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ORIGINAL ARTICLE

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

T. Sumathi [a,*], P. Shanmugasundaram [b], G. Chandramohan [c]

[a] *Department of Chemistry, B.N.M. Institute of Technology, P.B. No. 7087, BSK 2nd Stage, Bangalore 560 070, India*
[b] *TÜV Rheinland (India) Pvt. Ltd., Sigma Tech Park, White Field Main Road, Bangalore 560 066, India*
[c] *P.G. and Research Department of Chemistry, A.V.V.M. Sri Pushpam College, Poondi 613 503, Tamil Nadu, India*

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Abstract The kinetics of oxidation of L-methionine and *N*-acetyl L-methionine by Ce(IV) in sulfuric acid–sulfate media in the range of 288.1–298.1 K has been investigated. The major oxidation products of methionine and *N*-acetyl L-methionine have been identified as methionine sulfoxide and *N*-acetyl methionine sulfoxide. The major oxidation products have been confirmed by qualitative analysis and boiling point. The reaction was first order with respect to L-methionine, *N*-acetyl L-methionine and Ce(IV). Increase in $[H^+]$, ionic strength and HSO_4^- did not affect the reaction rate. Under the experimental conditions, Ce^{4+} was the effective oxidizing species of cerium. Increase in dielectric constant of the medium decreased the reaction rate. Under nitrogen atmosphere, the reaction system can initiate polymerization of acrylonitrile, indicating the generation of free radicals. Activation parameters associated with the overall reaction have been calculated.

1. Introduction

The oxidation of amino acids is of utmost importance from a chemical point of view due to its bearing on the mechanism of amino acid metabolism. Kinetics of oxidation of amino acids by a variety of oxidants, such as Mn(III) (Beg and Kamaluddin, 1975), Co(III) (Usha et al., 1977), Os(VIII)-Fe$(CN)_6^{3-}$ (Upadhyay and Agrawal, 1977), chloramine-T (Mahadevappa et al., 1981), 1-chlorobenzotriazole (Hiremath et al., 1987), and *N*-bromosuccinimide (Gopalkrishnan and Hogg, 1985; Schonberg et al., 1951; Chappelle and Luck, 1957; Konigsberg et al., 1961) in acid and alkaline media has been reported. The oxidation of biologically important amino acid methionine and *N*-acetyl L-methionine is very important because it may

* Corresponding author. Tel.: +91 080 26711781/82 (office), +91 080 41632763 (Res.); mobile: +91 9972812978; fax: +91 80 26710881.
E-mail address: pranavsumathi@gmail.com (T. Sumathi).

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

Ce(IV) is a well known oxidant (Thabaj et al., 2006; Chimatadar et al., 2002, 2001) in acid media having the reduction potential (Day and Selbin, 1964) of the couple Ce(IV)/Ce(III): 1.70 V. The oxidation of organic compound by Ce(IV) in general seems to proceed via the formation of intermediate complexes (Yatsimiraskii and Luzan, 1965; Guilbault and McCurdy, 1963).

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

2. Experimental

2.1. Materials

Double distilled water was used for preparing the solutions. L-methionine and *N*-acetyl L-methionine (SRL) were used as such. Stock aqueous solutions of L-methionine and *N*-acetyl L-methionine were prepared by dissolving it in water. The Ce(IV) stock solution was obtained by dissolving cerium(IV) ammonium sulfate (E. Merck) in 0.98 mol dm^{-3} sulfuric acid and standardized with iron(II) ammonium sulfate solution (Jeffery et al., 1996). Other chemicals and reagents, such as sodium sulfate, sulfuric acid, acetonitrile, acetone, hydrated copper sulfate and aluminum sulfate used were of analytical grade with 99.9% purity.

2.2. Kinetic measurements

Kinetic studies were carried out in sulfuric acid medium in the temperature range (288.1–298.1 K) under pseudo first order conditions with a large excess of L-methionine and *N*-acetyl L-methionine over Ce(IV). The reaction was followed by estimating the unreacted Ce(IV) as a function of time by titrating against ferrous ammonium sulfate solution employing ferroin as an indicator (Walden et al., 1933).

No precautions were taken to exclude the diffused light entering into the reaction mixture (Krishna and Sinha, 1959). The Ce(IV) solution was thermally quite stable (Grant, 1964) in the visible region and undergoes photochemical decomposition (Heidt and Smith, 1948) only in the UV region. Since, the oxidation of Kolp and Thomas (1949) water even at 333 K by Ce(IV) was immeasurably slow and insignificant, no further precautions were taken to account for this.

From the titration values, plots of log [Ce(IV)] vs. time were made and from the slope of such plots, the pseudo first order rate constants k^1 (s^{-1}) were obtained. All the first order plots were linear, with a correlation coefficient of 0.996–0.999. The results were reproducible within an accuracy of ±5%

3. Results

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

At a constant [Ce(IV)] (8×10^{-3} mol dm^{-3}), [H^+] (5×10^{-2} mol dm^{-3}) and [Na_2SO_4] (1×10^{-1} mol dm^{-3}) the kinetic runs were carried out with various ($1–10 \times 10^{-2}$ mol dm^{-3}) concentrations of L-methionine and *N*-acetyl L-methionine which yielded rate constants whose values depended on [L-methionine] and [*N*-acetyl L-methionine]. The pseudo first

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

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

Effect of concentration of L-methionine, *N*-acetyl L-methionine and Ce(IV) on the pseudo first order rate constant $k^1$and second order rate constant k_2 substrates = L-met and *N*-A-L-Met [H^+] = 5×10^{-2} mol dm^{-3}, [Ce(IV)] = 8×10^{-3} mol dm^{-3}, [μ] – [Na_2SO_4] = 1×10^{-1} mol dm^{-3}.

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