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Kinetics and Mechanism of Bromide Catalysed Oxidation of L-Sorbose by Cerium(IV) in Aqueous Sulphuric Acid Solution

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Kinetics of oxidation of L-sorbose has been studied in presence of bromide catalyst in aqueous sulphuric acid medium at constant ionic strength. The reaction is first order each in L-sorbose and [Ce(IV)]. The rate of reaction decreases on increasing the concentration of hydrogen ion. The sulphate and bisulphate ions show retarding effect on reaction rate at constant ionic strength. The bromide ion shows positive catalytic effect on reaction rate. The value of activation energy has been calculated and a suitable mechanism conforming to the kinetic data is proposed.

INTRODUCTION

Ceric sulphate, ferricyanide, dichromate and vanadium (V) etc. have been used as oxidising agents in acid media[1–5]. Ceric oxidation of oxalic acid[6, 7], dextrose[8] and fructose[9] have been studied earlier. The present study deals with the kinetics and mechanism of bromide catalysed oxidation of L-sorbose by Ce(IV) in aqueous sulphuric acid solution.

EXPERIMENTAL

All the chemicals used in this work were of analytical reagent grade. A stock standard solution of sodium thiosulphate was prepared[10]. Ceric ammonium sulphate solution prepared in 2N H_2SO_4 and the prepared solution was standardised iodometrically against standard sodium thiosulphate solution using starch as an indicator. The kinetics were followed by removing 5 mL aliquot from the reaction mixture at different intervals and the reaction was arrested by adding 10 mL of 5% KI aqueous solution; the liberated iodine which is equivalent to the concentration of the unreacted cerium(IV) was determined by titration with standard solution of sodium thiosulphate.

The stoichiometry of reaction was determined by measuring the cerium(IV) disappearance by titrimetry and substrate dissappearance by measuring the volume of carbon dioxide formed, which was confirmed by lime water test. The stoichiometry thus determined was found to be 24 mols of Ce(IV) to one mol of L-sorbose; thus the overall stoichiometric equation could be written as:

$$C_6H_{12}O_6 + 24Ce^{4+} + Br^- + 6H_2O \longrightarrow 6CO_2 + 24Ce^{3+} + Br^- + 24H^+$$

RESULTS AND DISCUSSION

Under the conditions [Substrate] << [Ce(IV)], when –dc/dt values are plotted against Ce(IV) a straight line is obtained which passes through the origin showing that the reaction is first order with respect to [Ce(IV)] (Fig. 1A). The reaction was observed to show linear relationship between –dc/dt and [Substrate] indicating thus first order with respect to the substrate (Fig. 1B).

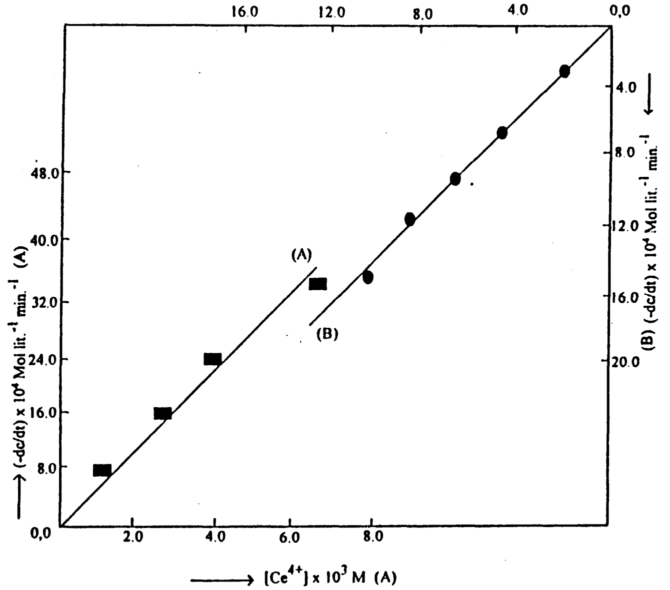


Fig. 1. (A) Plot of (–dc/dt) *vs.* $[Ce^{4+}]$ at 40°C; [L-Sorbose] = 12.5×10^{-3} M; $[Br^-] = 5.0\times10^{-3}$ M; $[H_2SO_4] = 5.0\times10^{-1}$ M; $\mu = 1.685$. (B) Plot of (–dc/dt) *vs.* (L-Sorbose) at 40°C; $[Ce^{4+}] = 2.5\times10^{-3}$ M; $\mu = 1.55$. Other conditions are same as in (A).

Effect of Hydrogen and Bromide Ions: The rate of reaction decreases on increasing the concentration of sulphuric acid (Fig. 2A) due to the conversion of reactive species $Ce(SO_4)_2$ to the unreactive species $Ce(SO_4)^{2+}$ as described in the equation

$$Ce(SO_4)_2 + H^+ \rightleftharpoons Ce(SO_4)^{2+} + HSO_4^- \qquad (1)$$

The addition of potassium bromide shows positive catalytic effect of bromide ion on reaction rate. The rate of reaction increases on increasing the concentration of $[Br^-]$ (Fig. 3A).

Effect of bisulphate and sulphate ions: Sulphate being a better ligand can combine with Ce(IV) to a varying degree forming various species. Several investigators[11–13] reported that in H_2SO_4 medium, ceric sulphate exists mainly as $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$ and $Ce(SO_4)_4^{4-}$ depending on the concentration of sulphate. From the study of the effect of $[HSO_4^-]$ or $[SO_4^{2-}]$ on the rate it was concluded that neutral $Ce(SO_4)_2$ is the reactive species. The inhibitory action of $[HSO_4^-]$ (Fig. 2B) and $[SO_4^{2-}]$ (Fig. 3B) is due to the conversion of reactive form of $Ce(SO_4)_2$ to the unreactive species $Ce(SO_4)_3^{2-}$ and $Ce(SO_4)_4^{4-}$.

Effect of Temperature: The reaction has been studied at different tempera-

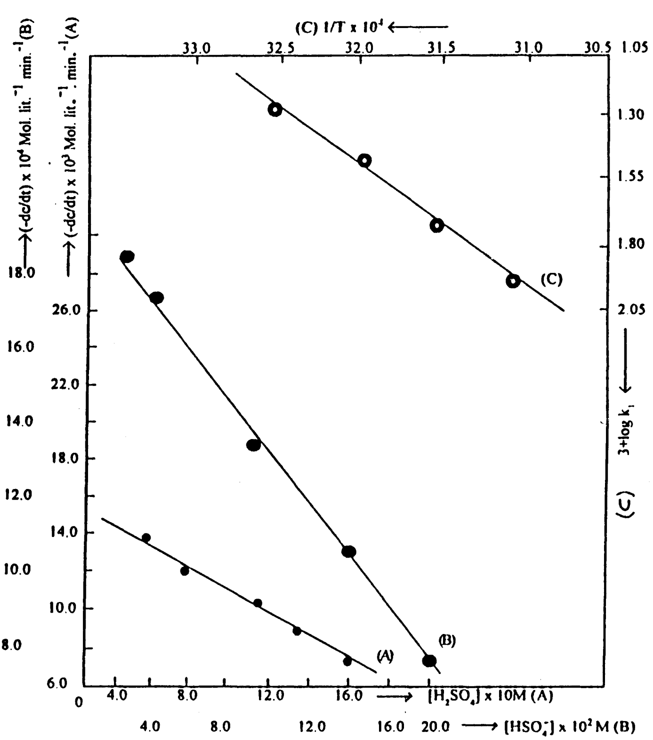
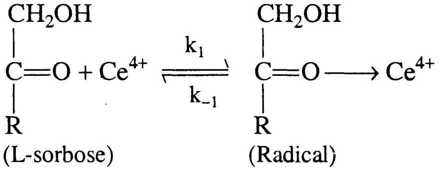


Fig. 2. (A) Plot of (–dc/dt) *vs.* $[H_2SO_4]$ at 40°C; [L-Sorbose] = 2.50×10^{-2} M; $[Ce^{4+}] = 2.50 \times 10^{-3}$ M; $[Br^-] = 5.0 \times 10^{-3}$. (B) Plot of (–dc/dt) *vs.* $[HSO_4^-]$; [L-Sorbose] = 12.50×10^{-3} M, $[H_2SO_4] = 5.0 \times 10^{-1}$ M, $\mu = 1.75$. Other conditions are same as in (A). (C) Plot of k_1 *vs.* 1/T.

tures and the activation parameters have been evaluated in the temperature range 35–50°C. The values of ΔE and ΔS^* were found to be 105.75 kJ mol^{-1} and -111.85 J K^{-1} mol^{-1} respectively. The fairly high negative value of ΔS^* suggestes the formation of more ordered activated complex[14]

Mechanism

On the basis of the results the following mechanism may be proposed in order to explain the mechanistic path of oxidation of L-sorbose:



$$\underset{\text{(L-sorbose)}}{\begin{array}{l}CH_2OH\\ |\\ C{=}O\\ |\\ R\end{array}} + Ce^{4+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Radical)}}{\begin{array}{l}CH_2OH\\ |\\ C{=}O\\ |\\ R\end{array}} \longrightarrow Ce^{4+} \qquad (2)$$

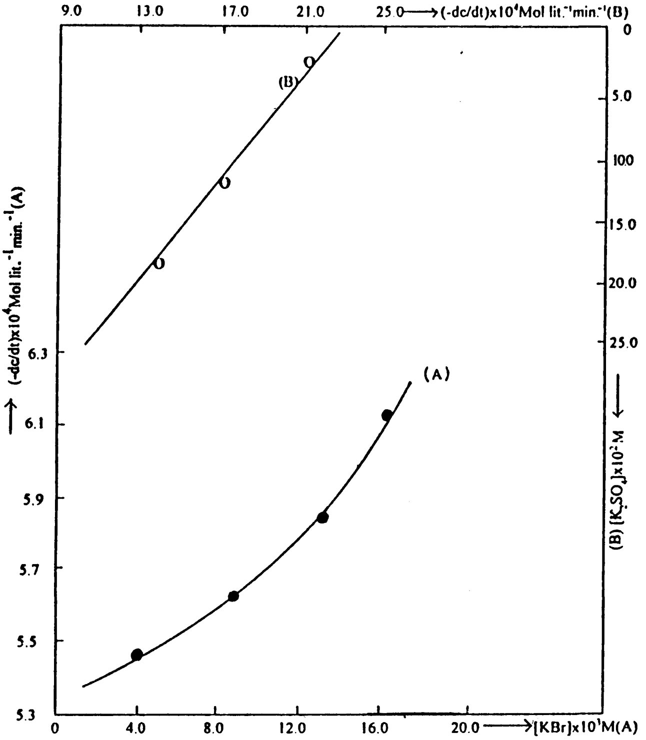
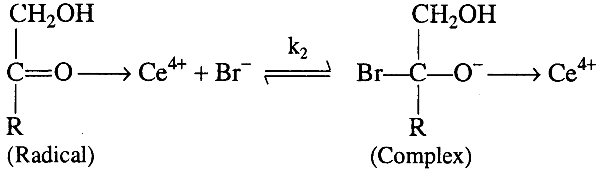
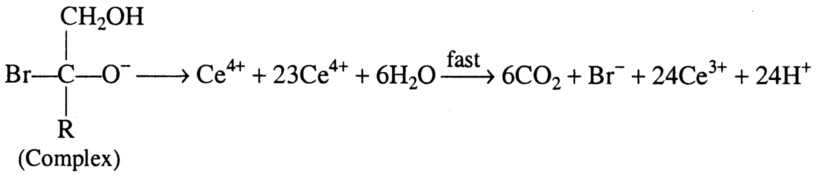


Fig. 3. (A) Plot of (–dc/dt) *vs.* [KBr] at 40°C; [L-Sorbose]= 3.125×10^{-3} M; $[Ce^{4+}] = 2.50 \times 10^{-3}$ M; $[H_2SO_4] = 5.0 \times 10^{-1}$ M, $\mu = 1.56$. (B) Plot of (–dc/dt) *vs.* $[K_2SO_4]$ at 40°C; $[KBr] = 5.0 \times 10^{-3}$ M; $[L\text{-Sorbose}] = 12.5 \times 10^{-3}$ M; $H_2SO_4 = 5.0 \times 10^{-1}$ M; $\mu = 2.225$



$$\underset{\text{(Radical)}}{\overset{CH_2OH}{\underset{R}{C}}}{=}O \longrightarrow Ce^{4+} + Br^- \overset{k_2}{\rightleftharpoons} \underset{\text{(Complex)}}{Br-\overset{CH_2OH}{\underset{R}{C}}-O^-} \longrightarrow Ce^{4+} \qquad (3)$$



$$\underset{\text{(Complex)}}{Br-\overset{CH_2OH}{\underset{R}{C}}-O^-} \longrightarrow Ce^{4+} + 23Ce^{4+} + 6H_2O \xrightarrow{\text{fast}} 6CO_2 + Br^- + 24Ce^{3+} + 24H^+ \qquad (4)$$

where R is carbohydrate chain.

The rate law derived on the basis of above mechanism is as follows:

$$d[R]/dt = K_1[S][Ce^{4+}] - K_{-1}[R] - K_2[R][Br^-] \qquad (5)$$

now at steady state,

$$K_1[S][Ce^{4+}] = [R](K_{-1} + K_2[Br^-])$$

or

$$[R] = K_1[S][Ce^{4+}]/(K_{-1} + K_2[Br^-]) \qquad (6)$$

Now at steady conditions the rate of disapperance of Ce^{4+} may be given as

$$-(d[Ce^{4+}]/dt) = K_2[R][Br^-] \qquad (7)$$

Substituting (6) into (7) gives

$$-(d[Ce^{4+}]/dt) = (K_1K_2[S][Br^-][Ce^{4+}])/(K_{-1} + K_2[Br^{-1}])$$

or

$$-(d[Ce^{4+}]/dt) = (K_1[S][Br^-][Ce^{4+}])/((K_{-1}/K_2) + [Br^-]) \qquad (8)$$

Since $K_2 \gg K_{-1}$ and hence K_{-1}/K_2 can be neglected.

Thus equation (8) assumes the form

$$-(d[Ce^{4+}]/dt) = K_1[S][Ce^{4+}] \qquad (9)$$

where S and R represent the L-sorbose and radical respectively.

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