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NOTE

Kinetics and Mechanism of Ru(VIII)-Catalysed Oxidation of Methyl Glycol by Ce(IV) in Perchloric Acid Medium

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The kinetics of ruthenium(VIII) catalysed oxidation of methyl glycol by ceric perchlorate in perchloric acid medium have been studied. The reaction exhibits zero-order kinetics in Ce(IV) and first order rate dependence with respect to each of methyl glycol and Ru(VIII). Negligible effect of $[H^+]$ and ionic strength of the medium has been observed. A suitable mechanism, consistent with the observed kinetic data, is proposed.

Although a good number of research papers have appeared on Ru(III) catalysis with many oxidants[1-3], but literature on Ru(III) catalysis is scanty.[4] This paper deals with Ru(VIII) catalysed oxidation of methyl glycol by Ce(IV) in perchloric acid medium. The kinetic aspects and mechanistic steps have been described.

The reagents employed were methyl glycol (E. Merck), ceric ammonium nitrate, ceric sulphate (both BDH, AR grade) and ruthenium trichloride (Johnson Matthey). All other reagents used were of AR grade. All the solutions were prepared in doubly distilled water. The ruthenium trichloride solution was prepared by dissolving the sample in very dilute HCl solution of known volume. The solutions of ceric ammonium nitrate and ceric sulphate were prepared in $HClO_4$ and H_2SO_4 (both acids of 1 N).

A thermostated bath was used to maintain the desired temperature within ±0.1°C. The kinetics were evaluated by estimating unconsumed Ce(IV) at different intervals of time with the help of ferrous ammonium sulphate solution and ceric sulphate solution using ferroin as an indicator. The reaction was studied for two half lives.

The reaction was studied at various initial concentrations of reactants (Table-1). The rates *i.e.* (–dc/dt) at different concentrations of Ce(IV) were nearly constant, establishing the zero order dependence of rate on [oxidant]. The plot of (–dc/dt) values against [methyl glycol] is linear and passes through the origin (figure not given), indicating first order kinetics with respect to methyl glycol. The value of (–dc/dt) is directly proportional to the concentration of Ru(VIII), showing also first order rate dependence on Ru(VIII). The change in ionic strength of the medium (adjusted and maintained by addition of suitable amount of

$NaClO_4$) did not bring about significant change in (–dc/dt) value, which proves negligible effect of ionic strength (μ) of the medium on rate of reaction. Variation in initial concentration of $HClO_4$ (used as source of H^+) in the reaction also had no effect on the value of (–dc/dt), showing thus negligble effect of $HClO_4$. The reate measurements were carried out at 30, 35, 40 and 45°C and energy of activation was calculated and found to be 19.68 kcal/mole from the plot of log (dc/dt) *vs.* (1/T).

TABLE-1
EFFECT OF VARIATION OF [REACTANTS] ON THE REACTION RATE AT 35°C
$[Hg(OAc)_2] = 3.00 \times 10^{-3}$ M

[a][Ce(IV)] $\times 10^3$ M	0.50	0.80	1.00	1.67	2.00	2.50
$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}	1.32	1.24	1.26	1.30	1.34	1.28
a → [Methyl glycol] = 2.00×10^{-2} M, $[HClO_4] = 0.80$ M, [Ru(VIII)] = 0.60×10^{-6} M						
[b][Methyl glycol] 10^2 M	0.75	1.50	2.00	2.50	3.00	4.00
$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}	0.46	0.98	1.26	1.64	1.91	2.56
$k_1 \times 10^6$ s^{-1}	6.12	6.53	6.30	6.56	6.36	6.40
b → [Ce(IV)] = 1.00×10^{-3} M, $[HClO_4] = 0.80$ M, [Ru(VIII)] = 0.60×10^{-6} M						
[c][Ru(VIII)] $\times 10^6$ M	0.30	0.60	0.90	1.20	1.50	1.80
$(-dc/dt) \times 10^7$ M L^{-1} s^{-1}	0.66	1.26	2.04	2.58	3.22	4.04
$k_1 \times 10$ s^{-1}	2.22	2.10	2.26	2.15	2.14	2.24
c → [Ce(IV)] = 1.00×10^{-3} M, $[HClO_4] = 0.80$ M, [Methyl glycol] = 2.00×10^{-2} M						
[d][$HClO_4$] M	0.40	0.80	1.60	2.40	3.00	4.00
$((-dc/dt) \times 10^7$ M L^{-1} s^{-1}	1.28	1.26	1.30	1.24	1.28	1.34
d → [Ce(IV)] = 1.00×10^{-3} M, [Methyl glycol] = 2.00×10^{-2} M, [Ru(VIII)] = 0.60×10^6 M						

Zero-order rate dependence on Ce(IV) clearly suggests involvement of Ce(IV) in the fast steps. Negligible effect of $[H^+]$ also suggests involvement of methyl glycol as such in the rate determining step. Ru(III), when mixed with an excess of cerium(IV), is oxidised[5–7] rapidly and quantitatively to Ru(VIII) as shown in eqn (1):

$$Ru(III) + 5Ce(IV) \rightarrow Ru(VIII) + 5Ce(III) \quad (1)$$

Ru(III) shows the same catalytic activity as ruthenium(VIII) when initially added to the reaction mixture[8] and the rate of Ru(III) catalysed reaction was also found[9] to be in good agreement with that of Ru(VIII) catalysed reaction for the same ruthenium content. Therefore, in the present investigation ruthenium is involved here as Ru(VIII) and not as Ru(III). The formation of free radical as an intermediate has also been reported earlier[10, 11] in oxidation of some organic substances by Ce(IV).

On the basis of the above facts and experimental results, the mechanistic steps for the title reaction are proposed as follows (Eqn. (1)–(4)):

$$S + Ru(III) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate (X)} \quad (1)$$

The forward reaction is slow and rate determining step.

$$X \longrightarrow F^{\bullet} + 2H^{+} + Ru(VI) \quad (2)$$

$$F^{\bullet} + Ce(IV) \xrightarrow[\text{fast}]{H_2O} \text{Product} + H^{+} + Ce(III) \quad (3)$$

$$Ru(VI) + Ce(IV) \longrightarrow Ru(VII) + Ce(III) \quad (4)$$

$$Ru(VII) + Ce(IV) \longrightarrow Ru(VIII) + Ce(III) \quad (5)$$

Here S represents methyl glycol and $F^{\bullet}$ (free radical) stands for $^{\bullet}CH_2CH_2OH$ in methyl glycol. The existence of unstable ruthenium(VI) and ruthenium(VII) species and their conversion back to ruthenium(VIII) with Ce(IV) in the fast steps has been reported in the literature.[12] The rate expression for the title reaction is represented as

$$\frac{-d[Ce(IV)]}{dt} = k_1[S][Ru(VIII)] \quad (6)$$

This is in agreement with the experimental results.

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