



## Silver(I)-Catalyzed Oxidation of L-Leucine by Cerium(IV) in Sulfuric Acid Medium: A Kinetic and Mechanistic Study

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The kinetics of the Ag(I) catalyzed oxidation of L-leucine by cerium(IV) in H<sub>2</sub>SO<sub>4</sub> medium has been investigated at 323 K. The reaction was first order with respect to L-leucine, inverse order with respect to Ce(IV) and a positive fractional order with respect to Ag(I). Increase in [H<sup>+</sup>] decreased the reaction rate. The added SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> decreased the rate of the reaction. Under the experimental conditions, the kinetically active species of cerium has been found to be Ce(SO<sub>4</sub>)<sub>2</sub>. The major oxidation product of L-leucine has been identified as pentanaldehyde which is confirmed by the IR spectrum. Effects of bivalent and trivalent catalyst have also been studied. Under nitrogen atmosphere, the reaction system can initiate the polymerization of acrylonitrile, indicating the generation of free radicals. A suitable mechanism involving the formation of an intermediate complex with silver catalyst has been proposed.

**Key Words:** Kinetics, Oxidation, L-Leucine, Ag(I) catalyst, Ce(IV).

### INTRODUCTION

The oxidative decarboxylation of amino acids is important both from a pure photochemical viewpoint and also from the viewpoint of mechanism of amino acid metabolism. Metallic ions play a significant role in the oxidative decarboxylation of amino acids. However, our preliminary observations indicate that 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)<sup>1</sup>, Co(III)<sup>2</sup>, Os(VIII)-Fe(CN)<sub>6</sub><sup>3-3</sup>, chloramine-T<sup>4</sup>, 1-chlorobenzotriazole<sup>5</sup>, N-bromo-succinimide<sup>6,7</sup> and peroxomonosulfate (PMS)<sup>8</sup> in acid and alkaline media has been reported. L-leucine is an active site residue of enzymes and help in maintaining the correct conformation of enzymes by keeping it in its proper ionic states. Thus, oxidation of this may help in understanding enzyme kinetics. The oxidation of amino acids is of interest as the products differ depending on the oxidants<sup>9</sup>.

Ce(IV) is a well known oxidant<sup>10</sup> in acid media having the reduction potential<sup>11</sup> 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<sup>12</sup>.

The sluggish reaction of Ce(IV) oxidation of L-leucine is catalyzed by a small amount of Ag<sup>+</sup> (10<sup>-6</sup> mol dm<sup>-3</sup>) in aqueous sulfuric acid medium. In sulfuric acid and sulfate media, several sulfate complexes<sup>10,13</sup> of Ce(IV) form exists such as Ce(OH)<sup>3+</sup>, Ce(SO<sub>4</sub>)<sup>2+</sup>, Ce(SO<sub>4</sub>)<sub>2</sub>, Ce(SO<sub>4</sub>)<sub>2</sub>HSO<sub>4</sub><sup>-</sup> and H<sub>3</sub>Ce(SO<sub>4</sub>)<sub>4</sub><sup>-</sup>, 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-leucine 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-leucine (E.Merck) was used as such. A stock solution of L-leucine was prepared by dissolving it in 0.98 mol dm<sup>-3</sup> 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<sup>-3</sup> sulfuric acid and standardized with iron(II) ammonium sulfate solution<sup>14</sup>. Other chemicals and reagents such as sodium sulfate, silver nitrate, sulfuric acid, acetonitrile,

TABLE-1  
EFFECT OF CONCENTRATION OF L-LEUCINE AND Ce(IV) ON THE PSEUDO FIRST ORDER RATE CONSTANT  $k^1$  AND SECOND ORDER RATE CONSTANT  $k_2$ ;  $[H^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[Ag^+] = 2.0 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[Na_2SO_4] = 10 \times 10^{-2} \text{ mol dm}^{-3}$

[L-Leucine] $\times 10^2$ (mol dm <sup>-3</sup> )	[Ce(IV)] $\times 10^3$ (mol dm <sup>-3</sup> )	$k^1 \times 10^3$ (s <sup>-1</sup> )			$k_2 \times 10^2$ (mol dm <sup>-3</sup> s <sup>-1</sup> )		
		313 K	318 K	323 K	313 K	318 K	323 K
1.0	4.0	0.56	0.90	1.23	5.65	9.08	12.29
2.0	4.0	1.21	1.77	2.42	6.06	8.85	12.09
3.0	4.0	1.85	2.69	3.64	6.17	8.98	12.12
4.0	4.0	2.44	3.43	4.90	6.10	8.57	12.26
5.0	4.0	3.01	4.30	6.17	6.03	8.61	12.34
6.0	4.0	3.63	5.48	7.25	6.06	9.13	12.09
7.0	4.0	4.14	6.17	8.52	5.92	8.81	12.17
8.0	4.0	4.74	7.18	9.69	5.93	8.98	12.11
9.0	4.0	5.52	8.29	10.89	6.14	9.21	12.10
10.0	4.0	6.05	9.02	12.36	6.05	9.02	12.36
4.0	1.0	–	–	199.5	–	–	–
4.0	2.0	–	–	39.81	–	–	–
4.0	3.0	–	–	13.88	–	–	–
4.0	4.0	2.44	3.43	4.90	6.10	8.57	12.26
4.0	5.0	–	–	2.94	–	–	–
4.0	6.0	–	–	1.58	–	–	–
4.0	7.0	–	–	1.00	–	–	–
4.0	8.0	–	–	0.63	–	–	–

acetone, hydrated copper sulfate and aluminum sulfate used were of analytical grade with 99.9 % purity.

**Kinetic measurements:** Kinetic studies were carried out in sulfuric acid medium in the temperature range (313-323 K) under pseudo first order conditions with a large excess of L-leucine 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<sup>15</sup>. No precautions were taken to exclude the diffused light entering into the reaction mixture<sup>16</sup>. The Ce(IV) solution was thermally quite stable<sup>17</sup> in the visible region and undergoes photochemical decomposition<sup>18</sup> only in the UV region. Since, the oxidation of water<sup>19</sup> even at 333 K by Ce(IV) was immeasurably slow and insignificant, no further precautions were taken to account for this. From the titre 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<sup>-1</sup>) were obtained. To evaluate  $k^1$ , generally 8-10 values at least up to 80 % completion of the reaction were used. Average values of at least two independent determinations of the pseudo first order rate constants  $k^1$  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  $\pm 5$  %.

## RESULTS AND DISCUSSION

**Effect of [L-leucine]:** The concentration of L-leucine varied from  $1 \times 10^{-2}$  to  $10 \times 10^{-2} \text{ mol dm}^{-3}$  at a constant [Ce(IV)] ( $4 \times 10^{-3} \text{ mol dm}^{-3}$ ),  $[H^+]$  ( $5 \times 10^{-2} \text{ mol dm}^{-3}$ ),  $[Na_2SO_4]$  ( $1 \times 10^{-1} \text{ mol dm}^{-3}$ ) and  $[Ag(I)]$  ( $2 \times 10^{-6} \text{ mol dm}^{-3}$ ). The plot of pseudo-first-order rate constants (Table-1)  $k^1$  (s<sup>-1</sup>) vs. [L-leucine] yielded a straight line passing through the origin indicating first-order dependence with respect to L-leucine (Fig. 1). The  $k_2$  (mol dm<sup>-3</sup> s<sup>-1</sup>) values thus obtained from such plots (Table-2) were in agreement with the corresponding values calculated from the factor  $k^1$  (s<sup>-1</sup>) / [L-leucine]. The plot of  $1/k^1$  vs.  $1/[L-leucine]$  exhibits excellent linearity (Fig. 2) with a positive slope. Observed reaction order  $n_{ap} = 0.99931$  ( $r = 0.999$ ).

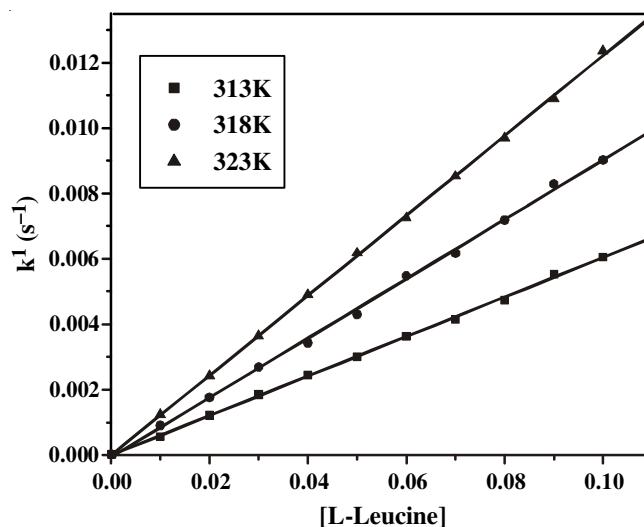


Fig. 1. Linear plot of  $k^1$  (s<sup>-1</sup>) vs. [L-leucine] confirms the first order reaction with respect to [L-leucine]

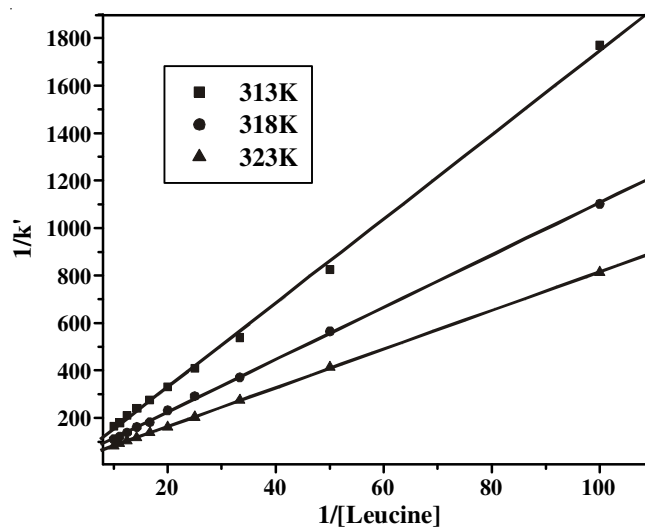


Fig. 2. Excellent linearity with a positive slope confirms the first order reaction with respect to [L-leucine]

TABLE-2  
COMPARISON OF GRAPHICALLY CALCULATED VALUE OF  $k_2$   
AND EXPERIMENTALLY CALCULATED VALUE OF  $k_2$

Temp. (K)	$k_2 \times 10^2$ (mol dm <sup>-3</sup> s <sup>-1</sup> ) Graphical	$k_2 \times 10^2$ (mol dm <sup>-3</sup> s <sup>-1</sup> ) Calculated
313	6.046	6.011
318	9.083	8.924
323	12.21	12.19

**Effect of [Ce(IV)]:** The concentration of cerium(IV) was varied from  $1 \times 10^{-3}$  to  $9 \times 10^{-3}$  mol dm<sup>-3</sup> at a constant [L-leucine]  $4 \times 10^{-2}$  mol dm<sup>-3</sup>, [H<sup>+</sup>] ( $5 \times 10^{-2}$  mol dm<sup>-3</sup>), [Na<sub>2</sub>SO<sub>4</sub>] ( $1 \times 10^{-1}$  mol dm<sup>-3</sup>) and [Ag(I)]  $2 \times 10^{-6}$  mol dm<sup>-3</sup>. The rate of the reaction was decreased with increase in [Ce(IV)] indicates that the order with respect to [Ce(IV)] was negative (-2.79391) as found from a plot of  $\log k^1$  vs.  $\log$  [Ce(IV)]. (Figs. 3 and Table-1). 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)]<sup>20,21</sup>. It is supported by a linear plot of  $k^1$  vs.  $1/[\text{Ce(IV)}]$ .

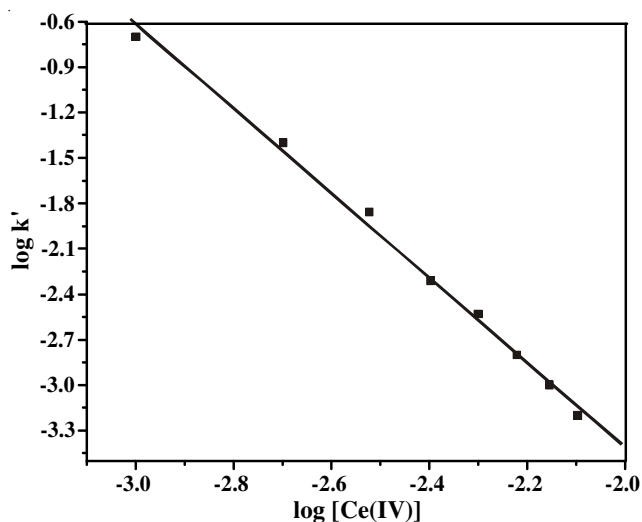


Fig. 3. Linear plot of  $\log k^1$  vs.  $\log$  [Ce(IV)] confirms that the reaction is negative order with respect to [Ce(IV)]

**Effect of [H<sup>+</sup>]:** Hydrogen ion concentration was varied from  $3.5 \times 10^{-2}$  to  $7.0 \times 10^{-2}$  mol dm<sup>-3</sup> at constant [L-leucine] ( $4.0 \times 10^{-2}$  mol dm<sup>-3</sup>), [Ce(IV)] ( $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>), [Na<sub>2</sub>SO<sub>4</sub>] ( $1 \times 10^{-1}$  mol dm<sup>-3</sup>) and [Ag(I)] ( $2 \times 10^{-6}$  mol dm<sup>-3</sup>). The rate of the reaction was decreased with increase in H<sup>+</sup> concentration (Table-3). The order with respect to [H<sup>+</sup>] was negative (-2.06119) as found from a plot of  $\log k^1$  vs.  $\log$  [H<sup>+</sup>] (Fig. 4).

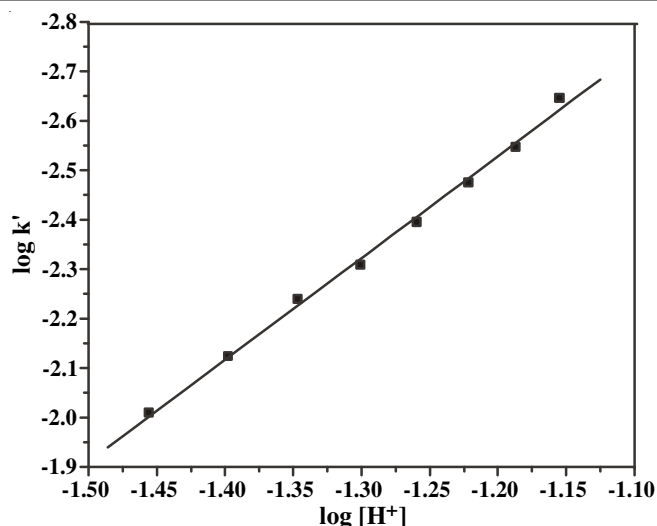
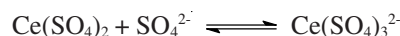


Fig. 4. Linear plot of  $\log k^1$  vs.  $\log$  [H<sup>+</sup>] confirms that the reaction is negative order with respect to [H<sup>+</sup>]

**Effect of [ionic strength]:** The effect of ionic strength was studied by varying the concentration of sodium sulfate from  $5.0 \times 10^{-2}$  to  $60 \times 10^{-2}$  mol dm<sup>-3</sup> at [L-leucine] ( $4.0 \times 10^{-2}$  mol dm<sup>-3</sup>), [Ce(IV)] ( $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>), [H<sup>+</sup>] ( $5 \times 10^{-2}$  mol dm<sup>-3</sup>) and [Ag(I)] ( $2 \times 10^{-6}$  mol dm<sup>-3</sup>). The rate of the reaction was decreased with increase in [ionic strength] (Table-4). The effect of sulfate ions may be explained<sup>22</sup> as due to the removal of the reactive species as Ce(SO<sub>4</sub>)<sub>3</sub><sup>2-</sup>.



**Effect of [HSO<sub>4</sub><sup>-</sup>]:** The effect of HSO<sub>4</sub><sup>-</sup> was studied by varying the concentration of HSO<sub>4</sub><sup>-</sup> from  $5 \times 10^{-2}$  to  $50 \times 10^{-2}$  mol dm<sup>-3</sup> at [L-leucine]  $4 \times 10^{-2}$  mol dm<sup>-3</sup>, [Ce(IV)] ( $4 \times 10^{-3}$ ) mol dm<sup>-3</sup>, [H<sup>+</sup>] ( $5 \times 10^{-2}$  mol dm<sup>-3</sup>) and [Ag(I)] ( $2 \times 10^{-6}$  mol dm<sup>-3</sup>). The rate of the reaction was decreased with increase in [HSO<sub>4</sub><sup>-</sup>] indicates that the order with respect to [HSO<sub>4</sub><sup>-</sup>] was negative (-1.27336). This is confirmed by the linear plot of  $1/k^1$  vs. [HSO<sub>4</sub><sup>-</sup>]. Therefore HSO<sub>4</sub><sup>-</sup> shows rate retarding effect. The plot of  $1/k^1$  vs. [HSO<sub>4</sub><sup>-</sup>] was found to be linear with positive slope. Thus the hydrogen sulfate dependence can be represented as eqn. 1:

$$k^1 = \frac{a}{b + c [\text{HSO}_4^-]} \quad (1)$$

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-leucine by Ce(IV) was studied in acetonitrile

TABLE-3  
EFFECT OF CONCENTRATION OF H<sup>+</sup> ON THE PSEUDO FIRST ORDER RATE CONSTANT  $k^1$

[L-leucine] $\times 10^2$ (mol dm <sup>-3</sup> )	[Ce(IV)] $\times 10^3$ (mol dm <sup>-3</sup> )	[H <sup>+</sup> ] $\times 10^2$ (mol dm <sup>-3</sup> )	[Ag <sup>+</sup> ] $\times 10^6$ (mol dm <sup>-3</sup> )	[μ] [Na <sub>2</sub> SO <sub>4</sub> ] $\times 10^2$ (mol dm <sup>-3</sup> )	$k^1 \times 10^3$ (s <sup>-1</sup> ) 323 K
4.0	4.0	3.5	2.0	10	9.78
4.0	4.0	4.0	2.0	10	6.40
4.0	4.0	4.5	2.0	10	5.73
4.0	4.0	5.0	2.0	10	4.90
4.0	4.0	5.5	2.0	10	4.03
4.0	4.0	6.0	2.0	10	3.36
4.0	4.0	6.5	2.0	10	2.85
4.0	4.0	7.0	2.0	10	2.25

TABLE-4  
EFFECT OF IONIC STRENGTH,  $\mu$  ON THE  
PSEUDO FIRST ORDER RATE CONSTANT,  $k^1$   
[H<sup>+</sup>] =  $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [Ag<sup>+</sup>] =  $2.0 \times 10^{-6}$  mol dm<sup>-3</sup>

[L-Leucine] $\times 10^2$ (mol dm <sup>-3</sup> )	[Ce(IV)] $\times 10^3$ (mol dm <sup>-3</sup> )	[HSO <sub>4</sub> <sup>-</sup> ] $\times 10^2$ (mol dm <sup>-3</sup> )	[Na <sub>2</sub> SO <sub>4</sub> ] $\times 10^2$ (mol dm <sup>-3</sup> )	$k^1 \times 10^3$ s <sup>-1</sup> 323 K
4.0	4.0	-	5.0	5.45
4.0	4.0	-	10.0	4.90
4.0	4.0	-	20.0	0.94
4.0	4.0	-	30.0	0.75
4.0	4.0	-	40.0	0.66
4.0	4.0	-	50.0	0.52
4.0	4.0	-	60.0	0.36
4.0	4.0	-	70.0	0.20
4.0	4.0	5.0	-	1.54
4.0	4.0	10.0	-	1.20
4.0	4.0	20.0	-	0.92
4.0	4.0	30.0	-	0.60
4.0	4.0	40.0	-	0.47
4.0	4.0	50.0	-	0.35
4.0	4.0	60.0	-	0.24

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<sup>23</sup>. 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  $\Delta S^\ddagger$  values obtained in this work.

**[Ag(I)] Dependence:** The concentration of silver(I) was varied from  $2 \times 10^{-6}$  to  $12 \times 10^{-6}$  mol dm<sup>-3</sup> at [L-leucine] ( $4.0 \times 10^{-2}$  mol dm<sup>-3</sup>), [Ce(IV)] ( $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>), [Na<sub>2</sub>SO<sub>4</sub>] ( $0.1$  mol dm<sup>-3</sup>) and [H<sup>+</sup>] ( $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>). The rate of the reaction was increased with increase in [Ag<sup>+</sup>]. (Table-6). The order with respect to [Ag<sup>+</sup>] was  $n_{app} = 0.45345$  as found from a plot of  $\log k^1$  vs.  $\log [Ag^+]$ . A plot of  $1/k^1$  vs.  $1/[Ag^+]$  at constant [H<sup>+</sup>] and [L-leucine] yielded a good linear plot through origin as shown in Fig. 5 passing nearly through origin<sup>24</sup>.

**Effect of Cu<sup>2+</sup> and Al<sup>3+</sup> catalyst:** The concentration of Cu<sup>2+</sup> and Al<sup>3+</sup> catalyst varied from  $2 \times 10^{-6}$  to  $12 \times 10^{-6}$  mol dm<sup>-3</sup> at [L-leucine] ( $4.0 \times 10^{-2}$  mol dm<sup>-3</sup>), [Ce(IV)] ( $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>), [Na<sub>2</sub>SO<sub>4</sub>] ( $1 \times 10^{-1}$  mol dm<sup>-3</sup>) and [H<sup>+</sup>] ( $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>).

The rate of the reaction was increased with increase in [Cu<sup>2+</sup>] and [Al<sup>3+</sup>]. It is observed that the rate of the reaction

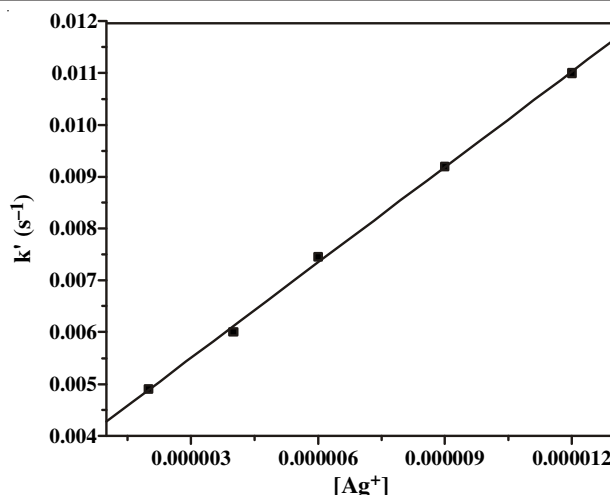


Fig. 5. Linear plot of rate constant  $k^1$  (s<sup>-1</sup>) vs. [Ag<sup>+</sup>] with non zero intercept confirms that the reaction is fractional order with respect to [Ag<sup>+</sup>]

was not much influenced with increase in [Al<sup>3+</sup>]. It is observed that the catalytic efficiency of Ag<sup>+</sup> is much higher than the Cu<sup>2+</sup> (Table-6).

TABLE-6  
EFFECT OF CONCENTRATION OF Ag<sup>+</sup>, Cu<sup>2+</sup> AND  
Al<sup>3+</sup> ON THE PSEUDO FIRST ORDER RATE CONSTANT  $k^1$   
[L-Leucine]  $4 \times 10^{-2}$  (mol dm<sup>-3</sup>), [Ce(IV)]  $4 \times 10^{-3}$  (mol dm<sup>-3</sup>),  
[Na<sub>2</sub>SO<sub>4</sub>] =  $10 \times 10^{-2}$  mol dm<sup>-3</sup>

[H <sup>+</sup> ] $\times 10^2$ (mol dm <sup>-3</sup> )	[Ag <sup>+</sup> ] $\times 10^6$ (mol dm <sup>-3</sup> )	[Cu <sup>2+</sup> ] $\times 10^6$ (mol dm <sup>-3</sup> )	[Al <sup>3+</sup> ] $\times 10^6$ (mol dm <sup>-3</sup> )	$k^1 \times 10^3$ s <sup>-1</sup> 323 K
5.0	2.0	-	-	4.90
5.0	4.0	-	-	6.01
5.0	6.0	-	-	7.45
5.0	9.0	-	-	9.20
5.0	12.0	-	-	11.0
5.0	-	2.0	-	3.63
5.0	-	4.0	-	5.68
5.0	-	6.0	-	5.82
5.0	-	9.0	-	6.33
5.0	-	12.0	-	6.56
5.0	-	-	2.0	6.12
5.0	-	-	4.0	5.25
5.0	-	-	6.0	5.08
5.0	-	-	9.0	5.38
5.0	-	-	12.0	5.68

**Test for free radical intermediates:** The reaction mixture initiated polymerization of olefinic monomers, acrylonitrile and methyl methacrylate, indicating an *in situ* formation of free radicals.

TABLE-5  
EFFECT OF DIELECTRIC CONSTANT ON THE PSEUDO FIRST ORDER RATE CONSTANT  $k^1$   
[L-Leucine]  $4 \times 10^{-2}$  (mol dm<sup>-3</sup>), [Ce(IV)]  $4 \times 10^{-3}$  (mol dm<sup>-3</sup>)

[H <sup>+</sup> ] $\times 10^2$ (mol dm <sup>-3</sup> )	[Ag <sup>+</sup> ] $\times 10^6$ (mol dm <sup>-3</sup> )	[ $\mu$ ] [Na <sub>2</sub> SO <sub>4</sub> ] $\times 10^2$ (mol dm <sup>-3</sup> )	Acetonitrile (%) (v/v)	Acetone (%) (v/v)	$k^1 \times 10^3$ s <sup>-1</sup> 323 K
5.0	2.0	10	30	-	8.98
5.0	2.0	10	40	-	5.91
5.0	2.0	10	50	-	2.85
5.0	2.0	10	60	-	2.25
5.0	2.0	10	-	30	14.11
5.0	2.0	10	-	40	12.36
5.0	2.0	10	-	50	8.52
5.0	2.0	10	-	60	5.84

TABLE-7  
EFFECT OF TEMPERATURE VARIATION ON PSEUDO FIRST ORDER RATE CONSTANT  $k^1$  AND SECOND ORDER RATE CONSTANT  $k_2$ ;  $[H^+] = 5 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[Ag^+] = 2.0 \times 10^{-6} \text{ mol dm}^{-3}$ ,  $[Na_2SO_4] = 10 \times 10^{-2} \text{ mol dm}^{-3}$

[L-Leucine] $\times 10^2$ (mol dm <sup>-3</sup> )	[Ce(IV)] $\times 10^3$ (mol dm <sup>-3</sup> )	$k^1 \times 10^3 \text{ s}^{-1}$			$k_2 \times 10^2 \text{ (mol dm}^{-3} \text{ s}^{-1})$		
		313 K	318 K	323 K	313 K	318 K	323 K
1.0	4.0	0.56	0.90	1.23	5.65	9.08	12.29
2.0	4.0	1.21	1.77	2.42	6.06	8.85	12.09
3.0	4.0	1.85	2.69	3.64	6.17	8.98	12.12
4.0	4.0	2.44	3.43	4.90	6.10	8.57	12.26
5.0	4.0	3.01	4.30	6.17	6.03	8.61	12.34
6.0	4.0	3.63	5.48	7.25	6.06	9.13	12.09
7.0	4.0	4.14	6.17	8.52	5.92	8.81	12.17
8.0	4.0	4.74	7.18	9.69	5.93	8.98	12.11
9.0	4.0	5.52	8.29	10.89	6.14	9.21	12.10
10.0	4.0	6.05	9.02	12.36	6.05	9.02	12.36

$$E_a = 59.512 \text{ KJ mol}^{-1}, \Delta H^\ddagger = 56.82680274 \text{ KJ mol}^{-1}, \Delta S^\ddagger = -87.0863524 \text{ KJ mol}^{-1}, \Delta G^\ddagger = 84.9555 \text{ KJ mol}^{-1}$$

**Rate and activation parameters:** The reaction was studied at different temperatures (313-323 K) (Table-7) and the activation parameters were computed from Arrhenius and Eyring's plots (Figs. 6 and 7).

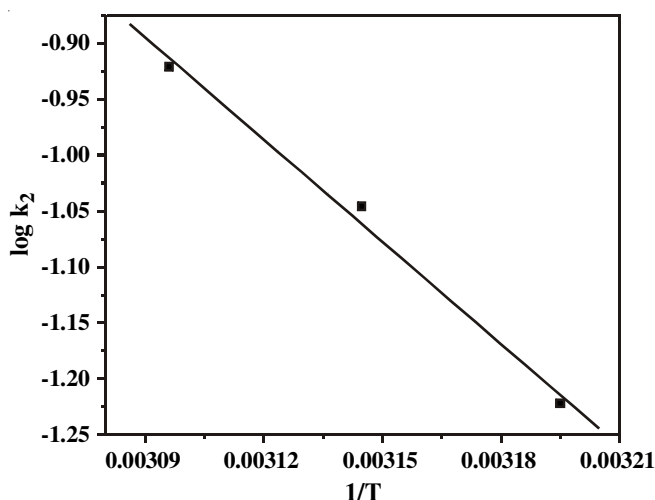


Fig. 6. Arrhenius plot shows the linear plot of  $\log k_2$  vs.  $1/T$ . From Arrhenius plot, energy of activation ( $E_a$ ) is calculated

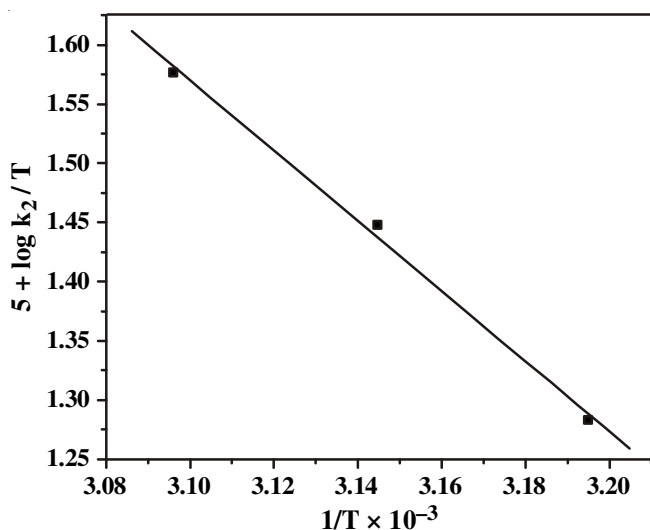
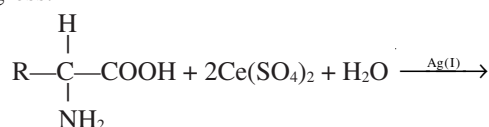


Fig. 7. Eyring's plot shows the linear plot of  $5 + \log k_2/T$  vs.  $1/T \times 10^{-3}$ . From Eyring's plot the value of  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$  is computed

**Stoichiometry and product analysis:** Different reaction mixtures with different sets of concentration of reactants, where  $[Ce(IV)]$  was in excess over  $[L\text{-leucine}]$  at constant ionic strength, acidity and at constant concentration of catalyst were kept for 24 h at 323 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  $CO_2$  (Baryta water test).

The product pentanaldehyde was quantitatively estimated to about 70%, which is evidenced by its 2,4-DNP derivative<sup>25</sup>. The nature of the aldehyde was confirmed by its IR spectrum<sup>26</sup> carbonyl stretching at  $1729 \text{ cm}^{-1}$  and aband at  $2928 \text{ cm}^{-1}$  due to the aldehydic stretching. Further, aldehyde group was confirmed with qualitative test such as Tollen's reagent<sup>22,27</sup> and Schiff's reagent. Nitrile test was negative, the product usually reported in the oxidation of amino acids. Therefore, the stoichiometry of the reaction with positive test of an aldehyde can be represented by the eqn. 2.

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



where  $R = -\text{CH}_2-\text{CHMe}_2$ .

The rate expression may thus be represented by eqn. 3:

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

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

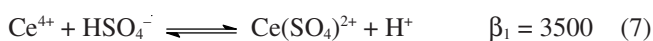
$$\frac{1}{k^1} = \frac{[\text{Ce(IV)}][\text{H}^+]}{kf[\text{Ag}^+]} + \frac{1}{kfK[\text{Leucine}][\text{Ag}^+]} \quad (4)$$

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

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

Eqn. 3 suggests that  $n_{ap} \approx 1.0$ ,  $0 < n_{ap}$  [leucine] which is consistent with the results of our experiments. Eqn. 5 suggests that  $1/k^1$  vs.  $1/[\text{leucine}]$  at constant  $[\text{H}^+]$  and  $[\text{Ag}^+]$  should be linear plots with positive intercept as shown in (Fig. 2). Eqn. 6 suggests that  $1/k^1$  vs.  $1/[\text{Ag}^+]$  at constant  $[\text{H}^+]$  and [L-leucine] 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  $\text{Ce}(\text{SO}_4)_4^{2+}$ ,  $\text{Ce}(\text{SO}_4)_2$ ,  $\text{HCe}(\text{SO}_4)_3^-$  and the relevant equilibria are Mishra and Gupta<sup>28</sup>.



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<sup>29</sup>. From the relationship between hydrogen sulfate and  $k^1$ ,  $\text{Ce}(\text{SO}_4)_2$  has been found as the kinetically active species in the present study. The concentration of  $\text{Ce}(\text{SO}_4)_2$  can be approximately obtained. According to the mass balance eqn. 10 is obtained.

$$[\text{Ce}(\text{IV})]_T = [\text{Ce}^{4+}] + [\text{Ce}(\text{SO}_4)^{2+}] + [\text{Ce}(\text{SO}_4)_2] + [\text{HCe}(\text{SO}_4)_3^-] \quad (10)$$

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

$$[\text{Ce}^{4+}] = \frac{[\text{Ce}(\text{SO}_4)^{2+}][\text{H}^+]}{\beta_1[\text{HSO}_4^-]}$$

$$[\text{Ce}(\text{SO}_4)^{2+}] = \frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]}{\beta_2[\text{HSO}_4^-]}$$

$$[\text{HCe}(\text{SO}_4)_3^-] = \beta_3[\text{HSO}_4^-][\text{Ce}(\text{SO}_4)_2]$$

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

$$[\text{Ce}(\text{IV})]_T = \frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]}{\beta_1[\text{HSO}_4^-]} + \frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]}{\beta_2[\text{HSO}_4^-]} + [\text{Ce}(\text{SO}_4)_2] + \beta_3[\text{HSO}_4^-][\text{Ce}(\text{SO}_4)_2] \quad (11)$$

By considering the relative magnitudes of the successive formation equilibrium constants which are in the order:

$$\beta_1 \gg \beta_2 \gg \beta_3, \text{ the value of } \frac{[\text{Ce}(\text{SO}_4)^{2+}][\text{H}^+]}{\beta_1[\text{HSO}_4^-]} \text{ and}$$

$$\frac{[\text{Ce}(\text{SO}_4)_2][\text{H}^+]}{\beta_2[\text{HSO}_4^-]} \text{ are much less than the other two terms.}$$

Therefore, we get eqn. 12 from eqn. 11.

$$[\text{Ce}(\text{IV})]_T \approx [\text{Ce}(\text{SO}_4)_2] + \beta_3[\text{HSO}_4^-][\text{Ce}(\text{SO}_4)_2] = [\text{Ce}(\text{SO}_4)_2](1 + \beta_3[\text{HSO}_4^-]) \quad (12)$$

$$\text{so, } [\text{Ce}(\text{SO}_4)^{2+}] = \frac{[\text{Ce}(\text{IV})]_T + [\text{H}^+]}{1 + \beta_3[\text{HSO}_4^-]} = f[\text{Ce}(\text{IV})]_T$$

$$f = \frac{1}{1 + \beta_3[\text{HSO}_4^-]} \quad (13)$$

Substituting eqn. 13 into eqn. 3 we get:

$$k^1 = \frac{kK[\text{leucine}][\text{Ag}^+]}{K[\text{Ce}(\text{SO}_4)_2](1 + \beta_3[\text{HSO}_4^-])([\text{H}^+][\text{leucine}] + 1)} \quad (14)$$

$$\text{Assuming that } m = \frac{kK[\text{leucine}][\text{Ag}^+]}{K[\text{Ce}(\text{IV})][\text{H}^+][\text{leucine}] + 1}$$

Eqn. 14 may be written as:

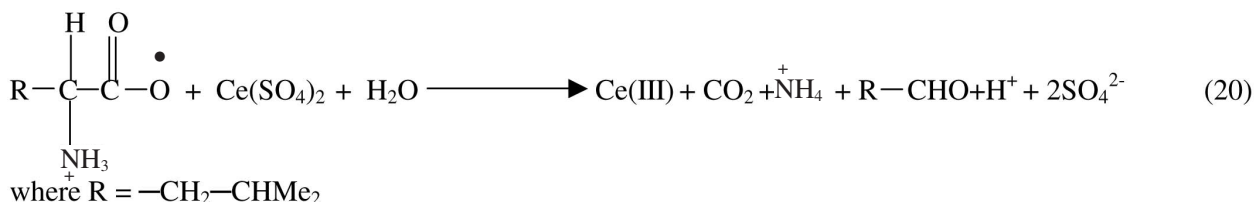
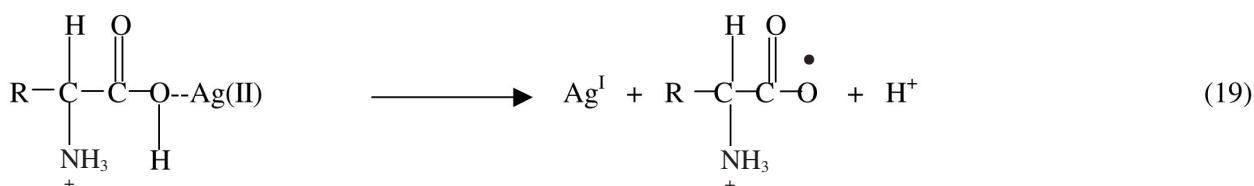
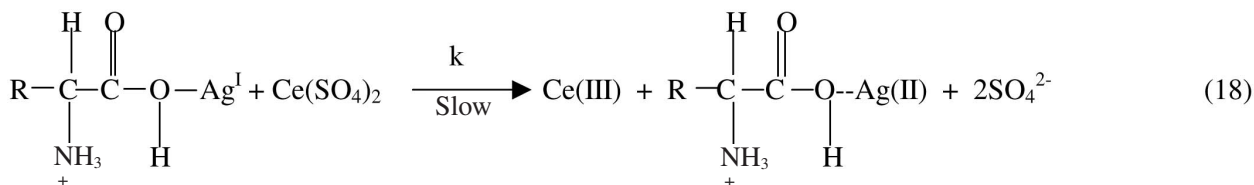
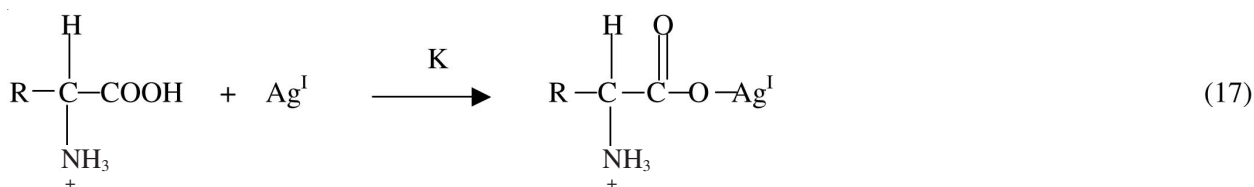
$$k^1 = \frac{m}{(1 + \beta_3[\text{HSO}_4^-])} \quad (15)$$

or

$$\frac{1}{k^1} = \frac{1}{m} + \frac{\beta_3}{m} [\text{HSO}_4^-] \quad (16)$$

Eqn. 16 is same as eqn. 1 which can explain well the negative order dependence on  $[\text{HSO}_4^-]$ . Eqn. 16 suggests that  $1/k^1$  vs.  $[\text{HSO}_4^-]$  should be linear and agrees with the experimental data. All the above result shows that  $\text{Ce}(\text{SO}_4)_2$  is the kinetically active species. Furthermore, the rate constants were decreased with increase in  $[\text{H}^+]$  (Table-3). This is due to the formation<sup>29,30</sup> of an active inhibitor  $\text{H}_2\text{Ce}(\text{SO}_4)_2^{2-}$ . The order with  $[\text{H}^+]$  was negative. As the sulfuric acid concentration increased in the reaction mixture, the  $[\text{H}^+]$  increased, but there is also a corresponding increase in  $[\text{HSO}_4^-]$ . If the rate is inversely dependent on the  $[\text{HSO}_4^-]$  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)<sup>25</sup> mandelic acid<sup>28,30,31</sup>, malic acid<sup>32</sup>, fructose<sup>33</sup> by cerium(IV). The observation that  $\text{SO}_4^{2-}$  ions retard the rate of oxidation coupled with the observation that increase in  $[\text{H}^+]$  decreased the rate, point to the fact that the neutral covalently bound  $\text{Ce}(\text{SO}_4)_2$  is the active species of oxidant<sup>19</sup>. In the oxidation of glutamic acid<sup>28</sup>, lactic acid<sup>34</sup> and mandelic acid<sup>29-31</sup> by cerium(IV) in sulfuric acid-sulfate media,  $\text{Ce}(\text{SO}_4)_2$ , had been identified as the active species, which supports the present work. Furthermore, the ionic strength has little effect on  $k^1$ . According to the principle of salt effect, there must be a neutral molecule in the rate determining step, which confirms  $\text{Ce}(\text{SO}_4)_2$  as the kinetically active species in the present study.

Amino acids are reported<sup>35</sup> to form an adduct with Ag(I) owing to availability of electron pair on oxygen atom. Therefore, an adduct between Ag(I) and leucine is initially formed that on further interaction with Ce(IV) yields another adduct of higher valent silver. Plot of  $1/k^1$  vs.  $1/[\text{L-leucine}]$  was linear with non-zero intercept confirms the complex between Ag(I) and L-leucine in a first step (Fig. 2). 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  $[\text{Ce}(\text{IV})][\text{Ag}(\text{I})]/\text{rate}$  vs.  $1/[\text{leucine}]$  (Fig. 8). Such complex formation has been observed already in the literature<sup>27,31</sup>. The results suggest that L-leucine combines with catalyst Ag(I) to form a complex, which then reacts in a slow step with one mole of  $\text{Ce}(\text{SO}_4)_2$  to give the product cerium(III), complex L-leucine,  $\text{H}^+$  and 2  $\text{SO}_4^{2-}$  with regenerating the catalyst Ag(I). The complex L-leucine reacts with another mole of  $\text{Ce}(\text{SO}_4)_2$  in a further fast step to give the products cerium(III), pentanaldehydeb, carbondioxide and ammonia. The results are given in **Scheme-I**.



Scheme-I

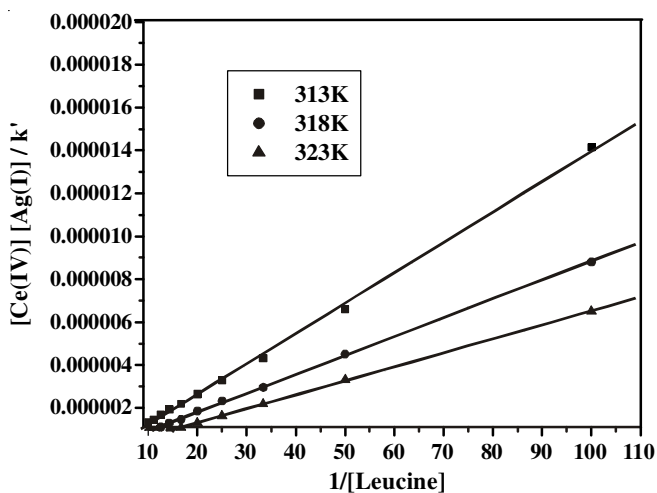


Fig. 8. Linear plot of  $[\text{Ce}(\text{IV})][\text{Ag}(\text{I})]/k'$  vs.  $1/[\text{Leucine}]$  with non-zero intercept confirms the formation of the complex between Ag(I) and L-leucine in a first step

## Conclusion

The reaction between cerium(IV) and L-leucine is sluggish in sulfuric acid medium at 323 K. The reaction occurs with measurable velocity in the presence of a small amount of ( $10^{-6}$  mol  $\text{dm}^{-3}$ ) of silver. The main active species of cerium(IV) is considered as  $\text{Ce}(\text{SO}_4)_2$ , 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 the experimental evidence.

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