

Kinetics and mechanism of iridium (III) catalysed oxidation of glycols by cerium (IV) in aqueous acidic media

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(Received: March 08, 2008; Accepted: April 17, 2008)

ABSTRACT

Kinetics and mechanism of iridium (III) catalysed oxidation of Glycols by cerium (IV) in aqueous sulphuric acid medium have been investigated at different temperatures [Glycols] \gg Ce (IV) \gg (IR) (10^{-5} mol/dm³) in 1 mol dm⁻³ sulphuric acid medium. The reactions are found to be the first order with respect to Ce (IV) ion and observed first order rate constant. From the [HSO₄] dependence, Ce (IV) has been found kinetically active the proposed mechanism involves a pre-equilibrium interaction between the catalyst and substrate. The process is acid catalysed. Activation parameters have been determined to investigate the effect of temperature; and probable rate law and mechanism has been proposed.

Key words : Catalysed oxidation, Glycols, iridium (III), cerium (IV).

INTRODUCTION

The use of Ir (III) and Ru (III) in trace amounts as an efficient catalysts in the homogeneous reactions involving Ce (IV) as an oxidant has been reported^{1,2} several kinetic investigations on redox reactions involving Ce (IV) and different organic and inorganic compounds including different alcohols have been carried out³⁻⁸.

Kinetic study on the oxidation of ethanol by Ce (IV) in perchloric acid media have been reported by glycols by Ce (IV) and oxalic acid²⁻⁴, malonic acid⁵, aliphatic ketones and aldehydes^{6,7}, isobutylic acid and 3-bromopropanoic acid^{8,7} have been studied⁹. Various investigations are also made on Ce(IV) aqueous H₂SO₄, where it forms strong sulphato complex¹⁰. Hence we reported here kinetics and mechanism of Iridium (III) catalysed oxidation of glycols by Ce(IV) in aqueous acidic medium.

The kinetic study shows that oxidation of

Glycols by Ce (IV) in aqueous sulphuric acid media is slow but gets catalysed by Ir (III) at trace concentration (10^{-5} mol dm⁻³). It prompted us to explore the kinetic behaviour of the title reaction in detail on metal ion catalysis in Ce (IV) oxidation.

MATERIAL AND METHODS

Cerium (IV) stock solution was obtained by dissolving Ce (IV) (Himedia A.R.) in 1.0 mol dm⁻³ sulphuric acid. The stock solutions were kept at room temperature for more than 48 hours to attain equilibrium and was standardised with ammonium iron (II) sulphate solution using ferroin as an indicator. Glycols were of Across Organics grade. Doubly distilled water was used throughout the experiment. Ir (III) solution was prepared in 1 mol dm⁻³ H₂SO₄ solution.

Procedure and kinetic measurements

Kinetic measurements were carried out on a Elico (CL 157 Colorimeter). The progress of the reaction was monitored by measuring absorbance

of at 350 nm. The kinetic study were carried out under pseudo-first order conditions using [Glycols] \gg [Ce (IV)]. To a thermally equilibrated solution containing Ce (IV), H₂SO₄, Ir (III) and glycol solutions were added to form the reaction mixture and progress of the reaction was monitored at regular time intervals by observing variation of optical density with time. H⁺ ion concentration was maintained by the addition of required amounts of H₂SO₄. The pseudo first order rate constants were computed by the graphical method and the experimental values were reproducible within $\pm 3\%$.

RESULTS AND DISCUSSION

Under varying concentration of [Glycols] and [Ce(IV)] kinetics of Ir (III) catalysed oxidation of Glycols by Ce (IV) in aqueous sulphuric acid media was investigated at several concentrations of the reactants indicating first order kinetics with each glycol. The results are shown in Table 1.

The rate of the reactions were studied under varying [Ce (IV)]. Plots of log [O.D.] versus time were linear indicating a zero order dependence in [Ce(IV)] from the pseudo-first order rate constants were computed.

The rates were increased with increase in [Glycols]. From the plots of log [O.D.] versus time, the Pseudo-first order rate constants (K_{obs}) were evaluated at, different values of [Glycols]. The order in [Glycols] was found to be first order indicating the formation of a complex between Ir(III) and [Glycols]. The fact is supported by the linearity of plot of $1/K_{obs}$ Versus $1/[Glycols]$ giving intercept.

Keeping [Ce(IV)] and [Glycols] constant, increase in Ir (III) increased the rate and the order in Ir (III) was found to be first order indicating the complex formation between them which has been confirmed by reciprocal plots of $1/K_{obs}$ Versus $1/Ir$ (III).

Table 1 : Pseudo-first order rate constants at 298.15 K for the Ir (III) catalysed oxidation of glycols by Ce (IV) in aqueous sulphuric acid medium 0.25 mol/dm³, [H⁺] = 0.1 mol dm⁻³ [Ir (III)] = 1 x 10⁻⁵ mol dm⁻³.

[Substrate] x 10 ⁻² mol dm ⁻³	$K_{obs} \times 10^2$ (min ⁻¹)	
	1,3-butane glycol	1,5-pentane glycol
6.48	0.342	7.587
7.40	0.388	8.256
8.33	0.431	8.792
9.25	0.475	9.139
10.18	0.546	10.467
10.61	0.666	11.684
11.38	0.864	13.374

At constant [Ce (IV)], [Glycols] and [Ir (III)], an increase in [H⁺] increased the rate of oxidation. These results could be explained by proposing the following equilibrium in which the neutral Ce (IV) was assumed to be the reactive species. The reactions were studied at different temperatures and rate constants at 15-45 °C (where used to

calculate K (specific rate constant)). ΔH and ΔS for the oxidation of each glycols and their values are reported in Table 2.

Under the experimental conditions, from an independent experiment, in the absence of substrate, it has been found that Ir (III) catalysed

Table 2 : Activation parameters at 298.15K for the Ir (III) catalysed oxidation of Glycols by Ce (IV) in aqueous H₂SO₄ medium.

Substrate	K _{obs} 10 ⁻⁴ Sec ⁻¹	Ea J Mol ⁻¹	ΔH [#]	ΔS [#]
1,3-butane glycol	1.153	2136.9879	1544.862	-49.8226
1,5-pentane glycol	13.062	7170.4450	6578.319	-33.5509

oxidation of water by Ce (IV) is insignificant. Hence, this path was not taken into consideration to calculate the k_{obs}.

When Ir(III) is mixed with excess of Ce(IV) it is oxidized¹¹⁻¹³ rapidly to Ir(IV) by Ce(IV) as shown in equation (1).

Pseudo-first order rate constants at 298.15 K for the Ir (III) catalysed oxidation of glycols by Ce (IV) in aqueous sulphuric acid medium.

Mol dm⁻³, [H⁺] = 0.1 mol dm⁻³ [Ir (III)] = 1 x 10⁻⁵ mol dm⁻³

The effect of temperature has been studied from the range of 15°C to 45°C, under the experimental conditions. The energy of activation was computed by the Arrhenius plots. The calculated pseudo-first order rate constants at 298.15 k are shown in Table 2.

Generally electron-donating groups like – OCH₃, –CH₃ increase the rate of the oxidation. Based on experimental facts such as the rate data, induced

polymerization, orders of the species of activation parameters, the most probable mechanism, proposed is as shown in Scheme 1.

Scheme 1

Scheme 1 leads to rate law which is in the form of the experimentally observed one – Where k obtained from experimentally from the effect of [substrate] on k_{obs}.

At constant [Ir (III)] the plot of 1/K_{obs} Versus 1/[substrate] was found to be linear and from the slope and intercept of which the values of formation constant K and bimolecular rate constants k were calculated.

Constancy in the calculated values of ΔG[#] for these oxidation reactions indicates that the same type of the reaction mechanism could be operative for the oxidation reactions. The complex formation between Substrate and Ir (III) takes place & finally the complex decomposes into products as per detailed proposed mechanism of oxidation as shown in Scheme 1.

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