



ORIGINAL ARTICLE

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

T. Sumathi <sup>a,\*</sup>, P. Shanmuga Sundaram <sup>b</sup>, G. Chandramohan <sup>c</sup>

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

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

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

Received 7 June 2010; accepted 3 July 2010

Available online 8 July 2010

## KEYWORDS

Kinetics;  
Oxidation;  
L-Alanine;  
Ag(I) catalysis;  
Ce(IV);  
H<sub>2</sub>SO<sub>4</sub> medium

**Abstract** The kinetics and mechanism of Ag(I)-catalyzed oxidation of L-alanine by cerium (IV) in sulfuric acid media have been investigated by titrimetric technique of redox in the temperature range of 298–313 K. It is found that the reaction is of first order with respect to Ce(IV) and L-alanine, and it is of a positive fractional order with respect to Ag(I). It is found that the pseudo first order ( $[L\text{-alanine}] \gg [Ce(IV)] \gg [Ag(I)]$ ) rate constant  $k'$  increases with the increase of  $[H^+]$ . The major oxidation product of alanine has been identified as acetaldehyde by an <sup>1</sup>H NMR and IR spectroscopy. Under the experimental conditions, the kinetically active species has been found to be Ce<sup>4+</sup>. Under nitrogen atmosphere, the reaction system can initiate the polymerization of acrylonitrile, indicating generation of free radicals. On the basis of the experimental results, a suitable mechanism has been proposed. The rate constants of the rate-determining step together with the activation parameters were evaluated.

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

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

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

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

Peer-review under responsibility of King Saud University.

doi:10.1016/j.arabjc.2010.07.002



## 1. Introduction

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

et al., 1977), Os(VIII)-Fe(CN)<sub>6</sub><sup>3-</sup> (Upadhyay and Agrawal, 1977), Chloramine-T (Mahadevappa et al., 1981), 1-chlorobenzotriazole (Hiremath et al., 1987), *N*-bromosuccinimide (Gopalkrishnan and Hogg, 1985; Schonberg et al., 1951), and Peroxomonosulfate (PMS) (Ramachandran and Vivekanandan, 1984) in acid and alkaline media has been reported. Oxidation of alanine has received much attention because of the involvement in the biological process such as stability of glucose in the system and is associated with chronic fatigue as well as Epstein-Barr virus, when alanine level becomes excessive (Shanmugam, xxxx).

Ce(IV) is a well known oxidant (Thabaj et al., 2006) in acid media having the reduction potential (Day and Selbin, 1964) of the couple Ce(IV)/Ce(III): 1.70 V. The oxidation of organic compounds by Ce(IV) in general seems to proceed via the formation of an intermediate complex (Yatsimirskii and Luzan, 1965).

The sluggish reaction of Ce(IV) oxidation of L-alanine is catalyzed by a small amount of Ag<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 (Thabaj et al., 2006; Kharzeeva and Serebrennikov, 1967) of Ce(IV) form exist such as Ce(OH)<sup>3+</sup>, Ce(SO<sub>4</sub>)<sub>2</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, increase in the rate of reaction with increasing sulfuric acid concentration has not been understood. The mechanism may be quite complicated due to the formation of different Ce(IV) complexes in the form of active species. Hence, Ag(I)-catalyzed oxidation of L-alanine by Ce(IV) has been investigated in order to understand the behavior of active species of oxidant in sulfuric acid media and a suitable mechanism is proposed.

## 2. Experimental

### 2.1. Materials

In the present work, double distilled water was used for preparing the solutions. L-alanine (E. Merck) was used as such. A stock solution of L-alanine was prepared by dissolving it in water. The Ce(IV) stock solution was obtained by dissolving cerium (IV) ammonium sulfate (E. Merck) in 0.98 mol dm<sup>-3</sup> sulfuric acid and was standardized with iron (II) ammonium sulfate solution (Jeffery and G.H., 1996). Other chemicals and reagents such as sodium sulfate, potassium sulfate, potassium bisulfate, silver nitrate, sulfuric acid, acetonitrile, acetone, hydrated copper sulfate, and aluminum sulfate used were of analytical grade with 99.9% purity.

### 2.2. Kinetic measurements

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

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

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

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

## 3. Results

Factors influencing the rate of oxidation of L-alanine by Ce(IV) such as effects of (i) [L-alanine], (ii) [Ce(IV)], (iii) [H<sup>+</sup>], (iv) ionic strength, (v) dielectric constant, (vi) monovalent (Ag<sup>+</sup>), and (vii) Bivalent (Cu<sup>2+</sup>) and trivalent (Al<sup>3+</sup>) catalysts have been studied. Rate and activation parameters were evaluated.

### 3.1. Effect of [L-alanine]

At a constant [Ce(IV)] (6 × 10<sup>-3</sup> mol dm<sup>-3</sup>), [H<sup>+</sup>] (0.05 mol dm<sup>-3</sup>) [Na<sub>2</sub>SO<sub>4</sub>] (0.1 mol dm<sup>-3</sup>) and [Ag<sup>+</sup>] (6 × 10<sup>-6</sup> mol dm<sup>-3</sup>) the kinetic runs were carried out with various initial concentrations of L-alanine, which yielded rate constants whose values depended on [L-alanine]. The pseudo first order rate constants  $k'$  (s<sup>-1</sup>) thus obtained were found to increase with [L-alanine] (Table 1) over a range of [L-alanine] used (2–10 × 10<sup>-2</sup> mol dm<sup>-3</sup>). This shows that the reaction obeys first order with respect to [L-alanine]. This was confirmed by the linear plots of  $k'$  (s<sup>-1</sup>) vs. [L-alanine] which yielded a straight line passing through the origin. Fig. 1. The plot of 1/ $k'$  vs. 1/[L-alanine] exhibits an excellent linearity (Fig. 2) with a positive slope. Observed reaction order  $n_{ap}$  = 1.01 ( $r$  = 0.998). The values of  $k_2$  (mol dm<sup>-3</sup> s<sup>-1</sup>) were evaluated from the slope of  $k'$  (s<sup>-1</sup>) vs. [L-alanine] plots (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  $k'$  (s<sup>-1</sup>)/[L-alanine].

### 3.2. Effect of [Ce(IV)]

The kinetics of oxidation of L-alanine has been investigated under pseudo first order conditions, keeping the concentrations of L-alanine always in large excess (nearly 10-folds) over that of [Ce(IV)]. When the log [Ce(IV)]<sub>T</sub> was plotted against 't', very good straight line plots were obtained indicating that the reaction was of first order with respect to [Ce(IV)] (Table 1). Effect of varying [Ce(IV)] (2–10 × 10<sup>-3</sup> mol dm<sup>-3</sup>) on the rate of oxidation has been studied at constant [L-alanine] (6 × 10<sup>-2</sup> mol dm<sup>-3</sup>), [H<sup>+</sup>] (0.05 mol dm<sup>-3</sup>) [Na<sub>2</sub>SO<sub>4</sub>] (0.1 mol dm<sup>-3</sup>), and [Ag<sup>+</sup>] (6 × 10<sup>-6</sup> mol dm<sup>-3</sup>). The pseudo first order rate constants  $k'$  were found to be independent of [Ce(IV)], confirming the first order dependence of rate on [Ce(IV)].

Download English Version:

<https://daneshyari.com/en/article/1250801>

Download Persian Version:

<https://daneshyari.com/article/1250801>

[Daneshyari.com](https://daneshyari.com)