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A KINETIC STUDY OF THE SOLVENT EFFECT ON THE MECHANISM OF CATALYSED OXIDATION OF GLYCOL BY BrO^-_3 IN ALKALINE MEDIUM

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ABSTRACT

The kinetic data obtained in ruthenium(VI) catalysed oxidation of methyldiethylene glycol (MDG) in alkaline medium using potassium bromate as oxidant and ruthenium tetroxide as a homogenous catalyst. In this kinetic reaction mercuric acetate acts as a liberated bromide ion scavenger. The result shows first order with respect to $KBrO_3$, Glycol, [(MDG] and [Ru(VI)] respectively. It shows zero order dependences of the reaction on solven, which is used as medium of the reaction and also zero effect of mercuric acetate. In this catalysed reaction ionic strength has positive effect. The corresponding acid was found to be main oxidation product. A plausible reaction mechanism in agreement with kinetic results was put forward.

KEYWORDS: Oxidation, Kinetics and Mechanism, Glycol, Potassium Bromate, Ruthenium (VI) Homogeneous Catalysis

Potassium bromate with redox potential 1.44 V is a very strong oxidant and it has been used in the oxidation of many organic substrates (Patel *et al.*, 2017; Srivastava *et al.*, 2008; Srivastava *et al.*, 2004) Apart from its action as oxidant, in presence of bromide ion, potassium bromate acts as a resource of bromine in the reaction. Mercuric acetate (Subramanian and Thigarajan, 1969; Bailer, 1964; Singh *et al.*, 2003) eliminates the possibility of complex reaction, which would be formed during the redox reaction of potassium bromate and bromide ion (reaction product). The use of transition metal ions (Sergar *et al.*, 2007; Srivastava *et al.*, 2008; Singh *et al.*, 2009; Singh *et al.*, 1993; Singh *et al.*, 2007; Singh *et al.*, 2005; Singh *et al.*, 2011) such as Osmium(VIII), Ruthenium(III), Ruthenium(VI), Ruthenium(VIII) and Iridium(III) as homogenous catalysts in the oxidation of various organic substrates by different oxidising agent has generated greater role in the industries. The kinetics of redox reaction (Lone Arafat *et al.*, 2018; Rao *et al.*, 2020; Reddy and Kumar, 2007) incorporating certain transition metal ions, viz Os(VIII), Ru(III), Ru(VI) and Pd(II) as homogeneous catalyst has been extensively investigated. The redox reaction catalyzed by transition metal ion is of immense interest (Bhat *et al.*, 2002) and it plays significant role in the mechanism of such redox reaction. Generally transition metal halides and oxides have been used as a homogeneous catalyst in most of the redox reaction (Srivastava *et al.*, 2001). The transition metal chloride such as ruthenium, rhodium and iridium use as homogeneous catalyst. In these catalyst, ruthenium is highly toxic where as rhodium and iridium are moderately toxic. But several researcher (Srivastava *et al.*, 2001) investigate ruthenium (III) chloride used as a non toxic catalyst. However, the reaction involving Ru(VI) as homogeneous catalyst (Singh *et al.*, 2013) have not been much investigated. There seems to be few reports on the Ru(VI) as homogeneous catalyst. The oxidation of Methyl Diethylene Glycol (MDG) by $KBrO_3$ is very slow in alkaline medium. In view of scant kinetic information about catalytic reactivity, biological properties and potential applications of Ru(VI) as well as due to importance of Potassium Bromate in industries, Aspects of thermodynamic parameters with A kinetic approach of transition metal catalysed by potassium bromate oxidation of methyl diethylene glycol (MDG) in alkaline medium with main aims we have (a). The reactive species of $KBrO_3$ in alkaline medium, (b). Reactive species of Ruthenium (VI), (c). The role of mercuric acetate, trapping agent for Br^- ions scavenger and it is not involved as catalyst and finally (d). To elucidate the mechanistic paths and derive the rate law consistent with kinetic results have been reported.

EXPERIMENTAL

Methyl Diethylene Glycol (MDG), potassium bromate, mercuric acetate, NaOH and other regents used were of A.R. grade, double distilled water was used throughout. Aqueous solution of ruthenium tetroxide was prepared by dissolving its one gram sample (Johnson and Matthey) in 0.1N standard NaOH solution and for final strength of ruthenium tetroxide, this solution was diluted

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to one liter. Sodium hydroxide (E. Merch) was used to maintain alkalinity of the solution and to maintain ionic strength (µ) of the medium, sodium perchlorate (E. Merch) was employed.

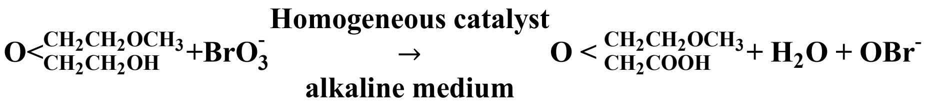
KINETIC MEASUREMENTS

The reaction mixture containing requisite amount of all other reactants of redox reaction, except oxidant, were taken in reaction vessel (blackened conical flask) which was kept in an electrically operated thermostatic water bath set at desired temperature ($\pm 0.1^0$C). The requisite volume of oxidant was also taken in another black coated vessel which was also placed in the same thermostate for thermal equilibrium. The reaction was initiated by rapid addition of oxidant to the reaction mixture and mixing them by vigorous shaking. The progress of the reaction was monitored volumetrically and the amount of unconsumed $KBrO_3$ periodically by iodometric titration using starch as an indicator.

STOICHIOMETRY AND PRODUCT ANALYSIS

Different concentration ratio sets were carried out, $[KBrO_3]$: [MDG] ratios under $[KBrO_3] \gg [MDG]$ for 48 hours or 72 hours. Estimation of unreacted $KBrO_3$ showed that one mol of MDG consumes one mol of $KBrO_3$. This result show that 1:1 stoichiometry.

The oxidation product of MDG was identified with the help of spot tests (Fiegl F, 1996), equivalence kinetic studies and thin layer chromatography (TLC) (Singh and Verma, 2006). The stoichiometric determination indicated the overall reaction (Scheme a).



$$O<\begin{smallmatrix}CH_2CH_2OCH_3\\ CH_2CH_2OH\end{smallmatrix} + BrO_3^- \xrightarrow[\text{alkaline medium}]{\text{Homogeneous catalyst}} O<\begin{smallmatrix}CH_2CH_2OCH_3\\ CH_2COOH\end{smallmatrix} + H_2O + OBr^-$$

……… (a)

Methyl Diethylene Glycol

RESULTS AND DISCUSSION

The kinetics result obtained as several initial concentrations of reactants are reported in Table 1. The plot of (-dc/dt) versus $[KBrO_3]$ shows first order with respect to potassium bromate (Fig 1). Linear increase is first order rate constant (k_{obs}) within the concentration of MDG clearly shows first order kinetics of the reaction on [MDG]. From the plot of $\log k_{obs}$ versus log [Ruthenium(VI)] which gives slope of 1.04, confirming first order in [Ru(VI)]. (Fig 2).

Negligible effect of the successive addition of mercuric acetate was observed. The variation of concentration of sodium hydroxide showed zero effect on the rate constant, while positive effect of variation of ionic strength of the medium (affected by addition of suitable amount of $NaClO_4$) has been observed (Table 2). The values of activation energy (Ea), entropy of activation (ΔS^*) and free energy of activation (ΔG^*) were calculated at 25^0C, 30^0C, 35^0C and 40^0C, and corresponding values found as 70.85 kJ mol^{-1}, 51.83 JK^{-1} and 52.30 kJ mol^{-1} respectively.

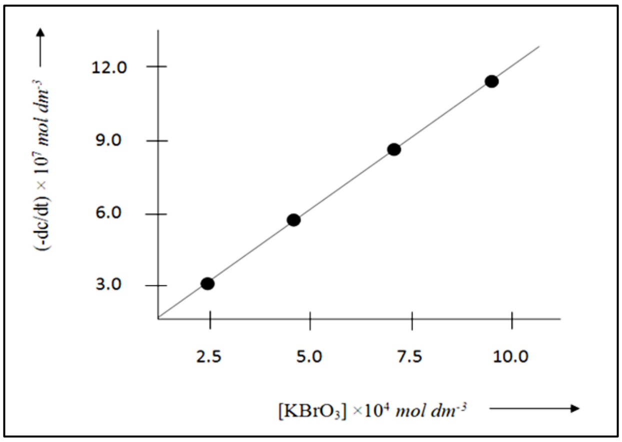


Figure 1: Plot of (-dc/dt) Vs $[KBrO_3]$ at 35^0C

[MDG] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-5} mol dm^{-3}

[NaOH] = 1.00×10^{-3} mol dm^{-3}

$[Hg(OAc)_2]$ = 3.34×10^{-3} mol dm^{-3}

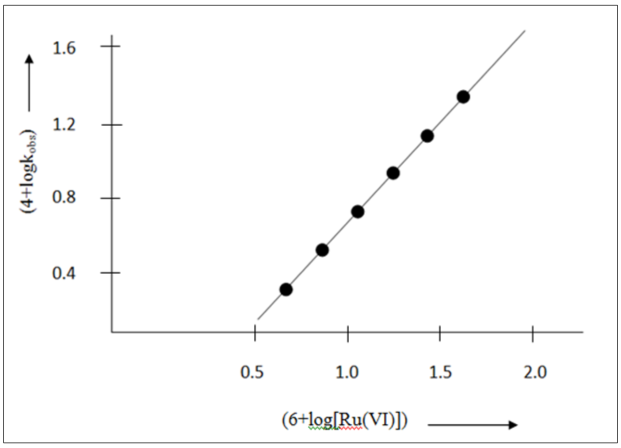


Figure 2

$[KBrO_3]$ = 4.16×10^{-4} *mol dm*$^{-3}$

$[MDG]$ = 5.00×10^{-2} *mol dm*$^{-3}$

$[NaOH]$ = 1.00×10^{-3} *mol dm*$^{-3}$

$[Hg(OAc)_2]$ = 3.50×10^{-3} *mol dm*$^{-3}$

The negligible effect of successive addition of mercuric acetate on reaction rate indicates that it is playing as trapping agent for bromide ions produced in the reaction and thus has its limited role as Br^-ions scavenger and it is not involved as catalyst. Its role as oxidant is also neglected as in the absence of $KBrO_3$ reaction does not progress with mercuric acetate. Thus mercuric acetate eliminates the parallel oxidation by free bromine which could have been formed by the interaction of potassium bromate with bromide ion produced as reaction product. Ruthenium tetroxide, prepared in carbonate free 0.1N NaOH solution is reduced by hydroxide ions to rethenate ions according to the following equilibria :

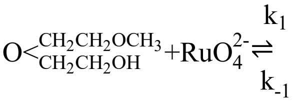
$$4RuO_4+4OH^- \rightleftharpoons 4RuO_4^- + 2H_2O + O_2 \ \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

$$4RuO_4^- + 4OH^- \rightleftharpoons 4RuO_4^{-2} + 2H_2O + O_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(ii)}$$

Electronic spectral studies (Connick and Fine, 1960) shows that lower oxidation states of ruthenium are present as hydrated species, but higher oxidation states of ruthenium need not to be hydrated. It has been reported (Syman and Corvington, 1960) that the coordination of hydroxyl ions with perruthenate occurred to a lower negligible extent because ruthenium represents an intermediate case between osmium and Rhenium. Therefore, ruthenate ions, i.e. Ru(VI), may coordinate with hydroxide ions to a negligible lower extent. Therefore, most of Ru(VI) remains as ruthenate ion RuO_4^{-2}, which can be taken to be the catalytic species of Ru(VI).

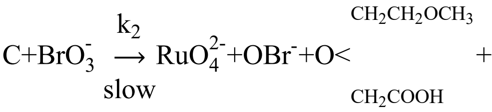
MECHANISM AND DERIVATION OF RATE LAW

Considering the reactive species of Ru(VI) along with all other kinetic effects the following reaction mechanism is proposed by alkaline potassium bromate oxidation of MDG catalysed by Ru(VI) in which BrO_3^- is assumed to be oxidative species of potassium bromate in alkaline medium as reported by earlier workers (Hiremath *et al.*, 2006).



$$O{<}\begin{matrix}CH_2CH_2OCH_3\\CH_2CH_2OH\end{matrix} + RuO_4^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex [C]} \ \ldots\ldots\ldots\ldots\ldots \text{(1)}$$

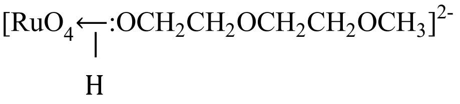
(MDG)



$$C + BrO_3^- \underset{\text{slow}}{\overset{k_2}{\longrightarrow}} RuO_4^{2-} + OBr^- + O{<}\begin{matrix}CH_2CH_2OCH_3\\CH_2COOH\end{matrix} + H_2O \ \ldots\text{(2)}$$

$$OBr^- + BrO_3^- \xrightarrow{k_3} 2Br^- + 2O_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

where complex [C] may be written as :



$$[RuO_4 \leftarrow :\underset{\displaystyle H}{\underset{|}{O}}CH_2CH_2OCH_2CH_2OCH_3]^{2-}$$

The oxygen atom containing lone pair of electrons in MDG forms a coordinate bond with RuO_4^{2-} species of [Ru(VI)] giving rise to above complex [C] formation step (1) which interacts with BrO_3^-. It is a slow step reaction and therefore it is rate determining step (2).

Now considering steady state approximation to [C], the rate law (4) in terms of rate of loss of $[BrO_3^-]$ may be written as –

$$\frac{-d[BrO_3^-]}{dt} = \frac{k_{-1}k_2[RuO_4]^{2-}[BrO_3^-][MDG]}{k_{-1}+k_2[BrO_3^-]} \ \ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Since step (2) is slow and rate determining step hence $k_2[BrO_3^-] << k_{-1}$ inequality may be assumed. Therefore in the light of this inequality rate law (4) may be written as rate law (5).

$$\frac{-d[BrO_3^-]}{dt} = k_{obs}[BrO_3^-][MDG][Ru(VI)] \ldots\ldots\ldots\ldots\ldots\text{(5)}$$

where $k_{obs} = \frac{k_1 k_2}{k_{-1}}$

Table 1: Effect of variation of reactants concentration at 35^{0}C

$[\mathrm{KBrO_3}] \times 10^4 \mathrm{mol\ dm^{-3}}$	$[\mathrm{MDG}] \times 10^2 \mathrm{mol\ dm^{-3}}$	$\mathrm{k_{obs}} \times 10^4 \mathrm{s^{-1}}$
1.67	5.00	13.40
2.67	5.00	13.20
3.34	5.00	13.06
4.16	5.00	13.21
6.67	5.00	13.56
8.34	5.00	13.30
4.16	1.25	3.32
4.16	2.50	6.74
4.16	3.75	10.28
4.16	5.00	13.21
4.16	6.25	16.74
4.16	7.50	20.76
3.34	5.00	5.82^a
3.34	5.00	8.66^b
3.34	5.00	19.92^c
^{a}Temperature 25^{0}C	^{b}Temperature 30^{0}C	^{c}Temperature 40^{0}C

[Ru(VI)] = 4.80 × 10^{-5} mol dm^{-3}, [NaOH] = 1.00 × 10^{-3} mol dm^{-3}, [Hg(OAc)$_2$] = 3.50 × 10^{-3} mol dm^{-3}, μ = 12.3× 10^{-3} mol dm^{-3}.

Table 2: Effect of variation of [NaOH], [Hg(OAc)$_2$] and ionic strength (μ) at 35^{0}C

$[\mathrm{Hg(OAc)_2}] \times 10^3 \mathrm{mol\ dm^{-3}}$	$[\mathrm{NaOH}] \times 10^3 \mathrm{mol\ dm^{-3}}$	$(\mu) \times 10^3 \mathrm{mol\ dm^{-3}}$	$\mathrm{k_{obs}} \times 10^4 \mathrm{s^{-1}}$
0.50	1.00	13.34	13.08
0.75	1.00	13.34	13.04
1.00	1.00	13.34	12.98
2.00	1.00	13.34	13.10
3.00	1.00	13.34	13.02
4.00	1.00	13.34	13.00
3.50	0.50	13.34	12.80
3.50	1.50	13.34	13.00
3.50	2.00	13.34	13.20
3.50	2.50	13.34	13.10
3.50	3.50	4.34	4.32
1.00	1.00	6.34	6.76
1.00	1.00	8.34	9.00
1.00	1.00	10.34	11.08
1.00	1.00	13.34	12.28
1.00	1.00	16.34	13.04

[KBrO$_3$]= 3.34 × 10^{-4}mol dm^{-3}, [MDG] = 5.00 × 10^{-2}mol dm^{-3}, [Ru(VI)] = 4.80 × 10^{-5}mol dm^{-3}

CONCLUSION

The present study shows that in Ru (VI)-catalysed oxidation of MDG by potassium bromate in alkaline medium, BrO$_3^-$ is reactive species of potassium bromate in alkaline medium and ruthenate ion RuO$_4^{-2}$ can be taken to be catalytic species of Ru (VI) in alkaline medium. The formation of a reactive complex between reactive species of Ru (VI) and reducing MDG molecule in alkaline medium is well supported by the observed kinetic results.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

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