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Kinetics and Mechanism of the Ir(III) Catalyzed Oxidation of Methyl Diethylene Glycol by Ce(IV) in Sulphuric Acid Medium

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In present studies, the iridium (III) catalysis in ceric sulphate oxidation of methyl diethylene glycol [MDG] in sulphuric acid medium has been investigated. The reaction is found to be zero-order with respect to cerium (IV) ion and positive effect of hydrogen ion. Zero-order dependence of [Ce(IV)] clearly suggests its involvement in the first step. First-order kinetics with respect to methyl diethylene glycol [MDG] and iridium (III) chloride has been observed. There is insignificant effect of ionic strength potassium sulphate and sodium hydrogen sulphate ($NaHSO_4$) 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. On the basis of the experimental findings a suitable mechanism has been proposed. The reaction product was identified, and the results were also confirmed by statistical regression analysis data.

Key Words: Kinetics, Mechanism, Oxidant Ce(IV), Methyl-diethylene-glycol, Ir(III) Catalyst.

INTRODUCTION

Ceric sulphate [Ce(IV)] has been used as an oxidising agent in the quantitative estimation of a large number of compounds. Various investigations on oxidation kinetics involving cerium (IV) and oxalic acid[1-3], malonic acid[4], maleic acid[5], fumaric acid[6], aliphatic ketones and aldehydes[7,8], isobutyric acid and 3-bromopropionic acid[9,10] have been reported. Although the oxidative capacity of cerium(IV) has been examined in several uncatalyzed and catalyzed reaction in acidic medium, it appears from the literature that no attempt has, so for, been made to explore, the catalytic potential of iridium (III) in ceric (IV) oxidation. Various investigations are also made on the cerium(IV) oxidation in aqueous H_2SO_4 where cerium(IV) froms strong sulfato complexes[11]. This prompted the authors to perform the present work, which constitutes on investigation on the kinetics and mechanism of the iridium(III) cataysed oxidation of methyl diethylene glycol by Ce(IV) in sulphuric acid medium.

EXPERIMENTAL

Ceric sulphate solution was prepared by warming it in sulphuric acid and double distilled water. The strength of sulphuric acid was maintained at least 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 Merck. Aqueous solution of methyl 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. Other chemical used were either analaR or chemically pure reagent. All the kinetic measurements were carried out at constant temperature (± 0.1ºC). 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 (35ºC) 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 sulfate solution and back titrating unreacted ferrous ion with standard Ce(IV) solution using ferrion as an internal indicator.

RESULTS AND DISCUSSION

The oxidation of methyl diethylene glycol by Ce(IV) studied over a wide range of concentration of the reactant showed that the reaction follows first-order with respect to methyl diethylene glycol (Fig. 1). It gives a straight line with unit slope, which confirms the first-order kinetics. A linear increase in first-order rate constant with an increase the initial concentration of iridium(III) was observed which shows the first order reaction with respect to 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. Addition of $NaHSO_4$ and Na_2SO_4 has no significant effect on the reaction rate.

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

[Methyl 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})
1.67	0.50	0.80	7.65	3.42	—
1.67	0.67	0.80	7.65	3.32	—
1.67	1.00	0.80	7.65	3.46	—

[Methyl 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})
1.67	1.25	0.80	7.65	3.36	—
1.67	1.67	0.80	7.65	3.48	—
1.67	2.00	0.80	7.65	3.40	—
0.56	2.00	0.80	7.65	1.10	1.96
0.84	2.00	0.80	7.65	1.68	2.00
1.25	2.00	0.80	7.65	2.50	2.00
1.67	2.00	0.80	7.65	3.40	2.04
2.50	2.00	0.80	7.65	4.88	1.95
3.34	2.00	0.80	7.65	6.72	2.01
1.67	2.00	0.80	1.90	0.86	4.53
1.67	2.00	0.80	3.80	1.75	4.60
1.67	2.00	0.80	5.70	2.48	4.35
1.67	2.00	0.80	7.65	3.46	4.52
1.67	2.00	0.80	11.50	5.00	4.35
1.67	2.00	0.80	15.30	6.96	4.55
1.67	2.00	0.50	7.65	2.58	—
1.67	2.00	0.80	7.65	3.68	—
1.67	2.00	1.00	7.65	4.78	—
1.67	2.00	1.21	7.65	6.92	—
1.67	2.00	1.50	7.65	8.08	—
1.67	2.00	2.25	7.65	10.88	—

TABLE-2

EFFECT OF IONIC STRENGTH, SO_4^{2-}, HSO_4^- AND TEMPERATURE

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})
—	3.015	0.20	0.00	3.34
—	3.615	0.40	0.00	3.36
—	4.215	0.60	0.00	3.40
—	4.815	0.80	0.00	3.38
—	5.415	1.00	0.00	3.34
—	8.415	2.00	0.00	3.42
—	14.415	3.00	0.10	3.36
—	3.412	2.00	0.12	3.46
—	3.412	2.00	0.14	3.40
—	3.412	2.00	0.16	3.48
—	3.412	2.00	0.18	3.36
—	3.412	2.00	2.00	3.32
—	3.412	2.00	0.00	3.42
30	3.024	0.20	0.00	2.42
35	3.024	0.20	0.00	3.40
40	3.024	0.20	0.00	5.06
45	3.024	0.20	0.00	7.96

TABLE-3
THERMODYNAMIC PARAMETERS AT 35°C

k_r (s^{-1})	E_a (kJ mol^{-1})	log A	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
1.74×10^{-4}	76.91	9.28	74.35	–16.93	79.56

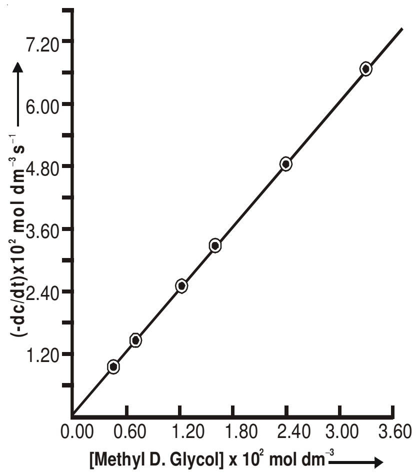


Fig. 1. Variation of substrate (methyl diethylene glycol) at 35°C

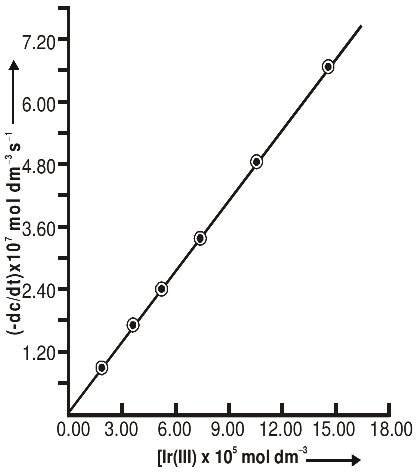


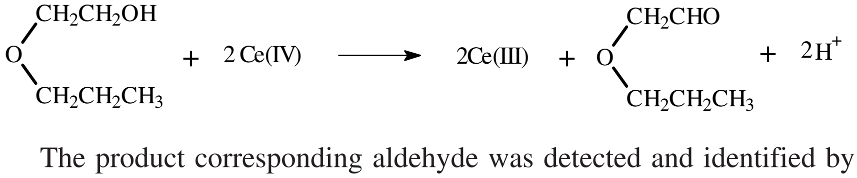
Fig. 2. Variation of catalyst at 35°C

[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}

[Ce(IV)] × 10^3 = 2.00 mol dm^{-3}
[H_2SO_4] = 0.80 mol dm^{-3}
[Methyl diethylene glycol] × 10^5 = 1.67 mol dm^{-3}
[Na_2SO_4] = 0.20 mol dm^{-3}
μ = 3.024 mol dm^{-3}

Stoichiometry and product analysis

Several reaction mixture of [oxidant] : [methyl diethylenen glycols] at fixed H^+ concentration were prepared under the condition [glycol] << [oxidant] *i.e.* [methyl 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 methyl diethylene glycol. The stoichiometric equation is as follows:



$$O(CH_2CH_2OH)(CH_2CH_2CH_3) + 2\,Ce(IV) \longrightarrow 2Ce(III) + O(CH_2CHO)(CH_2CH_2CH_3) + 2H^+$$

The product corresponding aldehyde was detected and identified by paper[12] and thin layer chromatography[13].

Mechanism

$$\mathrm{S + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} SH^+} \tag{1}$$

$$\mathrm{SH^+ + [IrCl_5H_2O]^{2-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X + H^+ + H_2O} \tag{2}$$

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

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

rate determining and slowest step.

$$\mathrm{S^+ + Ce(IV) \rightarrow Product\ (P) + Ce(III)} \tag{4}$$

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

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

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

$$-\frac{d[\mathrm{CeIV}]}{dt} = \mathrm{nk[IrCl_5S]^{2-}} \tag{6}$$

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

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

or

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

or

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

From equation (1) we have $[\mathrm{SH^+}] = \mathrm{K_1[S][H^+]}$ (8)

By equation (7) and (8) we have

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

or

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

or

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

Considering eqns. 1 and 9, we have

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

where $K^{l} = K_1/[H_2O]$

or

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

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 methyl diethylene glycol and Ir(III) and positive effect of $[H^+]$ on the rate of reaction. Here n is 2 for methyl diethylene glycol.

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