Oriental Journal of Chemistry Vol. **26**(3), 1183-1185 (2010)

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

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(Received: May 19, 2010; Accepted: July 02, 2010)

Kinetic and mechanism of iridium (III) catalyzed oxidation of Alcohol and Giycol by cerium (IV) in aqueous sulphuric medium have been investigated at different temperature [glycols]>>Ce(iv)>>(ir)(10-5 mol dm-3 sulphuric acid medium. The reactions are found to be the first order and zero order with respect to Ce (iv) ion and observed first order rate constant. From the [HSO_4] 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: Alcohol, Tridium (III), Glycois, Cerium (iv) and acidic medium.

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 cut[3-8].

Kinetic study on the oxidations of ethanol by Ce(IV) in perchloric acid media have been reported by glycols by Ce(IV) and oxalic acid[2-4] malonic acid5, aliphatic ketones and aldehyde[6-7].isobutylic acid and 3-brornopropanoic acid[8-7]. have been studies[9]. various investigations are also made on Ce(IV) aqueous H_2SO_4, where it forms strong sulhate complex[10]. Hence we reported here kinetics and mechanism of Iridiurn (III) catalysed oxidation of alcohol and glycol by Ce(IV) in aqueous acidic medium.

The kinetic study shows that oxidation of Alcohol and Glycol by Ce(IV) in aqueous sulphuric acid media is slow but gets catalysed by Ir(IV) at trace concentration (10^{-5} mol dm^{-3}) it prompled us to explore the kinetic behavior 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 hrs. to attain equilibrium and was standardized with ammonium iron (ii) sulphate solution using ferroin as an indicator Glycols were of Across Organics grade Doubly distilled water used throughout the experiment Ir (iii) solution was prepared in 1 mol dm^{-3} H_2SO_4, solution.

Procedure and kintetic measurement

Kinetic measurement were carried 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] >> [Ce (IV)]. To a thermally equilibrated solution

containing Ce(iv), H_2SO_4, 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 mainted by the addition of required amounts of H_2SO_4, the pseudo first order rate constants were computed by the graphical method and the experimental values were reproducible within $^{+3\%}$.

RESULTS AND DISCUSSION

Under varying concentration of [Alcohols], [Glycols]and [Ce(iv) kinetics of Ir(iii) catalysed oxidation of Alcohol and Glycol by Ce(iv) in aqueous sulphuric acid media was investigated at several concentration of the reactions indicating first order kinetics alcohols and first order with respect to giycol. 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 first order dependence in [Ce(iv)] from the pseudo-first order rate constants. Were computed. Under varying [Ce(IV)]. Plots of log [O.D] versus time were indicating first order dependence in [Ce(iv)] with respect to alcohol and zero order with respect to glycol.

The rates were increased with increase in [Glycols]. From the plots of log[O.D] versus time, the Pseduo-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. Under the kinetic conditions, at fixed [Ir] the plot of K_{obs}. Vs [substrate] indicating first order for substrate.

Keeping [Ce(iv)], [Alcohol] 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).

There results could be expained by proposing the following equilibrium in which the neutral Ce(iv) was assumed to be the reactive species. The reactions were studied at different temperature and rate constants at 15-45°C (where used to calculate K (specific rate constant). $\Delta H^{\#}$ and $\Delta S^{\#}$ for the oxidation of each alcohol and glycol 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 oxidation of water by Ce(iv) is insignificant Hence, this path was not taken into consideration to calculate the K_{obs} .

Table 1: Pseudo – first order rate constant at 298.15 K for the Ir(iii) catalysed oxidation of alcohol and glycol by Ce(iv) in aqueous sulphuric acid medium 0.25 mol/dm^3

[Substrate] x 10^{-2} mol dm^{-3}	K_{obs} x 10^2 (min^{-1})	
6.48	0.342	02.21
7.40	0.388	02.737
8.33	0.43.1	03.066
9.25	0.475	03.46
10.18	0.546	03.896
10.61	0.666	04.418
11.38	0.864	04.788

Table 2: Activation parameters at 298. 15K for the Ir(ii) catalysed oxidation of Alcohol and Glycol by Ce(iv) in aqueous H_2SO_4, medium

Substrate	$K_{obs}10^{-4}$ Sec^{-1}	Ea JMol^{-1}	$\Delta H^{\#}$ J^{-1} Mol^{-1}	$\Delta S^{\#}$J^{-1} Mol^{-1}
4-methhyl, 2-pentanol	1.153	2136.9879	1544.862	-49.8226
2- methyl 2,4-pentane glycol	7.782	9933.0736	9340.948	-24.1311

When Ir(III) is mixed with excess of Ce(iv) it is oxidized[11-13] rapidly to Ir(iv) by Ce(iv) as shown in equation (1).

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 completed by the Arrhenius plots. The calculated pseudo-first order rate constants at 298.15 k are shown in table 2.

$$\text{Ir (III)} + 2\text{Ce (IV)} \rightarrow \text{Ir(IV)} + \text{Ce(III)} \quad ...(1)$$

$$\text{S} + \text{Ir(III)} \rightleftarrows \text{Intermediate}$$

$$\text{Intermediate} \rightarrow \text{F} + 2\text{H} + + \text{Ir(IV)}$$

$$\text{F} + \text{Ce(IV)} \xrightarrow[\text{fast}]{\text{HOH}} \text{product} + \text{H} + + \text{Ce(III)}$$

$$\text{Ir} + \text{Ce(IV)} \xrightarrow{\text{fast}} \text{Ir(iv)} + \text{Ce(III)}$$

$$\text{Ir(IV)} + \text{Ce(IV)} \xrightarrow{\text{fast}} \text{Ir(III)} + \text{Ce(III)}$$

Where k obtained from experimentally from the effect of [substrate] on k_{obs}.

Based on experimental facts such as the rate data. Induced polymerization. Orders of the

$$\frac{-d[\text{Ce(IV)}]}{dt} = K_1[\text{S}]\ [\text{Ir(IV)}] \text{ Since Ir(IV) = Ir(I}$$

Hence it can be written as,

$$\frac{-d[\text{Ce(Iv)}]}{2} = \text{K1[s]}\ [\text{Ir(III)}]$$

species of activation parameters, the most probable mechanism, proposed is as shown in 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 "G 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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