Kinetics and mechanism of ruthenium(III) chloride catalysed oxidation of propane-1,3-diol by ceric sulfate in aqueous sulfuric acid medium

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A mechanism based on kinetic and spectral studies has been proposed for the oxidation of propanediol by cerium(IV)

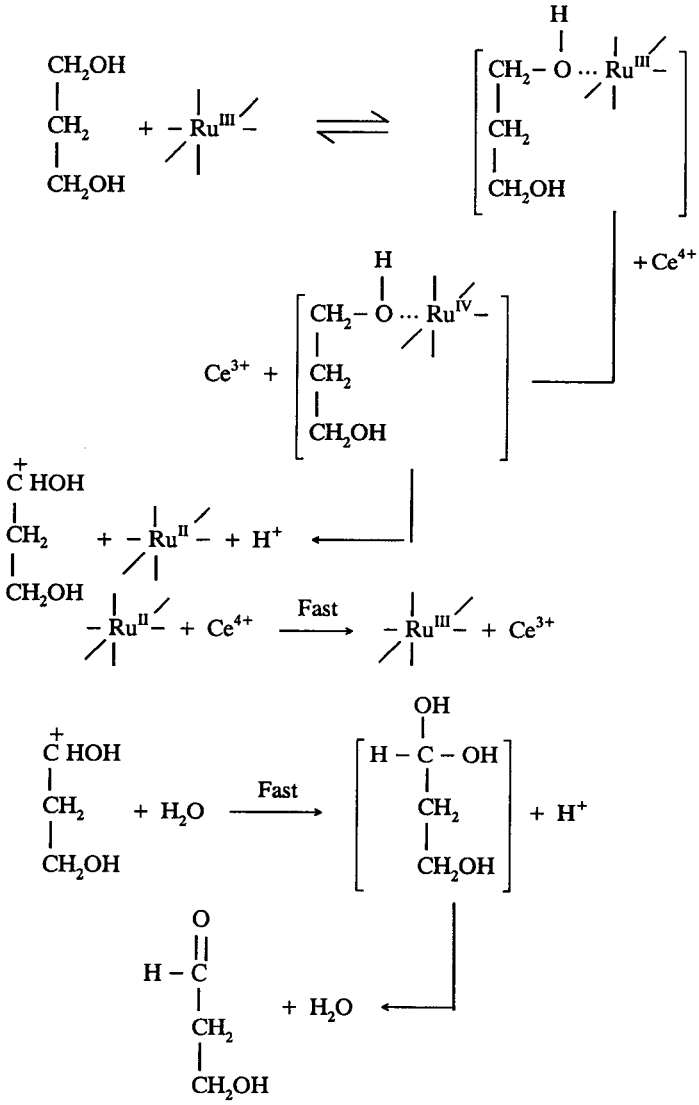
Keywords: ruthenium(III) chloride, propane-1,3-diol

The kinetics and mechanism of ruthenium(III) chloride catalysed oxidation of propane-1,3-diol (diol) by ceric sulfate in sulfuric acid medium have been studied. The stoichiometry corresponds to the reaction as represented by equation (1)

$$2\,Ce^{4+} + CH_2OH.CH_2.CH_2OH \longrightarrow 2\,Ce^{3+} + CH(O)CH_2CH_2OH + 2\,H^+ \quad (1)$$

The product 3-hydroxy propanal was identified and confirmed both spectrally and by determining the melting point of its hydrazone derivative.

The kinetics of the reaction were monitored by estimating cerium(IV) by titrating its known aliquot against ferrous ammonium sulfate solution employing ferroin as an indicator[7] free of interference from propanedio and its oxidation product. The kinetic results in triplicate were reproducible to within ±5%.



Scheme 1

* To receive any correspondence.

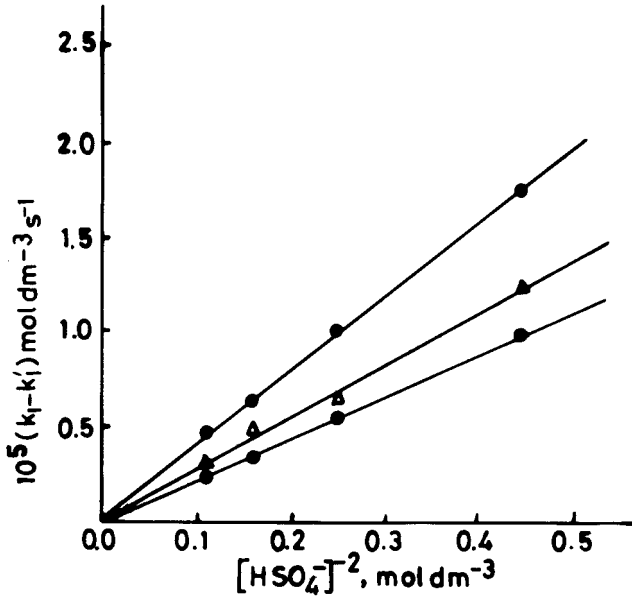


Fig. 1 Plot of $(k_1–k_1')$ versus $[HSO_4^-]^{-2}$ [diol] = 2.0×1.0^{-2} mol dm^{-3}; [Ce(IV)] 2.0×1.0^{-3} mol dm^{-3}; [Ru(III)] = 1.0×1.0^{-7} mol dm^{-3}; [H$^+$] = 1.0 mol dm^{-3}; ○, 30°C; Δ 35°C; ●, 40°C.

The kinetic orders with respect to the oxidant, diol and the catalyst are all one. The products do not affect the rate of the reaction. $CeSO_4^{2+}$ has been assumed to be the reactive form of cerium(IV) in view of the following equilibria[9] (2)–(4).

$$Ce^{4+} + HSO_4^- \overset{K_1}{\rightleftharpoons} CeSO_4^{2+} + H^+ \qquad (2)$$

$$CeSO_4^{2} + HSO_4^- \overset{K_2}{\rightleftharpoons} Ce(SO_4)_2 + H^+ \qquad (3)$$

$$Ce(SO_4)_2 + HSO_4^- \overset{K_3}{\rightleftharpoons} Ce(SO_4)_3H^- \qquad (4)$$

The concentration of $CeSO_4^{2+}$ species has been obtained as in eqn (8)

$$[CeSO_4^{2+}] = [Ce(IV)]\,[H^+]/K_2\,K_3\,[HSO_4^-]^2 \qquad (8)$$

A minor uncatalysed path observed in the reaction has been accounted for and the reaction mechanism consisting of steps (9) to (13) is envisaged.

$$Ce^{4+} + \text{diol} \xrightarrow{k_1'} \text{Products} \qquad (9)$$

$$Ru^{III} + \text{diol} \overset{K'}{\rightleftharpoons} [Ru^{III} – \text{diol}] \qquad (10)$$

$$[Ru^{III} – \text{diol}] + Ce^{4+} \xrightarrow{k'} [Ru^{IV} – \text{diol}] + Ce(III) \qquad (11)$$

$$[Ru^{IV} – \text{diol}] + Ce^{4+} \xrightarrow{\text{Fast}} [Ru^{V} – \text{diol}] + Ce(III) \qquad (12)$$

$$[Ru^{V} – \text{diol}] \xrightarrow{\text{Fast}} Ru^{III} + R – CHO + 2\,H^+ \qquad (13)$$

where $R = CH_2OH – CH_2–$

The loss of cerium(IV) leads to the rate law (15) or (16)

$$-\frac{1}{2}\frac{d\,[Ce(IV)]}{dt} = \frac{k'K'\,[Ce(IV)][diol][Ru^{III}][H^+]}{K_2K_3\,[HSO_4^-]^2\,(1 + K'\,[diol])} \qquad (15)$$

$$\text{or } (k_1 – k_1') = \frac{k[Ru^{III}]\,[H^+]}{K_2K_3\,[HSO_4^-]^2} \qquad (16)$$

where k_1 and k_1' are the observed second order rate constants for catalysed and minor uncatalysed path respectively. A plot of $(k_1 – k_1')$ versus $[HSO_4]^{2-}$ yields a straight line passing through the origin, the gredient of which yields k/K_2K_3. The mode of electron transfer has been suggested as in Scheme 1.

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References cited in this synopsis

7 A.I. Vogel, *Quantitative Inorganic Analysis*, 3rd Ed. Longman, London 1961, P. 319.
9 T.J. Hardwick and L. Robertson, *Can. J. Chem.* 1951, **29**, 828.