Research Article

Silver(I) Catalysis for Oxidation of L-Glutamine By Cerium(IV) in Perchlorate Solutions: Kinetics and Mechanistic Approach

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Abstract

The influence of silver(I) catalyst on the oxidation of L-glutamine (Gln) by cerium(IV) in perchlorate solutions was studied spectrophotometrically. The study was carried out at a constant ionic strength of 1.0 mod dm^{-3} and a temperature of 25^oC. In both uncatalyzed and Ag(I)-catalyzed paths, the reactions exhibited first order kinetics with respect to [Ce(IV)] and [Ag(I)], and less than unit order with respect to [Gln]. The reactions exhibited negative fractional-first order kinetics with respect to [H$^+$]. Increasing both ionic strength and dielectric constant increased the oxidation rates. Addition of cerium(III) ion as a reaction product did not affect the rates. The rate of Ag(I)-catalyzed oxidation was found to be about seven times higher than that of uncatalyzed one. $Ce(OH)3^+$ was suggested to be the kinetically active species of cerium(IV) under the experimental conditions. Probable mechanistic schemes for both uncatalysed and catalysed reactions are proposed. In both paths, the final oxidation products of L-glutamine are identified as formyl propanamide, ammonium ion, and carbon dioxide. The rate-law expressions consistent with the reactions mechanisms are derived. The activation parameters are evaluated and discussed.

Keywords: Kinetics; Mechanism; L-Glutamine; Cerium(IV); Oxidation; Silver(I)

Introduction

L-Glutamine is a non-essential α-amino acid that is employed in the biosynthesis of proteins. Glutamine plays an essential role in a variety of biochemical functions [1-3]. In human blood, glutamine is the most abundant free amino acid. Production of glutamine in the body often slows down with age and does not generate sufficient quantities. It also plays a decisive role in keeping a balanced acid-base ratio. Glutamine can be converted to glucose in the kidneys, without effecting glucagon or insulin levels. There are also indications that glutamine can reduce the demand for sugar and alcohol [2,3]. Generally, due to the biological importance of amino acids, the kinetics and mechanistic studies of their oxidation by a variety of oxidants have received considerable attention [4-24].

Cerium(IV) has been widely employed as an oxidant in mechanistic studies in acid media especially in sulphuric acid solutions [25-36]. Cerium(IV) is less stable in aqueous nitric and perchloric acid solutions [37-41]. The oxidant has rarely been employed in perchloric acid medium probably due to the presence of dimers and polymers of cerium(IV) in such medium [39-41]. Identification of kinetically active Ce(IV) species [26,27] is a problem during studies of the kinetics and mechanisms of cerium(IV) oxidation in aqueous sulphuric acid solutions using different types of organic and inorganic substrates. In aqueous sulphuric acid solutions, cerium(IV) can exist as a mixture of different types of sulphate species such as $Ce(SO4)^{2+}$, $Ce(SO_4)_2$, $HCe(SO_4)_3^-$ and $H_3Ce(SO_4)_4^-$ [25-30].
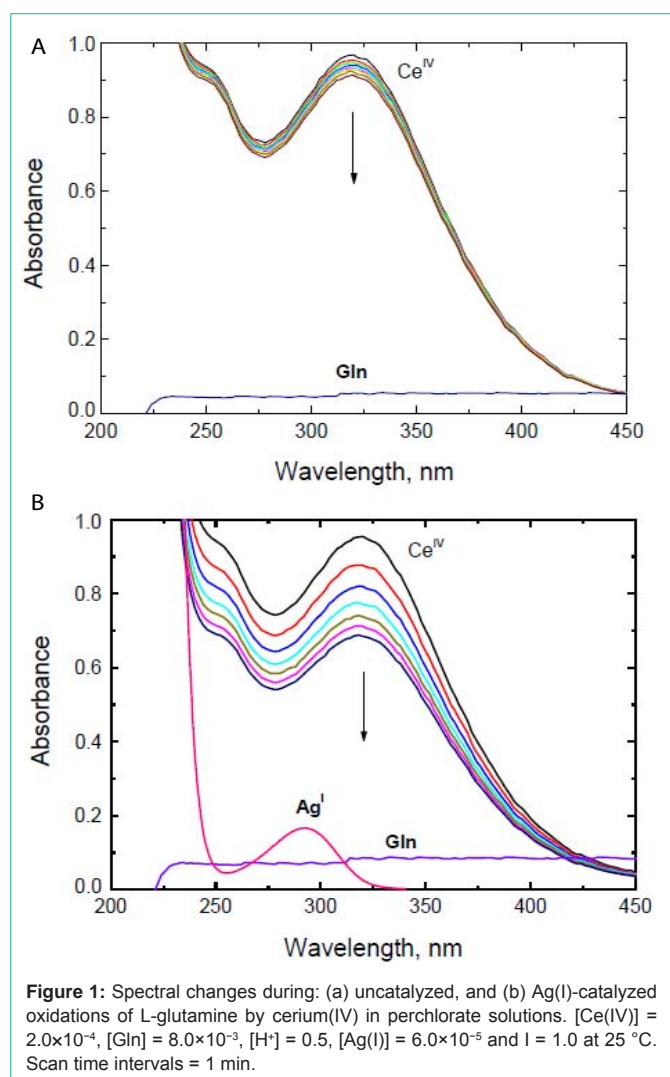
A Literature survey revealed no work has been done on the kinetics and mechanism of the oxidation of L-glutmine by cerium(IV) in the absence or presence of a catalyst. This observation prompted us to investigate the title reactions. We aim to investigate the selectivity of L-glutamine towards cerium(IV) in perchlorate solutions, to understand the active species of the oxidant in this medium, to check the catalytic activity of Ag(I) towards L-glutamine oxidation, and to elucidate plausible oxidation mechanisms.

Experimental and Methods

Materials

The stock solution of L-glutamine was prepared by dissolving the required amount of the sample (E. Merck) in double-distilled water. A solution of cerium(IV) was freshly prepared by dissolving ceric ammonium sulphate (S.D. Fine Chem.) in a 1.0 mol $dm-3$ sulfuric acid solution, then diluting with double-distilled water and kept overnight. The concentration of cerium(IV) solution was determined as reported earlier [42]. Cerium(III) solution was also prepared by dissolving cerium(III) acetate sample (S.D. Fine Chem.) in double-distilled water. Sodium perchlorate and acetic acid were used to vary the ionic strength and dielectric constant of the medium, respectively.

Kinetic measurements

The kinetic runs for uncatalyzed and catalysed reactions were followed under conditions in which [Gln] >> [Ce(IV)]. The progress of the reactions was followed by monitoring the decay of cerium(IV) absorbance as a function of time at its absorption maximum, λ =

Figure 1: Spectral changes during: (a) uncatalyzed, and (b) Ag(I)-catalyzed oxidations of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4}, [Gln] = 8.0×10^{-3}, [H$^+$] = 0.5, [Ag(I)] = 6.0×10^{-5} and I = 1.0 at 25 °C. Scan time intervals = 1 min.

315nm, where the other reactions constituents were not significantly absorbed at this wavelength. The absorbance measurements were conducted on a temperature-controlled Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer.
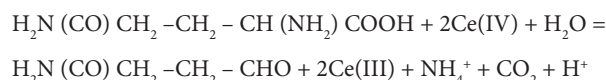
The observed first order rate constants of uncatalyzed and catalyzed reactions (k_U and k_C) were calculated using non-linear least-squares fitting to ln Abs. - time plots. The observed rate constants were the mean values of at least two kinetic run. The rate constants were reproducible to within 2-3%. Whereas the reaction between cerium(IV) and L-glutamine in perchlorate solutions proceeded with a slow rate in the absence of Ag(I) catalyst, the catalyzed reaction is thought to carried out in a parallel path with the contributions from both uncatalyzed and catalyzed paths. Therefore, the total rate constant (kT) is equal to $k_U + k_C$.

Results

Stoichiometry and product analysis

Different mixtures of the reactions with an excess of cerium(IV) concentration at [H$^+$] = 0.5 mol dm^{-3} and at I = 1.0 mol dm^{-3}, have been equilibrated for about 24h at room temperature. The stoichiometry, determined spectrophotometrically and by titration, indicated the

consumption of two Ce(IV) ions per one molecule of L-glutamine yielding the final products as in the following equation,

$$H_2N (CO) CH_2 - CH_2 - CH (NH_2) COOH + 2Ce(IV) + H_2O =$$

$$H_2N (CO) CH_2 - CH_2 - CHO + 2Ce(III) + NH_4^+ + CO_2 + H^+$$

The above stoichiometric equation is consistent with the results of product analysis. The products were identified as the corresponding aldehyde (formyl propanamide) by spot test [43], ammonia by Nessler's reagent [44] and carbon dioxide by lime water. The product, formyl propanamide was also identified by 2,4-dinitophenyhydrazine [44].

Spectral changes

The spectral changes during the oxidation of L-glutamine by

Table 1: Effect of variation of [Ce(IV)], [Gln], [H$^+$], [Ag(I)] and I on the observed first order rate constants in the uncatalyzed and Ag(I)-catalyzed oxidations of L-glutamine by cerium(IV) in perchlorate solutions at 25 °C.

| 10^4 [Ce(IV)] (mol dm^{-3})	10^3 [Gln] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	10^5 [Ag(I)] (mol dm^{-3})	I (mol dm^{-3})	10^5 k_U (s^{-1})	10^5 k_C (s^{-1})
0.5	8.0	0.5	6.0	1.0	17.6	119.8
1.0	8.0	0.5	6.0	1.0	16.5	121.0
2.0	8.0	0.5	6.0	1.0	17.3	122.4
3.0	8.0	0.5	6.0	1.0	17.7	121.7
4.0	8.0	0.5	6.0	1.0	15.9	120.0
5.0	8.0	0.5	6.0	1.0	17.8	122.6
2.0	**2.0**	0.5	6.0	1.0	5.6	43.1
2.0	**4.0**	0.5	6.0	1.0	9.5	73.7
2.0	**6.0**	0.5	6.0	1.0	13.0	97.4
2.0	**8.0**	0.5	6.0	1.0	17.3	122.4
2.0	**10.0**	0.5	6.0	1.0	21.7	148.0
2.0	**12.0**	0.5	6.0	1.0	24.9	171.2
2.0	8.0	**0.1**	6.0	1.0	41.7	214.1
2.0	8.0	**0.3**	6.0	1.0	25.2	159.3
2.0	8.0	**0.5**	6.0	1.0	17.3	122.4
2.0	8.0	**0.7**	6.0	1.0	13.4	95.0
2.0	8.0	**0.9**	6.0	1.0	10.2	77.1
2.0	8.0	**1.0**	6.0	1.0	8.9	68.4
2.0	8.0	0.5	**2.0**	1.0	17.3	39.6
2.0	8.0	0.5	**4.0**	1.0	17.3	80.4
2.0	8.0	0.5	**6.0**	1.0	17.3	122.4
2.0	8.0	0.5	**8.0**	1.0	17.3	159.7
2.0	8.0	0.5	**10.0**	1.0	17.3	195.1
2.0	8.0	0.5	**12.0**	1.0	17.3	229.7
2.0	8.0	0.5	6.0	**1.0**	17.3	122.4
2.0	8.0	0.5	6.0	**1.4**	19.8	129.7
2.0	8.0	0.5	6.0	**1.8**	23.1	136.1
2.0	8.0	0.5	6.0	**2.2**	25.9	143.2
2.0	8.0	0.5	6.0	**2.6**	28.2	149.7
2.0	8.0	0.5	6.0	**3.0**	30.4	154.0

Experimental error ±3%.

cerium(IV) in perchlorate solutions in the absence and presence of Ag(I) catalyst are shown in Figure 1a and 1b, respectively. In both cases, the spectra indicate gradual disappearance of the Ce(IV) band at its absorption maximum as a result of its reduction to Ce(III).

Order of reactions

The order of uncatalyzed and catalyzed reactions with respect to the reactants was determined from the slopes of the plots of log k_U and log k_C versus log(concentration) by varying the concentrations of L-glutamine, perchloric acid, and Ag(I) catalyst, in turn, while keeping all other conditions constant.

The concentration of the oxidant, cerium(IV), was varied in both uncatalyzed and catalyzed reactions in the range of 0.5×10^{-4} to 5.0×10^{-4} mol dm^{-3}, keeping all other variables constant. Plots of ln(absorbance) versus time were linear up to about two-half lives of the reaction completion. Furthermore, an increase in the initial oxidant concentration did not alter the oxidation rates of L-glutamine as listed in Table 1. These results indicate that the order of reactions with respect to [Ce(IV)] is one.

The observed rate constants were determined at different initial concentrations of the reductant L-glutamine while other variables were kept constant. Increasing [Gln] increases the rates of the reactions as listed in Table 1. Plots of the observed first order rate constants versus [Gln] are linear with positive intercepts as shown in Figure 2, confirming less than unit order kinetics on [Gln].
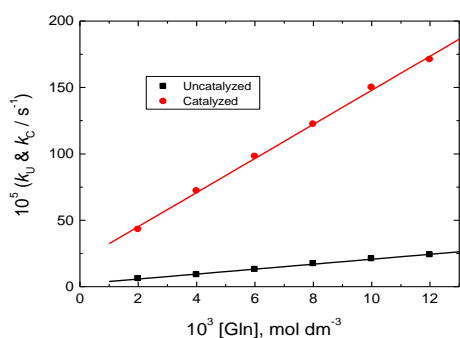
Figure 2: Effect of [Gln] on the observed first order rate constants in the uncatalyzed and Ag(I)-catalyzed oxidations of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4}, [H$^+$] = 0.5, [Ag(I)] = 6.0×10^{-5} and I = 1.0 mol dm^{-3} at 25 °C.
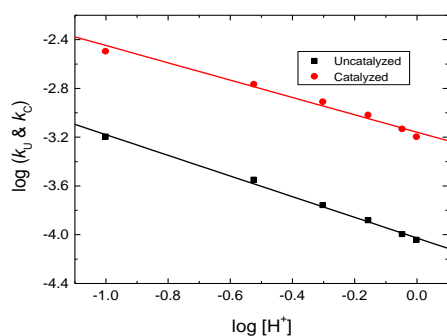
Figure 3: Plots of log k_U and log k_C versus log [H$^+$] in the uncatalyzed and Ag(I)-catalyzed oxidations of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4}, [Gln] = 8.0×10^{-3}, [Ag(I)] = 6.0×10^{-5} and I = 1.0 mol dm^{-3} at 25 °C.
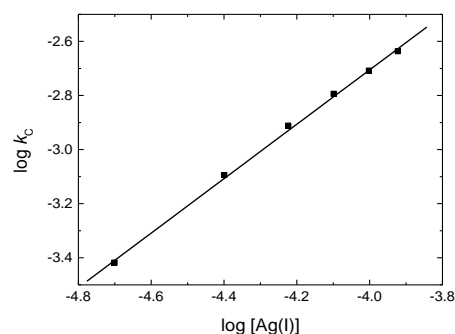
Figure 4: Plot of log k_C versus log [Ag(I)] in the Ag(I)-catalyzed oxidations of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4}, [Gln] = 8.0×10^{-3}, [H$^+$] = 0.5 and I = 1.0 mol dm^{-3} at 25 °C.

In order to study the effect of hydrogen ion concentration on the rates of the reactions, kinetic runs were carried out by varying the perchloric acid concentration (0.1 – 1.0 mol dm^{-3}) keeping the concentrations of all other reactants constant. It was observed that the rates of the reactions decrease with increasing [H$^+$] in both cases (Table 1). Plots of log k_U and log k_C versus [H$^+$] were linear with negative slopes of less than unity (Figure 3) confirming negative fractional-first order dependences with respect to [H$^+$].

To evaluate the reaction orders with respect to the concentrations of Ag(I) catalyst, the reaction rate was measured at various [Ag(I)], $(2.0–12.0) \times 10^{-5}$ mol dm^{-3}, while other variables were kept constant. The reaction rate increased as [Ag(I)] increased (Table 1). The order with respect to Ag(I) was found to be less than unity, as determined from the plot of log k_C versus log [Ag(I)], as shown in Figure. 4.

Effect of ionic strength and dielectric constant

The effect of ionic strength on the rates of uncatalyzed and catalyzed reactions was studied by varying the ionic strength in the range of 1.0-3.0 mol dm^{-3} using sodium perchlorate while maintaining the concentrations of all other reactants constant, and at constant pH and temperature. Increasing the ionic strength of the medium increased the rates of reactions and the Debye–Huckel plots were linear with positive slopes (Figure 5a).

In order to determine the effect of the dielectric constant (D) of the medium on the reaction rates, the reactions were studied at different solvent compositions (vol%) of acetic acid and water. At different compositions, D of the medium was calculated using the D values for water (78.5) and acetic acid (6.15) at 25 °C. The rate constants clearly decreased as D of the solvent decreased (i.e., increasing acetic acid content). Plots of log k_U and log k_C versus 1/D were linear with negative slopes (Figure 5b).

Effect of initially added product

The effect of added cerium(III) was studied over the concentration range $(0.5 – 5.0) \times 10^{-4}$ mol dm^{-3} at fixed concentrations of other reactants. Addition of Ce(III) did not affect significantly the rates of both uncatalysed and catalysed reactions.

Effect of temperature

The rates of the reactions were carried out at five different temperatures (288 - 308 K) at constant concentrations of the reactants and all other conditions being constant. The results indicate that the
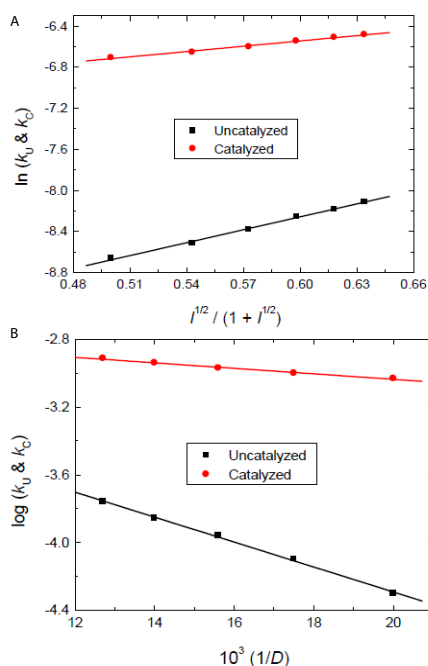
Figure 5: Effect of a) ionic strength, and b) dielectric constant of the reaction medium on the rate constants in the uncatalyzed and Ag(I)-catalyzed oxidations of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4}, [Gln] = 8.0×10^{-3}, [H+] = 0.5, [Ag(I)] = 8.0×10^{-5} and I = 1.0 mol dm^{-3} at 25 °C.

rate constants increased with the rise in temperature. The activation parameters of the second order rate constant (k') are calculated using Arrhenius Eyring plots and are listed in Table 2.

Table 2: Activation parameters of k' in the uncatalyzed and Ag(I)-catalyzed oxidations of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4}, [Gln] = 6.0×10^{-3}, [H+] = 0.5, [Ag(I)] = 8.0×10^{-5} and I = 1.0 mol dm^{-3}.

Reaction	$\Delta S^{\neq}$, Jmol^{-1}K^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta G^{\neq}_{298}$, kJ mol^{-1}	$E_a^{\neq}$, kJ mol^{-1}
Uncatalyzed	−94.08	49.12	77.15	52.11
Catalyzed	−112.14	37.7	71.11	39.02

Experimental error = ±3.0.

Test for free radical intermediates

Known quantities of acrylonitrile scavenger were added to samples of the reactions mixtures that had been kept in inert atmosphere for about 6h. White precipitates were formed upon diluting the reactions mixtures with methanol indicating free radicals intervention in the reactions. When the experiments were repeated in the absence of L-glutamine under similar conditions, the tests were negative. These tests indicated that the reactions proceeded through free radical paths.

Discussion

It was reported earlier [45-47] the active species of Ce(IV) in perchloric acid medium was suggested to be either Ce^{4+}, Ce(OH)$^{3+}$ and Ce(OH)$_2^{2+}$ or (Ce–O–Ce)6$^+$ and (HOCe–O–CeOH)$^{4+}$. However, it showed from the spectrophotometric studies [48] that Ce^{4+} is proposed to the predominant species at [H+] ≥ 1.0 mol dm^{-3} up to [Ce(IV)] = 1.5 x 10^{-3} mol dm^{-3}, whereas the other species are more predominant at [H+] < 0.8 mol dm^{-3}. Under the present experimental

conditions of low [H+] and deceasing rates of reactions with the increase in [H+], Ce(OH)$^{3+}$ may be considered as the active species of Ce(IV) according to the equilibrium,

$$Ce^{4+} + H_2O \xrightarrow{K_{OH}} Ce(OH)^{3+} + H^+$$

Also, it is reported [22,24,49,50] that in acid solutions, amino acids exist in zwitterions and predominantly tend to protonate at higher acid concentrations according to the following equilibria,

$$R\text{-}CH(NH_2)COOH \rightleftharpoons R\text{-}CH(^+NH_3)COO^- \quad \text{(zwitterion)}$$

$$R\text{-}CH(NH_3)^+COO^- \xrightarrow{H^+} R\text{-}CH(NH_3)^+COOH \quad \text{(protonated species)}$$

Where R-CH(NH$_2$)COOH and R-CH(+NH$_3$)COOH denote the amino acid and its protonated form.
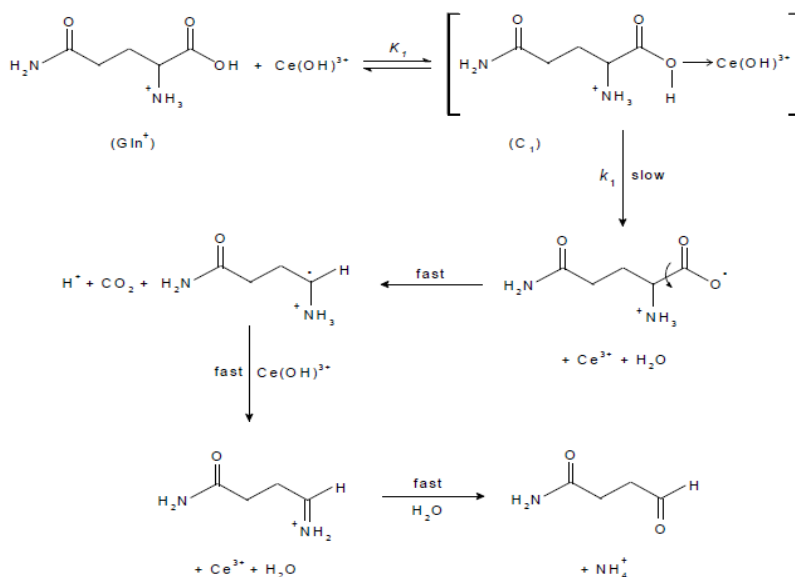
Mechanism of uncatalyzed oxidation

The reaction between L-glutamine and cerium(IV) in perchlorate solutions in the absence of silver(I) catalyst has a stoichiometry of 1:2, i.e., one mole of Gln requires two moles of Ce(IV). The reaction exhibits a first order dependence with respect to [Ce(IV)], less than unit order with respect to [Gln] and negative fractional order in [H+]. The less than unit order with respect to L-glutamine concentration may be interpreted by formation of an intermediate complex (C_1) between the protonated L-glutamine (Gln$^+$) and the kinetically active species of cerium(IV), Ce(OH)$^{3+}$. Increasing the oxidation rate with increasing both ionic strength and dielectric constant supports that the reaction was between two similarly charged ions [51,52]. Formation of an intermediate complex is proved kinetically by the non-zero intercept of the plot of $1/k_U$ versus $1/[Gln]$ (Figure 6).
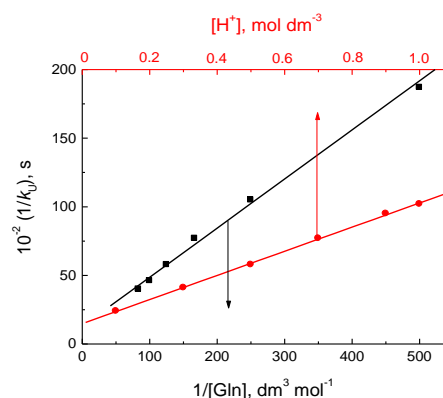
Figure 6: Plots of $1/k_U$ versus $1/[Gln]$ and [H+] in the uncatalyzed oxidation of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4} and I = 1.0 mol dm^{-3} at 25 °C.

This kinetic result favours the possible formation of an intermediate complex between the oxidant and substrate [53]. Furthermore, complex formation was supported by the obtained negative value of the entropy of activation (Table 2), which corresponds to the decrease in the degrees of freedom accompanying the transition from the initial state to the transition state [54,55]. The positive values of both DH≠ and DG≠ indicate endothermic formation of the intermediary complex and its non-spontaneity, respectively.

The oxidation reaction is proposed to be a one-electron process in the rate-determining step, which leads to decomposition of

Scheme 1: Mechanism of uncatalyzed oxidation of L-glutamine by cerium(IV) in perchlorate solution.

the intermediate complex forming an intermediate radical and Ce(III) ion. The formation of a free radical is evident through the acrylonitrile polymerization test. The rate was not affected by Ce(III), suggesting that the reaction step involving decomposition of the intermediate complex into L-glutamine free radical and Ce(III) ion may not be a reversible process. The rate-determining step should be irreversible, which is generally the case for one electron oxidants [56]. Next, decarboxylation of the free radical occurred, forming a new radical intermediate and the latter was rapidly attacked by another Ce(OH)$^{3+}$ species to yield the final oxidation products. The suggested mechanism was illustrated in Scheme 1.

The suggested mechanism leads to the following rate law expression (Appendix A),

$$\text{Rate} = \frac{k_1 K_{OH} K_1 [\text{Ce(IV)}][\text{Gln}]}{[\text{H}^+] + K_{OH} + K_{OH} K_1 [\text{Gln}]} \quad (1)$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (2),

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = K_U [\text{Ce(IV)}] \quad (2)$$

Comparing Eqs. (1) and (2), the following relationship is obtained,

$$k_U = \frac{k_1 K_{OH} K_1 [\text{Gln}]}{[\text{H}^+] + K_{OH} + K_{OH} K_1 [\text{Gln}]} \quad (3)$$

The rate law (3) is consistent with all the observed orders with respect to different species, which can be verified by rearranging to the following equations,

$$\frac{1}{k_U} = \left(\frac{[\text{H}^+] + K_{OH}}{k_1 K_{OH} K_1} \right) \frac{1}{[\text{Gln}]} + \frac{1}{k_1} \quad (4)$$

$$\frac{1}{k_U} = \left(\frac{1}{k_1 K_{OH} K_1 [\text{Gln}]} \right)[\text{H}^+] + \frac{1}{k_1 K_1 [\text{Gln}]} + \frac{1}{k_1} \quad (5)$$

According to Eqs. (4) and (5), the plots of $1/k_U$ versus $1/[\text{Gln}]$ at constant [H$^+$], and $1/k_U$ versus [H$^+$] at constant [Gln] should be linear with positive intercepts and are found to be so as shown in

Figure 6. From the slopes and intercepts of such plots, the values of k_1, K_1 and K_{OH} are calculated to be 7.2 x 10^{-4} s^{-1}, 1.8 x 10^3 dm^3 mol^{-1} and 22.2 x 10^{-3}, respectively.

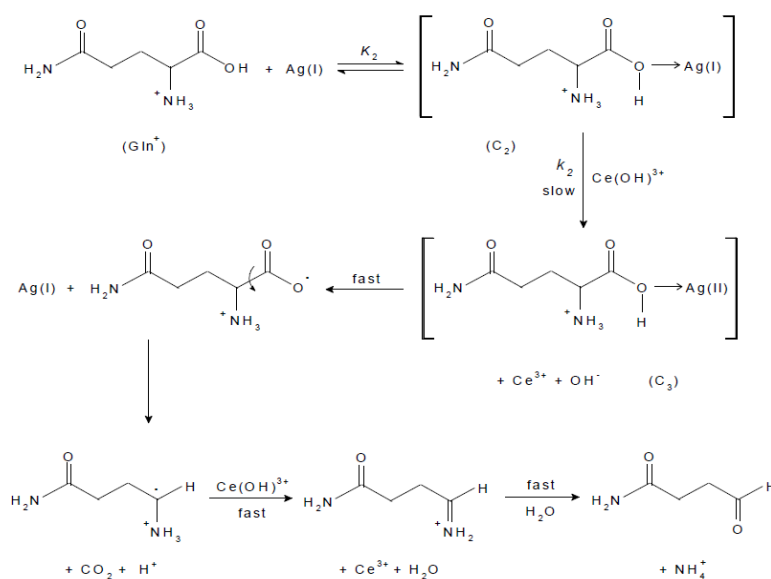## Mechanism of silver(I)-catalyzed oxidation

The kinetics of the oxidation of L-glutamine by cerium(IV) in perchlorate solutions in the presence of small amounts of silver(I) catalyst is similar to that for the uncatalyzed reaction. In addition, the reaction shows a first order dependence with respect to silver(I) concentration. The less than unit order for the concentration of Gln suggests formation of a complex between the protonated glutamine and Ag(I) catalyst prior to reaction with the oxidant. Complex formation was also proved kinetically by non-zero intercepts of the plots of [Ag(I)]/kC versus 1/[Gln] (Figure 7). The complex reacts in a slow step with Ce(OH)$^{3+}$ to give rise to the intermediate radical and Ce(III) ion with regeneration of the catalyst. This is followed by decarboxylation of Gln free radical, forming a new radical intermediate which is rapidly attacked by another Ce(OH)$^{3+}$ species
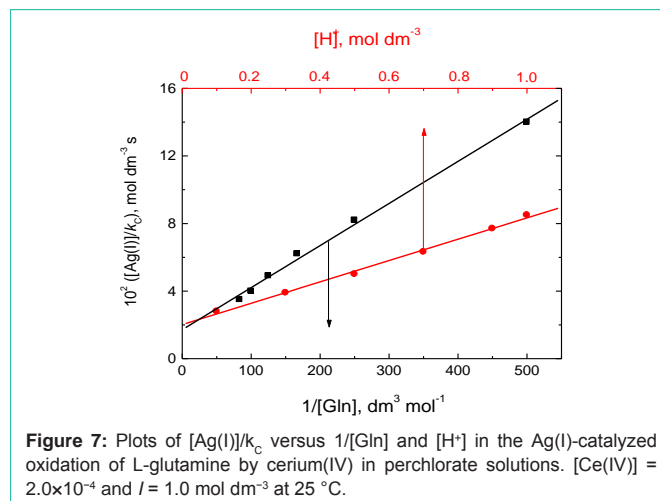
Figure 7: Plots of [Ag(I)]/k$_C$ versus 1/[Gln] and [H$^+$] in the Ag(I)-catalyzed oxidation of L-glutamine by cerium(IV) in perchlorate solutions. [Ce(IV)] = 2.0×10^{-4} and I = 1.0 mol dm^{-3} at 25 °C.
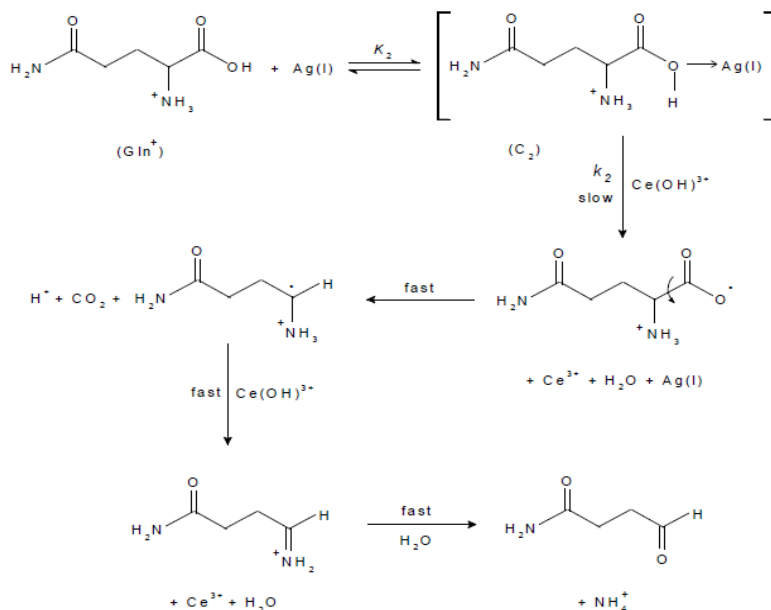
Scheme 2: Mechanism of Ag(I)-catalyzed oxidation of L-glutamine by cerium(IV) in perchlorate solution.

Scheme 3: An alternative mechanism of Ag(I)-catalyzed oxidation of L-glutamine by cerium(IV) in perchlorate solution.

to yield the final oxidation products as illustrated in Scheme 2.

An alternative reaction mechanism [27,57] for metal ion-catalyzed oxidation may be proposed. It involves formation of an intermediary complex between the metal ion catalyst, Ag(I), and the amino acid (C_2), that on further interaction with Ce(IV) in the rate-determining step yields another complex (C_3) of a higher valence silver ion, Ag(II), and Ce(III) ion. Such a complex rapidly decomposes giving rise to the intermediate radical with regeneration of the catalyst Ag(I), followed by subsequent fast steps to yield the final oxidation products as illustrated in Scheme 3.

In a similar manner to the uncatalyzed reaction, the proposed mechanism leads to the following rate law expression (Appendix B),

$$\text{Rate} = \frac{k_2 K_{OH} K_2 [\text{Ce(IV)}][\text{Gln}][\text{Ag(I)}]}{([\text{H}^+] + K_{OH})(1 + K_2[\text{Gln}])} \quad (6)$$

Under pseudo-first order condition, the rate-law can be expressed by Eq. (7),

$$\text{Rate} = \frac{-d[\text{Ce(IV)}]}{dt} = k_C[\text{Ce(IV)}] \quad (7)$$

Comparing Eqs. (6) and (7), the following relationship is obtained,

$$k_C = \frac{k_2 K_{OH} K_2 [\text{Gln}][\text{Ag(I)}]}{([\text{H}^+] + K_{OH})(1 + K_2[\text{Gln}])} \quad (8)$$

The rate law (8) is consistent with all the observed orders with respect to different species, which can be verified by rearranging to

the following equations,

$$\frac{[Ag(I)]}{k_C} = \left(\frac{[H^+] + K_{OH}}{k_2 K_{OH} K_2} \right) \frac{1}{[Gln]} + \frac{[H^+] + K_{OH}}{k_2 K_{OH}}$$

$$\text{(9)}$$

$$\frac{[Ag(I)]}{k_C} = \left(\frac{1 + K_2[Gln]}{k_2 K_{OH} K_2 [Gln]} \right) [H^+] + \frac{1 + K_2[Gln]}{k_2 K_2 [Gln]}$$

$$\text{(10)}$$

According to Eqs. (9) and (10), plots of $[Ag(I)]/k_C$ versus $1/[Gln]$ at constant $[H^+]$, and $[Ag(I)]/k_C$ versus $[H^+]$ at constant $[Gln]$ should be linear with positive intercepts on $[Ag(I)]/k_C$ axes and are found to be so as shown in Figure 7. From the slopes and intercepts of such plots, the values of K_2 and K_{OH} are calculated to be 70.8 dm^3 mol^{-1} and 23.2 x 10^{-3}, respectively. Also, the value of k_2 is evaluated form the slope or intercept of any plot to be 381.6 dm^3 mol^{-1} s^{-1}.

Conclusion

The catalytic effect of silver(I) ion on the oxidation of L-glutamine by cerium(IV) in perchlorate solutions was studied. The rate of Ag(I)-catalyzed oxidation was found to be about seven times higher than that of uncatalyzed one. Ce(OH)$^{3+}$ was suggested to be the kinetically active species of cerium(IV). In both paths, the final oxidation products of L-glutamine are identified as formyl propanamide, ammonium ion, and carbon dioxide.

Appendix

http://austinpublishinggroup.com/chemical-engineering/fulltext/ace-v3-id1037-Appendix.docx

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