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Kinetics and Mechanism of Oxidation of Ethyl Diethylene Glycol by Ce(IV) Catalyzed by Ir(III) in Aqueous Sulphuric Acid Media

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The kinetics of iridium(III) catalyzed oxidation of ethyl diethylene glycol by ceric sulphate has been investigated in sulphuric acid media. The result indicates zero order kinetics with respect to cerium(IV) ion and first order kinetics with respect to ethyl diethylene glycol and iridium(III) chloride. The dielectric constant of the medium shows positive effect on the reaction rate. There is insignificant effect of ionic strength of potassium sulphate on the reaction rate indicating interaction in the rate-determining step being an ion-dipole type and not an ion type. Elevation of temperature increases the rate of reaction. Various activation parameters have been calculated and recorded. A suitable mechanism in conformity with the above observation has been proposed.

Key Words: Kinetics, Mechanism, Oxidant Ce(IV), Ethyl diethylene glycol, Ir(III) catalyst and Suplhuric acid.

INTRODUCTION

Kinetic studies on oxidation of different types of organic compounds by cerium(IV) are well documented[1-3]. Different metal ion catalysts like silver(I)[4], manganese(II)[5,6], copper(II)[7], osmium(VIII)[8], mercury(II)[9], chromium(III)[10], ruthenium(III)[11], iridium(III)[6], *etc.* have been utilized in cerium(IV) oxidation reactions. Among the different metal ion catalysis, ruthenium(III) and iridium(III) have been found to catalyze even at trace quantities.

Iridium(III) catalysis in oxidation reactions by cerium(IV) in aqueous sulphuric acid media has been reported in few cases[12-15]. In different cases, different reaction mechanism have been proposed. Moreover, some previous workers have reported[16] iridium(III) catalyzed decomposition of cerium(IV) in aqueous sulphuric acid medium at elevated temperatures through the oxidation of water. The presence of such catalytic decomposition of cerium(IV) may complicate the interpretation of kinetic data. In fact, more work is needed to understand the mechanistic routes for iridium(III) catalysis in oxidation reaction by cerium(IV) in aqueous sulphuric acid medium. In present communication, the result of the kinetic and mechanism of Ir(III) catalyzed oxidation of ethyl-diethylene glycol by Ce(IV) in sulphuric acid media is reported.

EXPERIMENTAL

Reagent grade chemicals and doubly distilled water were used throughout. Aqueous solution of ceric sulphate was prepared by warming it in sulphuric acid and double distilled water. The strength of sulphuric acid was maintained at 0.5 N. The ceric sulphate solution standardized against ferrous ammonium sulphate using ferrion as an indicator. Ceric sulphate, ferrous ammonium sulphate and ferrion were all BDH, sulphuric acid was of AR-grade. Aqueous solution of ethyl diethylene glycol (BDH) was also prepared by dissolving a weighed quantity of the sample in double distilled water. Stock solution of iridium(III) chloride was prepared by dissolving the sample (Johnson and Matthey Chemical Ltd.) in a solution of HCl. The final concentration of hydrochloric acid and iridium(III) chloride were 4.00×10^{-3} and 3.80×10^{-3} mol dm^{-3}, respectively. All the kinetic measurements were carried out at constant temperature (± 0.1 ºC). All the reactants were mixed in a black coated conical flask. The reaction was initiated by mixing the pre-equilibrated reactant solution taken at desired temperature (35 ºC) and progress of reaction was followed by withdrawing known amount of aliquots (5 mL) of the reaction solution at regular time intervals, quenching the reaction by excess standardized ferrous ammonium sulphate solution and back titrating unreacted ferrous ion with standard Ce(IV) solution using ferrion as an internal indicator.

RESULTS AND DISCUSSION

The kinetics of oxidation of ethyl-diethylene glycol by cerium(IV) were investigated at several initial concentration of the reactants. The rate constant increase linearly on increasing the concentration of ethyl-diethylene glycol. It gives a straight line (Fig. 1) with unit slope, which confirms the first order kinetics with respect to ethyl diethylene glycol. The rate of reaction was found to be highly influenced by Ir(III). It was observed that with increasing Ir(III), the first order rate constant increase linearly, which proves first order dependence on Ir(III). The slope of straight line gives first-order rate constant whose values also confirms (Fig. 2). The reaction shows zero order kinetics with respect to Ce(IV). Increase in concentration of [H^+] has positive effect of the medium. Negligible effect of addition of $NaHSO_4$ and Na_2SO_4 has no significant effect on the reaction rate.

The reaction were carried out at 30, 35, 40 and 45 ºC and results at these temperatures led to compute energy of activation (E_a), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$) for the title reaction (Table-3).

Stoichiometry and product analysis: Several reaction mixture of [oxidant]: [ethyl diethylene glycols] at fixed H^+ concentration were prepared under the condition [glycol] << [oxidant] *i.e.* [ethyl diethylene glycol] << [Ce(IV)] and the reaction mixture was left for 72 h. Estimation of unreacted [Ce(IV)] shows that 2 moles of Ce(IV) were required for oxidation of each mole of ethyl diethylene glycol. The stoichiometric equation is as follows:

TABLE-1
EFFECT OF VARIATION OF [H^+], [Ce(IV)], ETHYL DIETHYLENE GLYCOL AND [Ir(III)] CATALYST ON REACTION RATE CONSTANT AT 35 ºC

[Ethyl D. glycol] × 10^2 (mol dm^{-3})	[Ce(IV)] × 10^3 (mol dm^{-3})	[H_2SO_4] (mol dm^{-3})	[Ir(III)] × 10^5 (mol dm^{-3})	[(-dc/dt)] × 10^7 (mol dm^{-3})	k_1 (s^{-1})
2.00	0.50	0.80	7.65	1.74	–
2.00	0.80	0.80	7.65	1.80	–
2.00	1.00	0.80	7.65	1.82	–
2.00	1.25	0.80	7.65	1.70	–
2.00	1.67	0.80	7.65	1.78	–
2.00	2.00	0.80	7.65	1.72	–
2.50	2.00	0.80	7.65	2.12	0.85
3.00	2.00	0.80	7.65	2.56	0.85
4.00	2.00	0.80	7.65	3.40	0.85
7.50	2.00	0.80	7.65	6.32	0.84
10.00	2.00	0.80	7.65	8.60	0.86
2.00	2.00	0.80	11.50	2.60	2.26
2.00	2.00	0.80	15.30	3.40	2.22
2.00	2.00	0.80	19.10	4.38	2.29
2.00	2.00	0.80	22.95	5.16	2.25
2.00	2.00	0.80	30.60	6.92	2.24
2.00	2.00	1.25	7.65	2.80	–
2.00	2.00	1.75	7.65	3.66	–
2.00	2.00	2.25	7.65	4.82	–
2.00	2.00	2.56	7.65	5.06	–
2.00	2.00	3.20	7.65	6.10	–

TABLE-2
EFFECT OF IONIC STRENGTH, SO_4^{2-}, HSO_4^- AND DIFFERENT TEMPERATURES

Temperature (ºC)	Ionic strength (μ) (mol dm^{-3})	Na_2SO_4 (mol dm^{-3})	$NaHSO_4$ (mol dm^{-3})	(-dc/dt) × 10^7 (mol dm^{-3})
35	3.012	0.20	0.00	1.82
35	3.612	0.40	0.00	1.84
35	4.212	0.60	0.00	1.80
35	4.812	0.80	0.00	1.78
35	5.412	1.00	0.00	1.86
35	8.412	2.00	0.00	1.84
35	3.912	0.00	0.20	2.58
35	3.912	0.00	0.40	2.66
35	3.912	0.00	0.60	2.62
35	3.912	0.00	0.80	2.68
35	3.912	0.00	1.00	2.70
35	3.912	0.00	1.50	2.66
30	3.024	0.20	0.00	1.16
35	3.024	0.20	0.00	1.72
40	3.024	0.20	0.00	2.46
45	3.024	0.20	0.00	3.72

TABLE-3
THERMODYNAMIC PARAMETERS AT 35 ºC

k_r (s^{-1})	E_a (kJ mol^{-1})	log A	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (Jk^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
0.88×10^{-4}	85.48	10.44	82.92	–11.67	86.51

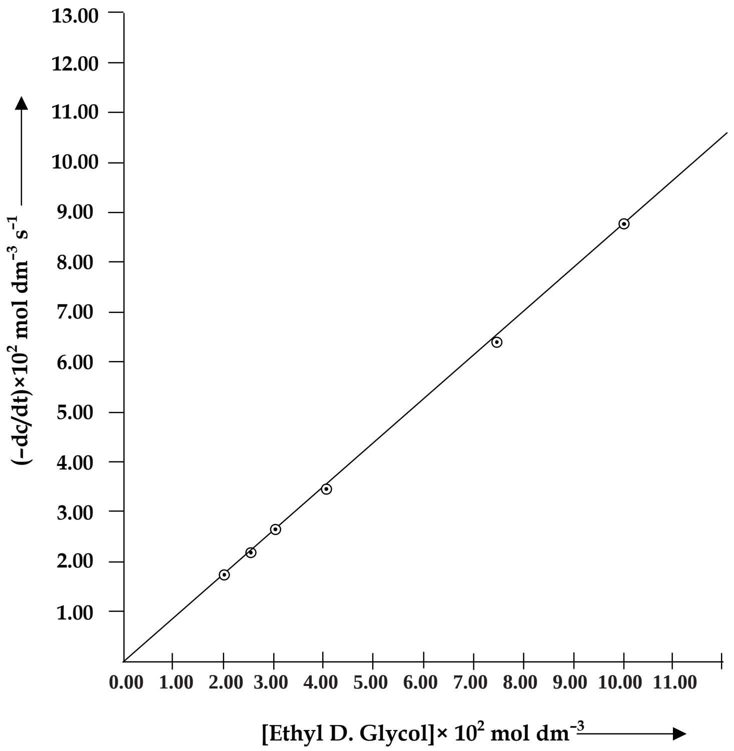
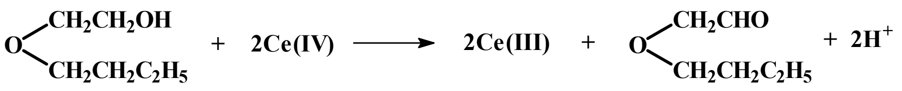


Fig. 1. Variation of substrate (ethyl diethylene glycol) at 35 ºC, [Ce(IV)] × 10^3 = 2.00 mol dm^{-3}; [H_2SO_4] = 0.80 mol dm^{-3}; [Ir(III)] × 10^5 = 7.65 mol dm^{-3}; [Na_2SO_4] = 0.20 mol dm^{-3} µ = 3.024 mol dm^{-3}



$$O(CH_2CH_2OH)(CH_2CH_2C_2H_5) + 2Ce(IV) \longrightarrow 2Ce(III) + O(CH_2CHO)(CH_2CH_2C_2H_5) + 2H^+$$

The product corresponding aldehyde was detected and identified by paper[17] and thin layer chromatography[18].

Mechanism

$$S + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} SH^+ \quad (1)$$

$$SH^+ + [IrCl_5H_2O]^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X + SH^+ + H_2O \quad (2)$$

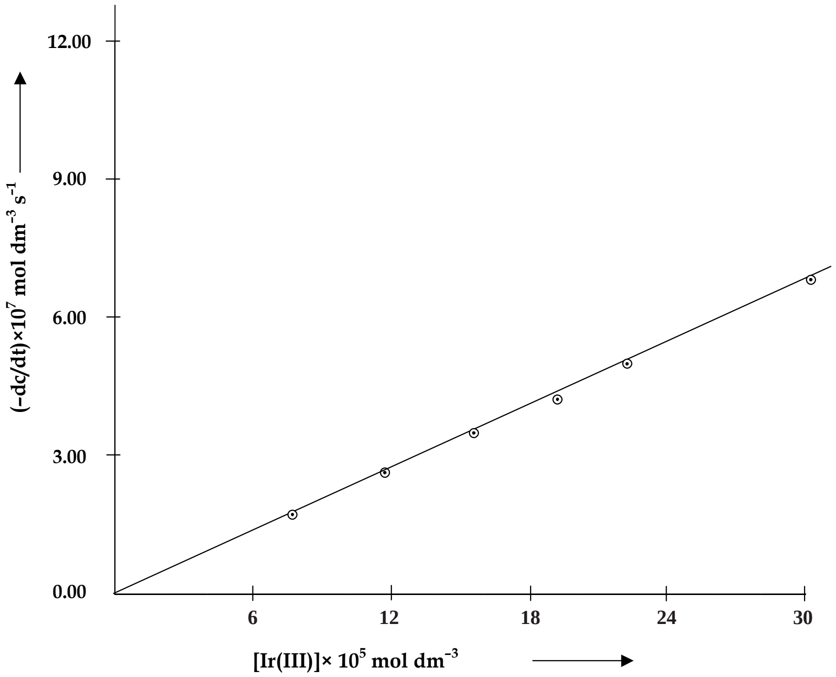


Fig. 2. Variation of catalyst at 35 ºC, $[Ce(IV)] \times 10^3 = 2.00$ mol dm^{-3}; $[H_2SO_4] = 0.80$ mol dm^{-3}; [ethyl diethylene glycol] × $10^5 = 2.00$ mol dm^{-3}; $[Na_2SO_4] = 0.20$ mol dm^{-3}; $\mu = 3.024$ mol dm^{-3}

where S is substrate *i.e.* ethyl diethylene glycol and X is $[IrCl_5.S]^{2-}$

$$[IrCl_5S]^{2-} + H_2O \xrightarrow{k} [IrCl_4(H_2O)H]^{2-} + S^+ + Cl^- \qquad (3)$$

rate determining and slowest step.

$$S^+ + Ce(IV) \longrightarrow \text{Product (P)} + Ce(III) \qquad (4)$$

$$Cl^- + [IrCl_4(H_2O)H]^{2-} + Ce(IV) \longrightarrow Ce(III) + H^+ + Y \qquad (5)$$

where Y is $[IrCl_5(H_2O)]^{2-}$

Considering above reaction steps, the rate of the reaction in terms of loss of concentration of Ce(IV) may be written as equation.

$$-\frac{d[Ce(IV)]}{dt} = nk[IrCl_5 \cdot S]^{2-} \qquad (6)$$

On applying steady state treatment to $[IrCl_5 \cdot S]^{2-}$, we have eqn. 7 with the help of eqns. 2 and 3

$$\frac{d[IrCl_5S]^{2-}}{dt} = 0 = k_2[SH^+H][IrCl_5H_2O]^{2-} - k_{-2}[H^+][IrCl_5S]^{2-}[H_2O] - k[IrCl_5S]^{2-}[H_2O]$$

or $$k_2[SH^+][IrCl_5H_2O]^{2-} = k_{-2}[IrCl_5S]^{2-}[H_2O][H^+] + k[IrCl_5S]^{2-}[H_2O]$$

or $$[IrCl_5S]^{2-} = \frac{k_2[SH^+][IrCl_5(H_2O)]^{2-}}{k_{-2}[H^+][H_2O] + k[H_2O]} \qquad (7)$$

From eqn. 1 we have

$$[SH^+] = K_1[S][H^+] \tag{8}$$

By eqns. 7 and 8 we have

or $$[IrCl_5S]^{2-} = \frac{k_2K_1[S][H^+][IrCl_5(H_2O)]^{2-}}{k_{-2}[H^+][H_2O] + k[H_2O]}$$

or $$[IrCl_5S]^{2-} = \frac{k_2K_1[S][H^+][IrCl_5(H_2O)]^{2-}}{H_2O\ \{k_{-2}[H^+] + k\}}$$

or $$[IrCl_5S]^{2-} = \frac{k_2K_1[S][H^+][IrCl_5(H_2O)]^{2-}}{k + k_{-2}[H^+]} \tag{9}$$

Considering eqns. 1 and9, we have

$$-\frac{d[Ce(IV)]}{dt} = \frac{nkk_2K'[S][H^+][IrCl_5(H_2O)]^{2-}}{k + k_{-2}[H^+]} \tag{10}$$

where $K' = K_1/[H_2O]$

or $$\text{Rate} = \frac{nkk_2K'[S][H^+][Ir(III)]}{k + k_{-2}[H^+]} \tag{11}$$

The rate law (11) is in agreement with all observed kinetics. The rate shows that the order of the reaction is zero-order in [Ce(IV)], first order in ethyl diethylene glycol and Ir(III) and positive effect of [H$^+$] on the rate of reaction. Here n is 2 for ethyl diethylene glycol.

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