



Kinetic and Mechanism of Uncatalytic Oxidation of DL-Threonine by Cerium (Iv) in Aqueous Acid Medium

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Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

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ABSTRACT

Kinetic of uncatalyzed oxidation of DL-Threonine has been studied by Ce (IV) in acidic medium has been investigated by spectrophotometer technique. The rate of reaction determined at three different temperatures ranging from 298 K to 318 K at the interval of 10 K. The reaction has been found to be a first order reaction in presence or in absence of KCl, CTAB, and SDS. The rate constant, decreases with increasing the concentration of $[\text{HSO}_4^-]$ and $[\text{H}^+]$ ion. The various thermodynamic parameters were calculated at 298 K, 308 K and 318 K. The proposed mechanism and results is discussed.

Keywords: Kinetics; oxidation; DL-threonine; cerium (IV); sulphuric acid; KCl; mechanism.

1. INTRODUCTION

The amino acids contain carbon, hydrogen, oxygen and nitrogen. We know that amino acids are molecules containing an amine groups, a

carboxylic acid group and side chain that varies between different amino acids. Oxidation reactions are very important in nature and key transformations in organic synthesis [1-3]. In the human body, four amino acid are used in genetic

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coding. Oxidation of amino acid is important for metabolic reaction. The oxidative deamination and decarboxylation by various reactions of amino acids are done [4,5].

The threonine present in central nervous system present is helpful for treating different types of depression. Metabolism of fat in the liver is caused by amino acids. Some amino acids in the form of protein help intestine in the digestion process. DL- Threonine cannot be synthesized by your body but is fulfilled in sources like beef, cottage cheese, fish, bleak and sesame seeds [6-8].

The Ce (IV) is a powerful oxidizing agent in acidic medium. Here the Ce (IV) in H₂SO₄ medium has been acting as oxidizing agent. Ce (III) is reduced by the transfer of one electron from Ce (IV) via the acidic medium. The intermediate complex is located at a higher concentration in the acid of Ce (IV) [9,10]. Many reports are available for the kinetics of oxidation of N- bromoanisamide, tributylammonium chlorochromate, tripropylammonium fluorochromate, iron (III)-1, 10-phenanthroline complex, chloramine-T, vanadium (V), manganese (III), n-bromosuccinimide, cerium (IV), pyridinium dichromate. The reaction of Ce(IV) with DL- threonine in aqueous acidic medium gives up many species like Ce(OH)³⁺, Ce(SO₄)₄²⁺, Ce(SO₄)₂ HSO₄⁻ and H₃Ce(SO₄), but their role has not attracted attention so far [11-17].

Ce(IV) species are reactive in oxidation of DL-threonine in H₂SO₄ has been the purpose in the present work. The attention has been drawn due to the natural characteristic of DL- threonine as a zwitter ionic in nature.

2. METHODOLOGY

All the solution used for the analysis was prepared with double distilled deionised water. Ce (IV) in stock solution was obtained by

dissolving cerium ammonium sulphate in presence of sulphuric acid 0.5 mol dm⁻³ solutions. The stock solution of DL-Threonine is made by E.Merck. The stock solution was prepared by salt NaCl and KCl by dissolving in double distilled deionised water. The SDS anionic surfactant and CTAB cationic surfactant by dissolving in double distilled deionised water [18,19].

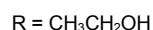
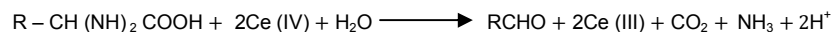
2.1 Kinetic measurements

Ce (IV) and other reactant in the water bath were allowed to be established in equilibrium solution. A definite concentration of Ce (IV), then mixed well with definite concentration of amino acid and quickly transferred to the absorbance cell. The progress of reaction was followed by quantification of Ce (IV) at various time intervals ($\lambda_{max}=360\text{nm}$) by using a visible spectrophotometer (systronic 105) [20]. Kinetic studies were done in the medium of sulphuric acid under the conditions of the pseudo first order at 298 to 318 K with excess of DL-threonine in Ce (IV). The response statuses of the application of Beer's law between 5.0×10^{-4} to 5.0×10^{-3} were verified of Ce (IV) and molar extinction coefficient was found to be 22622 mol dm⁻³. The observed rate constants were reproducible within the experimental error $\pm 5\%$ [21,22].

2.2 Stoichiometry and product analysis

DL- threonine was taken at different concentration in the presence of sulphuric acid containing an excess of Ce (IV) was kept at 318 K temperature for 24 hours. In which the absorbance of the Ce (IV) medium was measured spectrometric method. The results indicate that two moles of cerium (IV) were consumed by one mole of DL-threonine as given by equation [23].

Scheme-1



The oxidation products were identified as Ce (III), 2- hydroxyl propanal, ammonia and carbon dioxide. 2- Hydroxy propanal was confirmed by the IR spectrum of the corresponding species. The reaction mixture was treated with acidified 2, 4 - dinitrophenyl hydrazine solution, which

yielded a hydrazone, which indicates the presence of 2-hydroxy propanal. The other product ammonia was detected by Nessler's reagent test and CO₂ was qualitatively detected by passing the liberated gas through a tube containing lime water.

3. RESULTS

3.1 Cerium (IV) Dependence

Cerium (1.0×10^{-4}) was varied concentrations and other chemical was fixed concentration that is DL- Threonine (1.0×10^{-2}) mol dm⁻³, [H⁺] 1.0 mol dm⁻³ and at different temperatures 298 K to 318 K. In which Cerium was pseudo first order in different concentration and temperature. Pseudo first order graph was plotted K_{obs} vs cerium (IV) in slope of positive and intercept of zero as shown in Fig. 1.

3.2 DL-Threonine Dependence

Cerium (IV) in oxidant reagent of concentration (1.0×10^{-4}) mol dm⁻³ and, [H⁺] 1.0 mol dm⁻³ in fixed concentration. The oxidation of DL- Threonine was at different concentration (1.0×10^{-2}) to (5.0×10^{-2}) mol dm⁻³ at temperature range 298 K to

318 K. As the concentration of DL-threonine increase the absorbance decrease in time interval. The reaction is found to be pseudo first order by plotting graph k_{obs} vs DL-threonine as shown in Fig. 2.

3.3 Effect of [HSO₄]

The sulphuric acid concentration was varied between 1.0 and 2.5 mol dm⁻³ and fixed concentration of cerium (IV) (5.0×10^{-4}) mol dm⁻³, DL- Threonine (5.0×10^{-2}) mol dm⁻³ at different temperature 298 K to 318 K. The rate of reaction was decrease with increasing, the concentration of sulphuric acid. The graphical plot of k_{obs} vs [H₂SO₄] is found to be linear with negative intercept and slope and shown in Fig. 3. Results are given in Table 3.1

Table 1.1. Variation of Cerium ammonium sulphate

| 10^{-4} [Ce (IV)] ⁻¹ mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|--|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.154 | 0.265 | 0.520 | 0.767 | 0.925 |
| 10 | 0.147 | 0.254 | 0.495 | 0.725 | 0.875 |
| 20 | 0.143 | 0.246 | 0.478 | 0.690 | 0.838 |
| 30 | 0.139 | 0.238 | 0.456 | 0.671 | 0.803 |
| 40 | 0.135 | 0.229 | 0.447 | 0.653 | 0.784 |
| 50 | 0.131 | 0.221 | 0.435 | 0.633 | 0.757 |
| 60 | 0.128 | 0.217 | 0.424 | 0.615 | 0.735 |
| 70 | 0.125 | 0.212 | 0.416 | 0.607 | 0.723 |
| 80 | 0.123 | 0.208 | 0.409 | 0.597 | 0.712 |
| 10^{-4} (k _{obs}), s ⁻¹ | 1.78 | 1.69 | 1.58 | 1.44 | 1.40 |

$[Ce(IV)] = 5.0 \times 10^{-4}$ mol dm⁻³, [Thre] = 1.0×10^{-2}
[H⁺] = 1.0 mol dm⁻³, Temp. = 298K

Table 1.2. Variation of Cerium ammonium sulphate

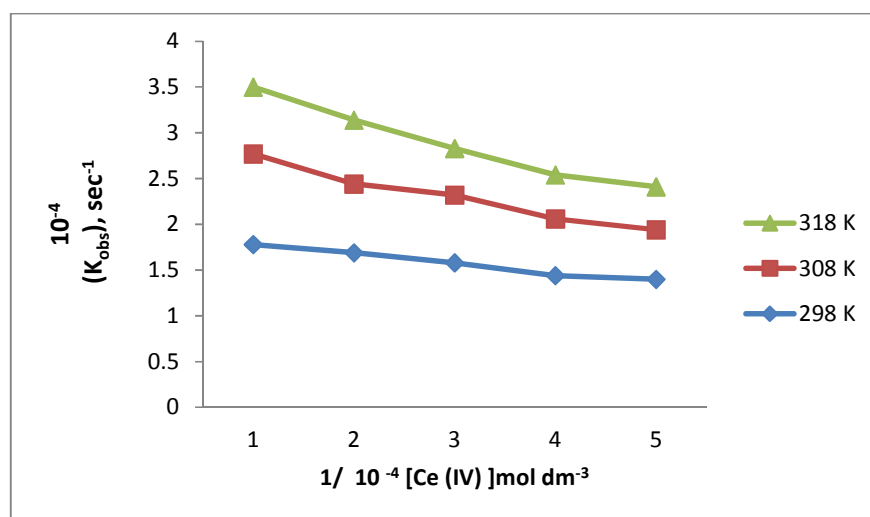
| 10^{-4} [Ce (IV)] ⁻¹ mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|--|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.130 | 0.375 | 0.465 | 0.545 | 0.960 |
| 10 | 0.125 | 0.335 | 0.415 | 0.458 | 0.790 |
| 20 | 0.115 | 0.303 | 0.375 | 0.428 | 0.735 |
| 30 | 0.108 | 0.288 | 0.354 | 0.401 | 0.656 |
| 40 | 0.101 | 0.273 | 0.334 | 0.389 | 0.635 |
| 50 | 0.096 | 0.265 | 0.321 | 0.365 | 0.603 |
| 60 | 0.092 | 0.258 | 0.316 | 0.347 | 0.590 |
| 70 | 0.087 | 0.247 | 0.309 | 0.338 | 0.574 |
| 80 | 0.084 | 0.239 | 0.301 | 0.327 | 0.554 |
| 10^{-4} (k _{obs}), s ⁻¹ | 0.99 | 0.75 | 0.74 | 0.62 | 0.54 |

$[Ce(IV)] = 5.0 \times 10^{-4}$ mol dm⁻³, [Thre] = 1.0×10^{-2} mol dm⁻³;
[H⁺] = 1.0 mol dm⁻³, Temp. = 308K

Table 1.3. Variation of Cerium ammonium sulphate

| $10^{-4} [\text{Ce (IV)}]^{-1} \text{ mol dm}^{-3}$ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---|-------------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.114 | 0.297 | 0.521 | 0.981 | 1.054 |
| 10 | 0.104 | 0.267 | 0.442 | 0.756 | 0.804 |
| 20 | 0.095 | 0.241 | 0.387 | 0.707 | 0.740 |
| 30 | 0.087 | 0.226 | 0.351 | 0.670 | 0.714 |
| 40 | 0.081 | 0.212 | 0.329 | 0.644 | 0.689 |
| 50 | 0.077 | 0.201 | 0.316 | 0.627 | 0.665 |
| 60 | 0.072 | 0.189 | 0.289 | 0.605 | 0.635 |
| 70 | 0.069 | 0.178 | 0.273 | 0.591 | 0.621 |
| 80 | 0.066 | 0.171 | 0.265 | 0.584 | 0.609 |
| $10^{-4} (k_{\text{obs}}), \text{ s}^{-1}$ | 0.73 | 0.70 | 0.51 | 0.48 | 0.47 |

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; $\text{Temp.} = 318\text{K}$

**Fig. 1. Variation of Cerium ammonium sulphate**

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; $\text{Temp.} = 298\text{K}, 308\text{K}, 318\text{K}$
 (Ref Table 1.1, 1.2 and 1.3)

Table 2.1. Variation of DL-Threonine

| $10^{-4} [\text{DL-threo}] \text{ mol dm}^{-3}$ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---|-------------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.925 | 0.527 | 0.556 | 0.483 | 0.376 |
| 10 | 0.908 | 0.518 | 0.544 | 0.472 | 0.361 |
| 20 | 0.905 | 0.514 | 0.541 | 0.468 | 0.357 |
| 30 | 0.898 | 0.507 | 0.537 | 0.464 | 0.353 |
| 40 | 0.888 | 0.504 | 0.533 | 0.460 | 0.351 |
| 50 | 0.883 | 0.501 | 0.530 | 0.457 | 0.349 |
| 60 | 0.879 | 0.498 | 0.527 | 0.454 | 0.347 |
| 70 | 0.876 | 0.497 | 0.524 | 0.452 | 0.345 |
| 80 | 0.870 | 0.496 | 0.521 | 0.450 | 0.343 |
| $10^{-4} (k_{\text{obs}}), \text{ s}^{-1}$ | 0.17 | 0.18 | 0.19 | 0.21 | 0.32 |

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; $\text{Temp.} = 298\text{K}$

Table 2.2. Variation of DL-Threonine

| 10^{-4} [DL-threo] mol dm^{-3} | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.590 | 0.545 | 0.690 | 0.593 | 0.562 |
| 10 | 0.577 | 0.489 | 0.607 | 0.510 | 0.479 |
| 20 | 0.550 | 0.463 | 0.577 | 0.463 | 0.414 |
| 30 | 0.480 | 0.438 | 0.557 | 0.440 | 0.378 |
| 40 | 0.465 | 0.420 | 0.536 | 0.424 | 0.353 |
| 50 | 0.455 | 0.410 | 0.512 | 0.405 | 0.327 |
| 60 | 0.447 | 0.400 | 0.502 | 0.395 | 0.312 |
| 70 | 0.440 | 0.390 | 0.496 | 0.386 | 0.290 |
| 80 | 0.435 | 0.385 | 0.494 | 0.380 | 0.287 |
| 10^{-4} (k_{obs}), s^{-1} | 1.00 | 1.09 | 1.15 | 1.49 | 1.97 |

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; Temp. = 308K

Table 2.3. Variation of DL-Threonine

| 10^{-4} [Ce (IV)] $^{-1}$ mol dm^{-3} | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 1.054 | 0.890 | 0.708 | 0.687 | 0.659 |
| 10 | 0.935 | 0.787 | 0.623 | 0.598 | 0.567 |
| 20 | 0.878 | 0.737 | 0.576 | 0.523 | 0.497 |
| 30 | 0.845 | 0.704 | 0.545 | 0.478 | 0.443 |
| 40 | 0.803 | 0.656 | 0.521 | 0.434 | 0.412 |
| 50 | 0.768 | 0.636 | 0.506 | 0.414 | 0.387 |
| 60 | 0.734 | 0.615 | 0.487 | 0.397 | 0.354 |
| 70 | 0.704 | 0.602 | 0.469 | 0.381 | 0.321 |
| 80 | 0.686 | 0.590 | 0.447 | 0.379 | 0.307 |
| 10^{-4} (k_{obs}), s^{-1} | 1.25 | 1.26 | 1.33 | 1.79 | 1.98 |

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; Temp. = 318K

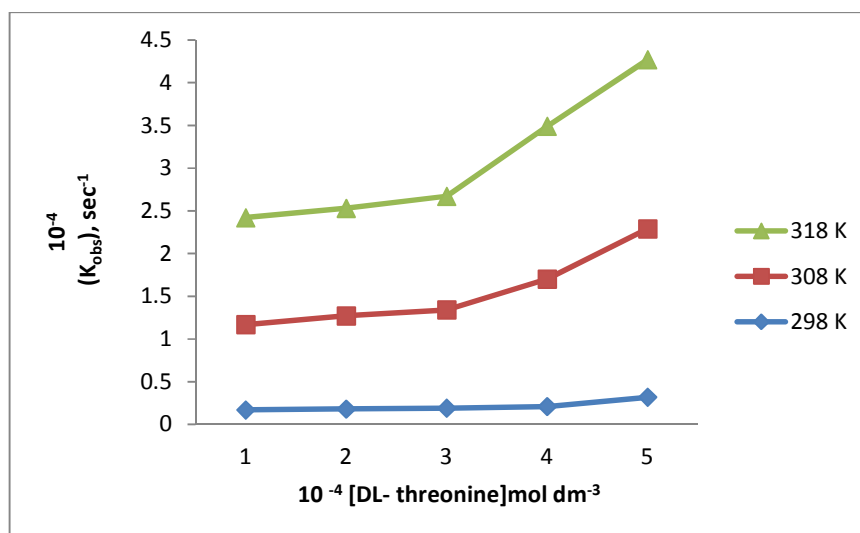


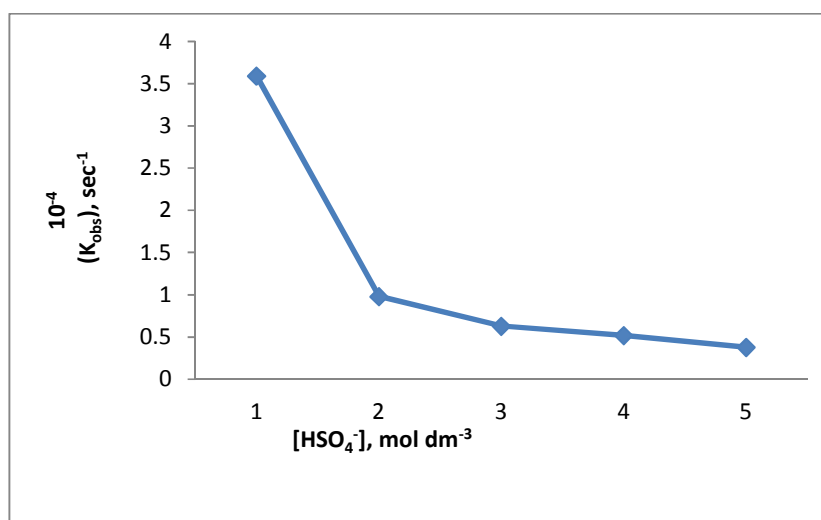
Fig. 2. Variation of DL – Threonine

$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$;
 $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$; Temp. = 298K, 308K, 318K
 (Ref Table 2.1, 2.2 and 2.3)

Table 3.1. Variation of sulphuric acid

| [HSO ₄ ⁻] mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 1.157 | 0.527 | 0.696 | 0.654 | 0.857 |
| 10 | 0.905 | 0.522 | 0.687 | 0.635 | 0.833 |
| 20 | 0.602 | 0.519 | 0.667 | 0.621 | 0.817 |
| 30 | 0.517 | 0.516 | 0.657 | 0.584 | 0.801 |
| 40 | 0.442 | 0.511 | 0.570 | 0.567 | 0.792 |
| 50 | 0.431 | 0.509 | 0.535 | 0.548 | 0.762 |
| 60 | 0.420 | 0.507 | 0.508 | 0.544 | 0.749 |
| 70 | 0.416 | 0.505 | 0.495 | 0.535 | 0.735 |
| 80 | 0.414 | 0.503 | 0.468 | 0.524 | 0.723 |
| 10 ⁻⁴ (k _{obs}), s ⁻¹ | 0.28 | 9.09 | 1.58 | 1.92 | 2.63 |

[Ce(IV)] = 5.0X10⁻⁴ mol dm⁻³; [Thre] = 1.0X10⁻² mol dm⁻³;
[H⁺] = 1.0 mol dm⁻³; Temp. = 298 K

**Fig. 3. Variation of sulphuric acid**

[Ce(IV)] = 5.0X10⁻⁴ mol dm⁻³; [Thre] = 1.0X10⁻² mol dm⁻³;
[H⁺] = 1.0 mol dm⁻³; Temp. = 298K,

3.4 Effect of Surfactant

a) CTAB Surfactant

CTAB is cationic surfactant; its concentration ranging from (1.0x10⁻²) to (5.0x10⁻²) mol dm⁻³ with constant concentration of Ce (IV) (1.0x10⁻⁴) mol dm⁻³ DL- Threonine (1.0x10⁻⁴) mol dm⁻³ and [H⁺] (1.0 mol dm⁻³) at different 298 K to 318 K temperatures. It is found that the absorbance decrease or increase with increase of the concentration of CTAB (Table 4.1). It indicates that the rate of reaction proceeds very slowly. The order of reaction was found to be first by plotting the graph k_{obs} vs CTAB concentration in Fig. 4.

b) SDS surfactant

SDS is an anionic surfactant; it was at different concentrations (1.0x10⁻³) to (5.0x10⁻³) mol dm⁻³ and fixed concentration of cerium (IV) (1.0x10⁻⁴)

mol dm⁻³ DL- Threonine (1.0x10⁻⁴) mol dm⁻³, [H⁺] 1.0 mol dm⁻³ at different 298 K to 318 K temperatures. The rate of reaction increases slowly in the same temperature and at different temperatures increases with the presence of SDS anionic surfactant in Fig. 5.

3.5 Effect of Product

The effect of initially added product, Ce (III) was studied from 1.0 x10⁻⁴ to 5.0x10⁻⁴ mol dm⁻³ at fixed concentration of Ce (IV) = 5.0 x10⁻⁴ mol dm⁻³, [DL- threonine] = 5.0 x10⁻² mol dm⁻³, [H⁺] = 0.5 to 2.5 mol dm⁻³ at 298 K to 318 K. The significant effect on the rate of reaction was observed.

3.6 Effect of Temperature

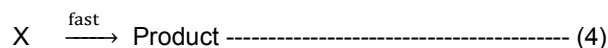
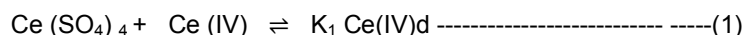
The effect of temperature was studied by varying the concentration of [DL- threonine] mol dm⁻³ to

1.0×10^{-2} to 5.0×10^{-2} mol dm⁻³ at fixed concentration of [H] = 1.0 mol dm⁻³ [Ce(IV)] = 5×10^{-3} mol dm⁻³ [SDS] = 5×10^{-3} mol dm⁻³ [CTAB] = 5×10^{-3} mol dm⁻³ [KCl] = 5×10^{-3} mol dm⁻³ at three temperature 298 K, 308 K and 318 K respectively. The rate of reaction initially increases with increasing the concentration of DL - threonine. The rate constant k of the slow step was obtained from the intercept of plot of k_{obs} vs. [DL - threonine]. The energy of activation was obtained by the plot of log k versus 1/T. The formation constant K of the first step was calculated from the plot of k_{obs} vs DL – threonine

at three temperatures. From different value of K at three temperatures, thermodynamics quantities were calculated from the plot of log k vs $\frac{1}{T}$ in Fig. 6.

4. DISCUSSION AND MECHANISM

An appropriate amount of continuous Ce (SO₄)₄ is taken to complicated Ce (IV) complex with so that cerium complex with amino acid. The following species are suggested for the oxidation of DL- threonine in presence of sulphuric acid.



$$\frac{-d[\text{Ce(IV)}]}{dt} = k_3 K_2 [\text{CAS}][\text{S}] \text{----- (5)}$$

It is expected that they are being used like the CAS; Ce (IV) with amino acids may remain in complex or diluent form [24]. The gradual disappearance rate of Ce (IV) is explained based on the equation.

$$k_{obs} = \frac{k_3 K_2 [\text{S}]}{k_3 K_2 [\text{S}] + K_1 \text{Ce(IV)}} \text{----- (6)}$$

The equation (6) can be rearranged as,

$$k_{obs} = \frac{1}{1 + \frac{K_1 [\text{Ce(IV)}]}{k_3 K_2 [\text{S}]}} \text{----- (7)}$$

The ratio of Ce and DL- threonine is 10^{-2} under experimental condition. For this equation (7) probably approximated to equation (8) without any serious errors.

$$k_{obs} = \frac{k_3 K_2 [\text{S}]}{K_1 \text{Ce(IV)}} \text{----- (8)}$$

The equation (8) is the rate law in agreement with our result. The graph plotted between 1/[Ce(IV)] vs k_{obs} is found to a straight line and its intercept value is not zero. Similarly the graph plotted between [DL - threonine] vs k_{obs} is linear.

At constant cerium (IV) concentration the rate law can be written as,

$$k_{obs} = A. [\text{DL- threonine}] \text{----- (9)}$$

Where $A = \frac{k_3 K_2 [\text{S}]}{K_1 \text{Ce(IV)}}$ is the slope value for the plot [DL- threonine] vs k_{obs} . The result suggest that DL- threonine combines with cerium (IV) to form complex, when the slow step with one mole of Ce(SO₄)₂ to gives the product cerium(IV), complex- DL – threonine and SO₄²⁻. It reacts with another mole of Ce (SO₄)₂ to give cerium (III), 3-imidazolepropanal, ammonia and carbon dioxide, as shown in scheme-1.

$$A' = \frac{k_3 K_2 [\text{S}]}{K_1}$$

It is interpreted as an indication for the correctness of the proposed mechanism that the slope values obtained for both curves should follow the relation.

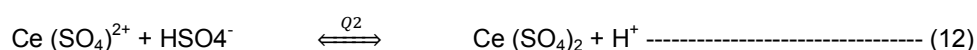
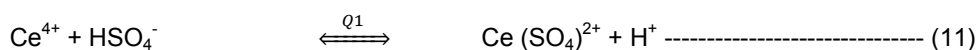
$$\frac{k_3 K_2}{K_1} = \frac{A'}{[\text{S}]} = A. [\text{Ce (IV)}] [\text{S}] = X \text{----- (10)}$$

The values of X calculated from the curves for the reactants and substrates. It is observed that there is a satisfactory agreement between these two values. The values are given as,

The reaction of Ce (IV) with DL- threonine in acidic medium show's a slow redox reaction to the present experimental condition. The concentration of H₂SO₄ increases when the concentration of HSO₄⁻ falls. Similarly the concentration of H⁺ increases the rate of reaction

decreases. It is inversely dependent on the HSO_4^- ion concentration rate. The rate of reaction was reducing on adding sulphuric acid. Added product Ce(III) inhibits the rate of reaction due to formation of Ce^{+4} to Ce^{+3} . The amino acid derived free radical again combines one molecules of Ce (IV) in a first step and gives the Ce (III) and ammonia. Under the experimental conditions cerium (IV) sulphato complex are in the form of $\text{Ce}(\text{SO}_4)^{2+}$, $\text{Ce}(\text{SO}_4)_2$ and $\text{HCe}(\text{SO}_4)_3$ and relevant equilibrium are as;

The value of equilibrium constants at 298 K Q_1 , Q_2 and Q_3 for the step (11) to (13) are reported to be 3500, 200 and 20 respectively through spectrophotometrically. Insignificant amount of unhydrolyzed species of cerium (IV) would also exist along with these sulphato complexes. This type of equation can be explained in equilibrium as a reactive species of bisulphate dependence generated form $\text{Ce}(\text{SO}_4)_2$ [25]. In which the concentration of this active species is given by the equation as;



$$[\text{Ce}(\text{SO}_4)_2] = \frac{[\text{Ce(IV)}]T}{1+Q_3[\text{HSO}_4^-]} = f[\text{Ce(IV)}]T \text{-----} (14)$$

Table 4.1. Variation of CTAB 298 K

| 10^{-4} [CTAB] mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.741 | 0.514 | 0.476 | 0.425 | 0.390 |
| 10 | 0.734 | 0.499 | 0.456 | 0.405 | 0.372 |
| 20 | 0.704 | 0.488 | 0.444 | 0.393 | 0.361 |
| 30 | 0.695 | 0.477 | 0.435 | 0.384 | 0.351 |
| 40 | 0.677 | 0.470 | 0.427 | 0.374 | 0.342 |
| 50 | 0.669 | 0.460 | 0.413 | 0.367 | 0.332 |
| 60 | 0.656 | 0.453 | 0.403 | 0.359 | 0.323 |
| 70 | 0.648 | 0.445 | 0.396 | 0.351 | 0.315 |
| 80 | 0.640 | 0.436 | 0.382 | 0.344 | 0.307 |
| 10^{-4} (k_{obs}), s ⁻¹ | 0.32 | 0.39 | 0.41 | 0.47 | 0.58 |

$$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}; [\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3};$$

$$[\text{H}^+] = 1.0 \text{ mol dm}^{-3}; \text{Temp.} = 298 \text{ K}$$

Table 4.2. Variation of CTAB 308 K

| 10^{-4} [CTAB] mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.763 | 0.641 | 0.586 | 0.523 | 0.485 |
| 10 | 0.734 | 0.601 | 0.523 | 0.453 | 0.409 |
| 20 | 0.696 | 0.539 | 0.471 | 0.408 | 0.364 |
| 30 | 0.667 | 0.490 | 0.437 | 0.367 | 0.331 |
| 40 | 0.620 | 0.449 | 0.405 | 0.345 | 0.302 |
| 50 | 0.595 | 0.427 | 0.377 | 0.314 | 0.283 |
| 60 | 0.558 | 0.359 | 0.341 | 0.289 | 0.257 |
| 70 | 0.520 | 0.339 | 0.317 | 0.265 | 0.235 |
| 80 | 0.490 | 0.320 | 0.298 | 0.234 | 0.209 |
| 10^{-4} (k_{obs}), s ⁻¹ | 0.82 | 1.42 | 1.59 | 1.85 | 2.04 |

$$[\text{Ce(IV)}] = 5.0 \times 10^{-4} \text{ mol dm}^{-3}; [\text{Thre}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3};$$

$$[\text{H}^+] = 1.0 \text{ mol dm}^{-3}; \text{Temp.} = 308 \text{ K}$$

Table 4. 3. Variation of CTAB 318 K

| 10^{-4} [CTAB] mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|---------------------------------------|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.233 | 0.221 | 0.207 | 0.195 | 0.156 |
| 10 | 0.202 | 0.196 | 0.167 | 0.153 | 0.121 |
| 20 | 0.159 | 0.151 | 0.153 | 0.123 | 0.098 |
| 30 | 0.126 | 0.146 | 0.139 | 0.115 | 0.086 |
| 40 | 0.115 | 0.132 | 0.128 | 0.098 | 0.074 |
| 50 | 0.103 | 0.122 | 0.117 | 0.091 | 0.067 |
| 60 | 0.092 | 0.109 | 0.108 | 0.083 | 0.058 |
| 70 | 0.084 | 0.081 | 0.097 | 0.075 | 0.051 |
| 80 | 0.076 | 0.062 | 0.089 | 0.069 | 0.047 |
| 10^{-4} mol dm ⁻³ | 1.42 | 2.19 | 2.32 | 2.87 | 3.15 |

[Ce(IV)] = 5.0×10^{-4} mol dm⁻³; [Thre] = 1.0×10^{-2} mol dm⁻³;
 [H⁺] = 1.0 mol dm⁻³; Temp. = 318 K

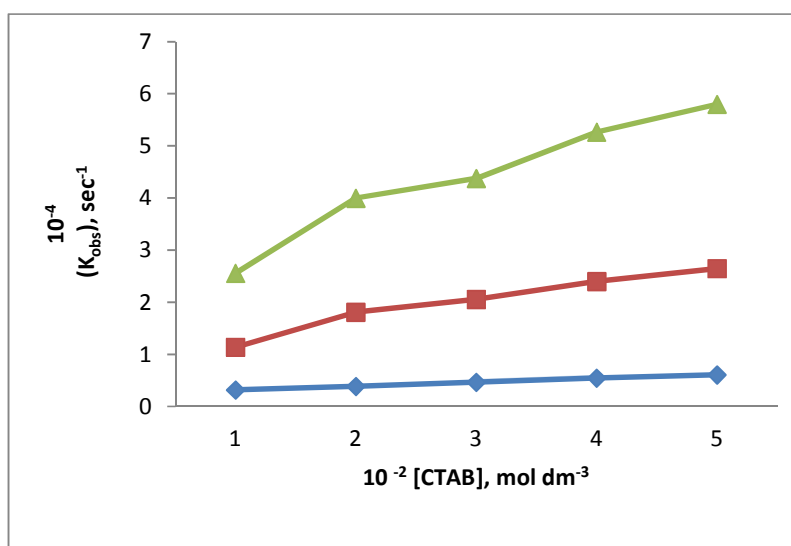


Fig. 4. Variation of CTAB

[Ce(IV)] = 5.0×10^{-4} mol dm⁻³; [Thre] = 1.0×10^{-2} mol dm⁻³;
 [H⁺] = 1.0 mol dm⁻³; Temp. = 298K, 308K, 318K
 (Ref Table 4.1, 4.2 and 4.3)

Table 5.1. Variation of SDS 298 K

| 10^{-4} [SDS] mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|--|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.291 | 0.264 | 0.257 | 0.249 | 0.231 |
| 10 | 0.286 | 0.256 | 0.249 | 0.241 | 0.223 |
| 20 | 0.282 | 0.252 | 0.245 | 0.237 | 0.219 |
| 30 | 0.278 | 0.250 | 0.241 | 0.239 | 0.215 |
| 40 | 0.274 | 0.245 | 0.237 | 0.226 | 0.211 |
| 50 | 0.270 | 0.244 | 0.234 | 0.223 | 0.207 |
| 60 | 0.266 | 0.242 | 0.231 | 0.222 | 0.203 |
| 70 | 0.263 | 0.241 | 0.238 | 0.220 | 0.200 |
| 80 | 0.260 | 0.240 | 0.228 | 0.217 | 0.197 |
| 10^{-4} (K _{obs}), s ⁻¹ | 0.25 | 0.30 | 0.34 | 0.36 | 0.40 |

[Ce(IV)] = 5.0×10^{-4} mol dm⁻³; [Thre] = 1.0×10^{-2} mol dm⁻³;
 [H⁺] = 1.0 mol dm⁻³; Temp. = 298 K

Table 5.2. Variation of SDS 308 K

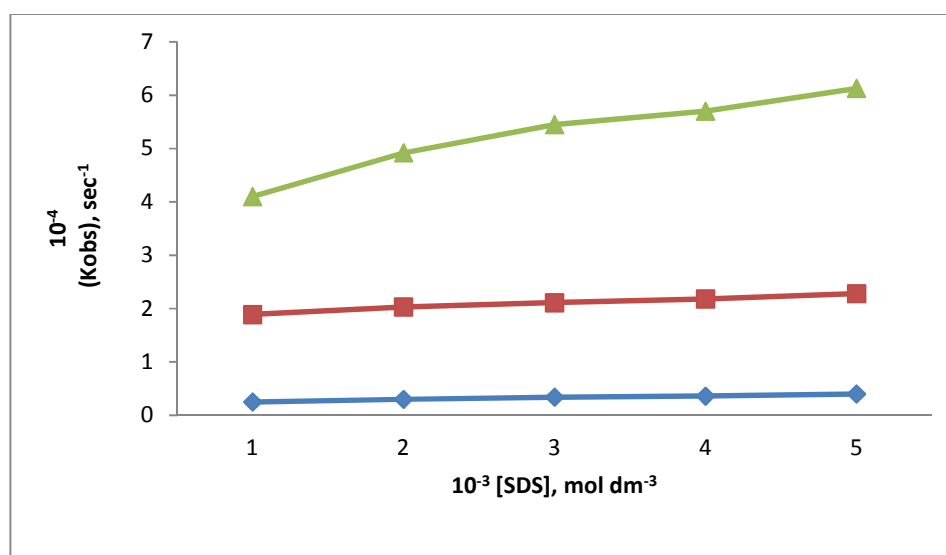
| 10^{-4} [CTAB] mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|--|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.663 | 0.470 | 0.434 | 0.277 | 0.239 |
| 10 | 0.573 | 0.401 | 0.371 | 0.236 | 0.203 |
| 20 | 0.523 | 0.374 | 0.341 | 0.215 | 0.185 |
| 30 | 0.485 | 0.337 | 0.311 | 0.196 | 0.168 |
| 40 | 0.446 | 0.315 | 0.289 | 0.182 | 0.157 |
| 50 | 0.421 | 0.291 | 0.267 | 0.169 | 0.146 |
| 60 | 0.401 | 0.272 | 0.249 | 0.156 | 0.135 |
| 70 | 0.388 | 0.261 | 0.234 | 0.148 | 0.123 |
| 80 | 0.384 | 0.249 | 0.227 | 0.141 | 0.118 |
| 10^{-4} (k _{obs}), s ⁻¹ | 1.64 | 1.73 | 1.77 | 1.82 | 1.85 |

$[Ce(IV)] = 5.0 \times 10^{-4}$ mol dm⁻³; $[Thre] = 1.0 \times 10^{-2}$ mol dm⁻³;
 $[H^+] = 1.0$ mol dm⁻³; Temp. = 308 K

Table 5.3. Variation of SDS 318 K

| 10^{-4} [CTAB] mol dm ⁻³ | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|--|------------|-------|-------|-------|-------|
| Time in minutes | Absorbance | | | | |
| 0 | 0.328 | 0.367 | 0.345 | 0.321 | 0.309 |
| 10 | 0.252 | 0.250 | 0.245 | 0.277 | 0.217 |
| 20 | 0.277 | 0.230 | 0.211 | 0.194 | 0.179 |
| 30 | 0.226 | 0.213 | 0.187 | 0.167 | 0.154 |
| 40 | 0.221 | 0.201 | 0.164 | 0.139 | 0.126 |
| 50 | 0.198 | 0.193 | 0.137 | 0.127 | 0.112 |
| 60 | 0.181 | 0.184 | 0.131 | 0.114 | 0.092 |
| 70 | 0.165 | 0.178 | 0.126 | 0.105 | 0.083 |
| 80 | 0.157 | 0.171 | 0.117 | 0.098 | 0.076 |
| 10^{-4} (k _{obs}), s ⁻¹ | 2.21 | 2.89 | 3.34 | 3.52 | 3.85 |

$[Ce(IV)] = 5.0 \times 10^{-4}$ mol dm⁻³; $[Thre] = 1.0 \times 10^{-2}$ mol dm⁻³;
 $[H^+] = 1.0$ mol dm⁻³; Temp. = 318 K

**Fig. 5. Variation of SDS**

$[Ce(IV)] = 5.0 \times 10^{-4}$ mol dm⁻³; $[Thre] = 1.0 \times 10^{-2}$ mol dm⁻³;
 $[H^+] = 1.0$ mol dm⁻³; Temp. = 298K, 308K, 318K
 (Ref Table 5.1, 5.2 and 5.3)

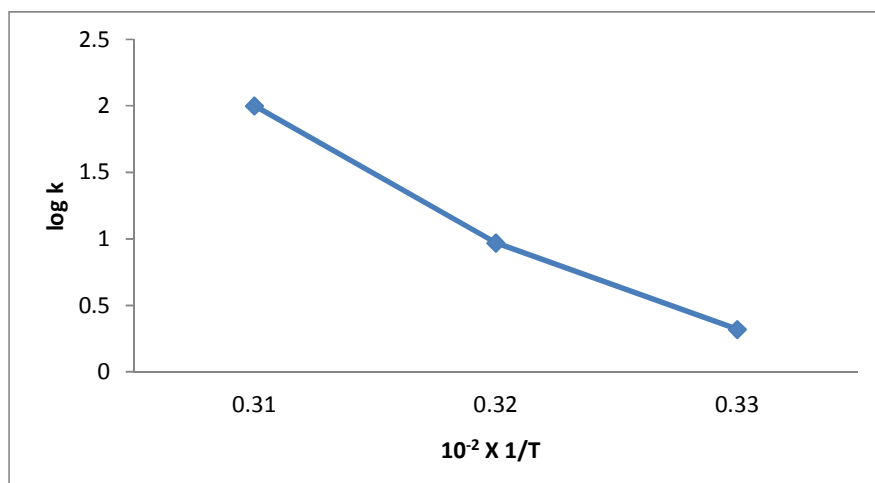


Fig. 6. plot of $\log k$ vs. $1/T$ that the reaction is Arrhenius plots shows the linear

Table 6. Kinetic and thermodynamic activation parameters for uncatalysed reaction at 298 K temperature

| Parameter | DL-threonine |
|--|--------------|
| E_a (kJ mol^{-1}) | 87.29 |
| ΔH^\ddagger (kJ mol^{-1}) | 91.03 |
| ΔS^\ddagger (J mol^{-1}) | -24.98 |
| ΔG^\ddagger (kJ mol^{-1}) | 97.30 |
| $\log A$ | 10.81 |

Thus equation (9) can be written as

$$K_{\text{obs}} = \frac{k_3 k_2 [S]}{k_1 [1 + Q_3 [HSO_3]} \quad \text{----- (15)}$$

$$\text{If } A = \frac{k_3 k_3 [S]}{k_1} \quad \text{----- (16)}$$

So equation become

$$K_{\text{obs}} = \frac{A}{1 + Q_3 [HSO_3]} \quad \text{----- (17)}$$

We have come to know by this equation that the plot in these forms a linear one by the k_{obs} vs $1/H_2SO_4$, who agree with the experimental data. The slope A/Q_3 and intercept $A/1$, which is in good agreement with the previously reported value. All of the above show the result of kinetics of the $Ce(SO_4)_2$ as a kinetically active species. The rate constant decreases with increasing $[H^+]$. This is due to formation of an active inhibition $H_2Ce(SO_4)_2^{2-}$. The thermodynamic parameters for uncatalysed have been evaluated. From Arrhenius plot, energy of activation (E_a) is calculated as shown in Fig. (6). The Table 6 shows that the value of k increase with increase of temperature indicates the reaction is

endothermic ($\Delta H^\ddagger > 0$). These have been assessed in the form of activation parameters to determine the rate as $E_a = 87.29 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 91.03 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -24.98 \text{ J mol}^{-1}$ and $\Delta G^\ddagger = 97.30 \text{ kJ mol}^{-1}$, $\log A = 10.81$ form the linear of plot of k versus $1/T$ Fig. (6). The major negative entropy of activation is in agreement with the formation of the activated complex involved in the reaction and the reaction of the compound are more ordered than the reactants. This supports the proposed mechanism. The value of the ΔH^\ddagger , and ΔS^\ddagger were indicates for electron transfer processes [26,27].

7. CONCLUSION

The oxidation of DL- threonine by Ce (IV) in acid medium has found to a slow rate, but by increasing the at temperature from 298 K to 318 K in uncatalyst, the rate of reaction increase. The oxidant and substrate under uncatalyst condition is found to first order. The thermodynamic physical parameter values are ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger increase with increase temperature. The main active species of cerium (IV) is considered as $Ce(SO_4)_2$, although other species are in lesser extent. The overall

mechanistic described here is consistent with product, kinetic and mechanistic study.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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