH)^{3+}]$, $[Ce(SO_4)^{2+}]$, $[Ce(SO_4)_2]$, $[Ce(SO_4)_2]$ HSO₄⁻] and $[H_3Ce(SO_4)_4^{-}]$, the complexes having the cumulative equilibrium constants, K_{OH} , β_1 , β_2 , β_3 , and β_4 as shown in Eq. (7).

$$\begin{split} [\mathrm{Ce}^{4+}]_{T} &= [\mathrm{Ce}^{4+}]_{F} \bigg\{ 1 + \frac{K_{\mathrm{OH}}}{\mathrm{H}^{+}} \beta_{1} [\mathrm{SO}_{4}^{2-}] + \beta_{2} [\mathrm{SO}_{4}^{2-}]^{2} \\ &+ \beta_{3} [\mathrm{SO}_{4}^{2-}]^{2} [\mathrm{HSO}_{4}^{-}] + \beta_{4} [\mathrm{SO}_{4}^{2-}]^{2} [\mathrm{HSO}_{4}^{-}]^{2} \\ &+ [\mathrm{H}^{+}] \bigg\} \end{split}$$
(7)

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 (2)–(6). The formation of $Ce(OH)^{3+}$ occurs to 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 effect of SO_4^{2-} and HSO_4^{-} (Table 5). The negligible effect of SO_4^{2-} and HSO₄ indicates the absence of the involvement of sulfato-Ce(IV) complexes as the reactive species. The rate also increases with increase in hydrogen ion rate increases with increasing hydrogen ion concentration, Ce⁴⁺ should be a more reactive species than sulfato-Ce(IV) complexes (Sharma et al., 1995). In the range of $[H^+]$ (5 × 10⁻² mol dm⁻³) used in this work, Ce⁴⁺ predominate whereas sulfato-Ce(IV) complexes are negligible. Further, the negligible effect of rate with increase in [H⁺] (Table 4) confirms that the reactive Ce(IV) species in this reaction is Ce⁴⁺. If the concentration of the monomeric cerium(1 V) species is calculated only 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(1V) 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, (Prakash et al., 1988) in this paper it is considered as a neutral molecule. This was confirmed by the influence of ionic strength on the reaction rate which was found to be negligible and also the rate of the reaction decreases with decrease in dielectric constant of the medium which indicates a transition state involving a more polar activated complex than the reactants. The results indicate that first Ce(IV) reacts with substrate to give a complex, which then decomposes in a slow step to give a free radical derived from substrate and Ce(III). This free radical reacts with another molecule of Ce(IV) species in further fast step to yield the products shown in Scheme 1. A similar mechanism has been already reported in the literature (Bilehal et al., 2003).

Since Scheme 1 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in a sequence of one electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work (Kampli et al., 1990; Bilehal et al., 2003) on the acidic Ce(IV) oxidations of various organic substrates. The formation of complex is proved kinetically by the non-zero intercept of the plot of 1/k' vs. 1/[substrate] (Michaelis–Menten plot) (Fig. 4(a and b)). The formation of the complex was also proved kinetically by a non zero intercept of the plot of [Ce(IV)]/rate vs. 1/[substrate] (Fig. 5). Such complex formation has been observed already in the literature (Meenakshisundaram and Vinothini, 2003; Duke and Parchen, 1956). The rate constant, k of the slow step of Scheme 1 was obtained from the intercepts and slopes of the plot of $[Ce(IV)]/k^1$ vs. 1/[substrate] at three different temperatures.

Scheme 1 leads to the rate law given in Eq. (8)

$$Rate = -\frac{d[Ce(IV)]}{dt}$$

=
$$\frac{kK[Ce(IV)][substrate]}{(1 + K[substrate])(K[Ce(IV)] + K^{2}[Ce(IV)][substrate]}$$
(8)

 $K[Ce(IV)] + K^2[Ce(IV)][substrate] \ll 1 + K[substrate])(K[Ce(IV)])$

$$H_{3}C-S-CH_{2}-CH_{2}-CH_{2}-CH-COOH + Ce(IV) \xrightarrow{K} H_{3}C-S-CH_{2}-CH_{2}-CH_{2}-CH-COOH$$

$$H_{3}C-S-CH_{2}-CH_{2}-CH_{2}-CH-COOH \xrightarrow{k} H_{3}C-S, -CH_{2}-CH_{2}-CH-COOH + Ce(III)$$

$$H_{3}C-S, -CH_{2}-CH_{2}-CH_{2}-CH-COOH + Ce(IV) + H_{2}O \xrightarrow{h} H_{3}C-S, -CH_{2}-CH_{2}-CH_{2}-CH-COOH + Ce(III) + 2H^{+}$$

Where
$$R = H$$
, COCH₃

Scheme 1



Figure 4 (a and b) Shows the linear plot of 1/k vs. 1/[substrate].

Eq. (8) can be written as,

$$Rate = -\frac{d[Ce(IV)]}{dt} = \frac{kK[Ce(IV)][substrate]}{1 + K[substrate]}$$
(9)

Eq. (9) can be written as,

$$\frac{\text{Rate}}{[\text{Ce}(\text{IV})]} = k = \frac{kK[\text{Ce}(\text{IV})][\text{substrate}]}{1 + K[\text{substrate}]}$$
(10)

Eq. (10) can be rearranged to give Eq. (11) which is suitable for verification.

$$\frac{1}{k} = \frac{1}{kK[\text{substrate}]} + \frac{1}{k} \tag{11}$$

According to Eq. (11), plots of 1/k vs. 1/[substrate] should be linear. This is verified in Fig. 4(a and b). From the slope and intercept of such a plot the calculated values of K and k were $9.77 \text{ dm}^3 \text{ mol}^{-1}$, 1.39 s^{-1} at 288.1 K, respectively. Using these values in Eq. (10), rate constants were calculated over a range of different conditions and compared with the experimental values as given in Table 2. There is reasonable agreement between the calculated and experimental rate constants, supporting the assumption in Scheme 1. The negligible effect of ionic strength on the rate of equation qualitatively explains the reaction between a positive and neutral species as shown in Scheme 1. The negative value of $\Delta S^{\#}$ indicates the formation of complex in the reaction, and the complex is more ordered than



Figure 5 (a and b) Are the linear plot of [Ce(IV)]]/k' vs. 1/ [substrate] (L-methionine and *N*-acetyl L-methionine] with non-zero intercept confirms the formation of the complex between Ce(IV) and substrate in a first step.

the reactants (Weissberger, 1974; Kulkarni et al., 2002). The observed modest enthalpy of activation and higher rate constant of slow step indicate that the oxidation presumably occurs by an inner-sphere mechanism (Halligudi et al., 2001; Moore and Hicks, 1975; Hicks, 1976; Martinez et al., 1996).

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