Asian Journal of Chemistry Vol. 7, No. 2 (1995), 450–452

NOTE

Mechanism of Ru(III) Catalysed Oxidation of Alanine by Ceric Perchlorate in Perchloric Acid Medium

P.N. RAM and JANAK PRASAD*
Department of Chemistry
Magadh University, Bodhgaya-824 234, India

A kinetic investigation of Ru(III) catalysed oxidation of alanine by ceric perchlorate in perchloric acid medium has been made and the results indicate first-order dependence on each of [Ce(IV)], [alanine], [Ru(III)] and [H^+]. These kinetic features have led to the conclusion that Ce(IV) first converts Ru(III) to Ru(VIII) quantitatively and Ru(VIII) reacts with protonated alanine to give an intermediate which is attached by Ce(IV) in a slow and rate determining step.

Amino acids have been reported to be probed extensively[1–3] by hexacyanoferrate(III), dichromate, periodic acid and other oxidants from kinetics viewpoint. Chloramine-T[4] and N-bromosuccinimide[5] have also been used in oxidation of amino acids. Amino acids have not been involved in Ru(III) catalysis by ceric perchlorate in acidic medium and the kinetic features are unknown. Keeping this in mind, an attempt has been made in the present communication to study the kinetics and mechanism of oxidation of alanine by ceric perchlorate in perchloric acid medium.

Aqueous solution of alanine (Fluka AG) was prepared by dissolving its desired quantity in distilled water. Ceric perchlorate solution was prepared by dissolving a weighed quantity of ceric ammonium nitrate in known strength of perchloric acid (E. Merck) solution. All other reagents were of available pure quality (A.R. Grade). A 1 g sample of ruthenium trichloride was dissolved in HCl solution of known concentration.

The kinetics of the reaction was followed by estimating the unreacted ceric perchlorate by adding it to excess ferrous ammonium sulphate solution and thereafter by titrating the unreacted ferrous ammonium sulphate solution with standard ceric sulphate solution. The reaction was initiated by quickly adding desired volume of ceric perchlorate in the reaction vessel (containing requisite volumes of alanine, perchloric acid, ruthenium(III) chloride and other reagents) maintained at a desired temperature in a thermostatic water bath (±0.1°C). The progress of the reaction was monitored by estimating unconsumed ceric perchlorate as described above at different intervals of time.

First-order kinetics with respect to Ce(IV) was observed for different initial concentrations of ceric perchlorate. The first-order rate constant was found to be directly proportional to the concentration of each of alanine, Ru(III) and H^+. This indicates first-order dependence on each of alanine, Ru(III) and H^+. The reaction was found to be independent of ionic strength of the medium which was maintained by addition of suitable amount of sodium perchlorate. Table-1 records the reaction velocity constant at different concentrations of various reactants. The reaction has been studied in the temperature range 30–45°C and energy of activation has been computed as 27.6 kcal/mole.

TABLE-1

EFFECT OF VARIATION OF [REACTANTS], IONIC STRENGTH OF MEDIUM (μ) AND TEMPERATURE ON REACTION RATE AT 35°C

$Ce(IV) \times 10^3$ M l^{-1}	1.00	1.25	2.00	2.50	4.00	5.00
$k_1 \times 10^4$ sec^{-1}	2.24	2.16	2.21	2.26	2.18	2.32
[Alanine] = 1.00×10^{-2} M, $[HClO_4]$ = 2.00 M, [Ru(III)] = 4.00×10^{-6} M, μ = 1.55 M						
[Alanine] $\times 10^2$ M l^{-1}	0.33	0.40	0.50	0.80	1.00	1.34
$k_1 \times 10^4$ sec^{-1}	0.75	0.88	1.14	1.79	2.21	3.02
$k_2 \times 10^2$ M^{-1} l sec^{-1}	2.27	2.20	2.28	2.24	2.21	2.25
[Ce(IV) = 2.00×10^{-3} M, $[HClO_4]$ = 2.00 M, [Ru(III)] = 4.00×10^{-6} M, μ = 2.55 M						
$[HClO_4]$ M l^{-1}	1.00	1.50	2.00	2.50	3.00	4.00
$k_1 \times 10^4$ sec^{-1}	1.15	1.80	2.21	2.95	3.60	4.64
$k_2 \times 10$ M^{-1} l sec^{-1}	1.15	1.20	1.15	1.18	1.20	1.16
[Ce(IV)] = 2.00×10^{-3} M, [Alanine] = 1.00×10^{-2} M, [Ru(III)] = 4.00×10^{-6} M, μ = 2.55 M						
[Ru(III)] $\times 10^6$ M l^{-1}	1.00	2.00	2.50	3.00	4.00	5.00
$k_1 \times 10^4$ sec^{-1}	0.58	1.10	1.36	1.62	2.21	2.70
$k_2 \times 10^{-2}$ M^{-1} l sec^{-1}	0.58	0.55	0.54	0.54	0.55	0.54
[Ce(IV)] = 2.00×10^{-3} M, [Alanine] = 1.00×10^{-2} M, $[HClO_4]$ = 2.00 M, μ = 2.55 M						

The real reactive species of ceric perchlorate in perchloric acid is reported[6] as $[Ce(H_2)_8]^{4+}$ which is written as Ce(IV) here for the sake of simplicity. Ruthenium(III), when mixed with an excess of Ce(IV) is oxidised[7–9] rapidly and quantitatively to ruthenium(VIII) as shown in Eq. (1).

$$Ru(III) + 5Ce(IV) \xrightarrow{\text{fast}} 5Ce(III) + Ru(VIII) \qquad (1)$$

Ruthenium(III) shows the same catalytic activity as ruthenium(VIII) when initially added to the reaction mixture[10] and the rate of ruthenium(III) catalysed reaction was also found to be in good agreement[11] with that of ruthenium(VIII) catalysed reaction for the same ruthenium content. Therefore, in the present investigations the active species[12] of the catalyst may be regarded as ruthenium(VIII).

Considering the kinetic features of the present investigations, the following reaction steps are suggested where S is alanine.

$$S + H^+ \overset{K_1}{\rightleftharpoons} (SH^+) \tag{I}$$

$$SH^+ + Ru(VIII) \overset{K_2}{\rightleftharpoons} \underset{\text{Intermediate}}{(X)} \tag{II}$$

$$(X) + Ce(IV) \xrightarrow[k]{\text{Slow}} \text{Products} + Ru(VII) \tag{III}$$

rate determining step

$$Ru(VII) + Ce(IV) \rightarrow Ce(III) + Ru(VIII) \tag{IV}$$

Considering above reaction steps the rate of reaction in terms of rate of loss of [Ce(IV)] may be written as Eq. (2)

$$\frac{-d\,[Ce(IV)]}{dt} = k\,K_1K_2[Ce(IV)][S][Ru(III)][H^+] \tag{2}$$

The rate law agrees well with the kinetic observations.

REFERENCES

1. S.K. Upadhyay and M.C. Agrawal, *Indian J. Chem.*, **16A**, 39 (1978).
2. C.S. Vishwanatham and G. Gopal Rao, *Curr. Sci.*, **12**, 327 (1943).
3. R.J. Falkova and J. Tanaka, *Proc. S. Dacota Acad. Soc.*, **41**, 184 (1961).
4. R. Sanehi, R.M. Mehrotra and S.P. Mushran, *Z. Naturfosch*, **28B**, 483 (1973).
5. S.P. Mushran, R.N. Tewari, A.K. Bose and K. Singh, *Indian J. Chem.*, **16A**, 35 (1978).
6. B.B.L. Saxena, C.P.S. Gaur, R.B. Singh and B. Singh, *J. Indian Chem. Soc.*, **50,** 136 (1988).
7. F.E. Beasmish and J.C. Vanloon, Recent Advances in the Analytical Chemistry of Noble Metals, Pergamon Press, London, p. 465 (1972).
8. C. Surasiti and E.B. Sondell, *Anal. Chem. Acta*, **22**, 261 (1960).
9. C.J. Keattek, *Talanta*, **8**, 620 (1961).
10. C. Surasiti and E.B. Sondell, *J. Phys. Chem.*, **63**, 890 (1959).
11. D.S.A. Dikshitulu, P. Vani and V. Hanumantha Rao, *Inorg. Nucl. Chem. Lett.*, **17**, 187 (1981).
12. A.K. Awasthi and S.K. Upadhyay, *Transition Met. Chem.*, **10**, 379 (1985).

(*Received:* 20 August 1994; *Accepted:* 18 October 1994) AJC-885

Industry-Education Initiatives in Chemistry

INTERNATIONAL SYMPOSIUM ON INDUSTRY-EDUCATION INITIATIVES IN CHEMISTRY

YORK, U.K.

August 28–September 2, 1995

Contact address:
PROFESSOR D.J. WADDINGTON
Department of Chemistry, University of York
Heslington, York, YO1 5DD, U.K.