



## Substrate Inhibition in Ruthenium(III) Catalyzed Oxidation of Propane-1,3-diol by Periodate in Acidic Medium: A Kinetic Study

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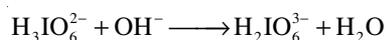
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Ruthenium(III) catalyzed oxidation of propane-1,3-diol by potassium periodate was studied in aqueous perchloric acid medium. Orders of reaction with respect to concentrations of oxidant, substrate, acid and catalyst were determined. First order in oxidant and catalyst concentrations, and inverse fractional order in acid medium were observed. In addition, substrate inhibition (*i.e.* a decrease in reaction rate with an increase in substrate concentration) was observed. Effect of addition of salt and solvent was studied. Based on the studies of temperature variation, Arrhenius parameters were calculated. Plausible mechanism was also proposed based on observed kinetics.

**Keywords:** Ruthenium(III), Propane-1,3-diol, Oxidation, Acidic medium, Potassium periodate, Kinetics.

### INTRODUCTION

Potassium periodate is a versatile oxidant that can oxidize a number of organic and inorganic compounds. Periodate is used both in alkaline and acidic media [1-5]. In acidic medium, the existing species is  $\text{H}_5\text{IO}_6$  and its non-existence was reported in the pH range of 5 to 9. In aqueous medium with a pH range of 6.1 to 7.3, the possible species of periodate are  $\text{IO}_4^-$ ,  $\text{H}_4\text{IO}_6^-$  and  $\text{H}_3\text{IO}_6^{2-}$ , whereas, the predominant species is  $\text{H}_4\text{IO}_6^-$  near pH = 7.0. In alkaline medium (0.005 to 0.1 M hydroxide concentration), trihydrogen paraperiodate ( $\text{H}_3\text{IO}_6^{2-}$ ) and dihydrogen paraperiodate ( $\text{H}_2\text{IO}_6^{3-}$ ) can be the expected predominant species. Due to participation in the following reaction, the expected species is  $\text{H}_2\text{IO}_6^{3-}$  in highly alkaline medium.



$\text{H}_2\text{I}_2\text{O}_{10}^{4-}$  is another species in alkaline medium. Periodate exists in its dimer form  $\text{I}_2\text{O}_9^{4-}$  at higher concentrations of periodate [6]. Oxidation of pharmaceutically important polyhydric compounds like polyethylene glycols was studied in alkaline medium [7,8]. In those PEG oxidations, transfer of one oxygen atom or two electrons was observed for each periodate, *i.e.* periodate was able to act as oxidant in these reactions till its conversion to iodate. Among the four species of periodate ( $\text{H}_2\text{IO}_6^{3-}$ ,  $\text{H}_3\text{IO}_6^{2-}$ ,

$\text{IO}_4^-$  and  $\text{H}_2\text{I}_2\text{O}_{10}^{4-}$ ) in alkaline medium, concentrations of the first two species are considerable, whereas the concentrations of the other two are trivial in the range of alkali from 0.05 to 0.5 M. Moreover, the predominant species is  $\text{H}_2\text{IO}_6^{3-}$  at higher concentration of alkali, however at low alkali concentration it is  $\text{H}_3\text{IO}_6^{2-}$ .

In addition to well-known trivalent, different oxidation states of ruthenium catalyst were proposed in different reactions. Ruthenium(IV) was the proposed reactive form of ruthenium in the oxidation of diols by peroxodiphosphate in acidic medium. Alteration of electrons availability at the oxidation site by the positive inductive effect was used to explain the reactivity order of ethane-1,2-diol < propane-1,2-diol < butane-1,2-diol. Some researchers [4,9] reported the quick conversion of trivalent ruthenium to octavalent by periodate in acidic medium.

Further reported the existence of Ru(VIII) in acidic medium in the form of  $\text{H}_2\text{RuO}_5$  or  $\text{RuO}_3(\text{OH})_2$ . The former was assumed to be active catalytic species in the kinetics of ruthenium(III) catalyzed oxidation of methyl glycol by periodate in perchloric acid [4] to form the corresponding monocarboxylic acid as the product. Participation of more powerful oxidant species Ru(V) was proposed for the observed catalysis in the oxidation of alanine [10] and monoethanolamine [11] by *N*-bromosucci-

nimide (NBS) in aqueous acetic acid-perchloric acid medium. Acceleration of NBS oxidation of monoethanolamine with the involvement of Ru(V) was substantiated with the presence and absence of catalysis with Ru(III) and Os(VIII), respectively. It indicates the absence of complexation in these reactions, but the formation of Ru(V) [11].

Oxidation of alcohols by various oxidants is well documented in literature. In the kinetics of oxidation of neopentyl glycol by diperiodatocuprate(III) [5], protonated form of  $\text{H}_2\text{IO}_6^{3-}$  coordinates with central copper ion in alkaline medium to form  $[\text{Cu}(\text{H}_2\text{IO}_6)_2]^{3-}$ , which further reacts with  $\text{OH}^-$  to give  $[\text{Cu}(\text{HIO}_6)]^-$ . So formed  $\text{Cu}^*(\text{III})$  was the active species to form the corresponding aldol as the final product. In the oxidation of aliphatic alcohols by iodate in acidic medium, reactions were explained based on the involvement of halic acid ( $\text{HIO}_3$ ) and hypoiodite ion ( $\text{IO}^-$ ). Order of reaction rate in that study was given as 1-hexanol < isobutyl alcohol < isopropyl alcohol < 1-butanol < 1-propanol. Length of chain and structural features of the substrates were taken into consideration to explain the reactivity. Compared to  $2^\circ$  aliphatic alcohols, the oxidation of  $1^\circ$  aliphatic alcohols was faster with an exception to 1-hexanol. An inverse proportionality in reaction rate was observed with respect to the chain length. Cadmium(II) was found to be the effective catalyst in those oxidations, among the studied transition metal ions. Aldehydes and ketones were the products in the oxidation of primary and secondary aliphatic alcohols [12].

In the oxidation of secondary cyclic alcohols by different inorganic oxidants (potassium bromate, potassium iodate and potassium periodate) in acidic medium, the corresponding halic acids ( $\text{HBrO}_3$ ,  $\text{HIO}_3$  and  $\text{HIO}_4$ ) were reported as active oxidizing species [13]. The oxidation products were the corresponding ketones and same reaction order was reported with all oxidants as menthol < isoborneol < borneol. Structural features (steric hindrance and isomeric) were considered to be the responsible for the observed sequence of secondary alcohols reactivity. High and low vulnerability of oxidation in borneol and menthol towards oxidation was explained based on the least and most hindered  $\alpha$ -hydrogen present in them respectively. The  $\text{H}_2\text{OBr}^+$  was the proposed active oxidising species to explain the enhanced reaction rate by the addition of bromide ion in the oxidation of *n*-butanol by *p*-methoxy-*n*-bromobenzamide in aqueous acetic acid [14].

Higher rate of ditelluratoargentate(III) oxidation of 2-(2-ethoxyethoxy)ethanol (EEE) compared to the oxidation of 2-(2-methoxy ethoxy)ethanol (MEE) in alkaline medium was described based on the higher electron-donating ability of the former compared to the latter [15]. The observed experimental results were explained based on a free radical mechanism. Similarly, higher rate of oxidation of 2-ethoxyethanol by  $\text{K}_2\text{FeO}_4$  in alkaline medium compared to the oxidation of methoxyethanol was based on electron donating ability [16].

Propane-1,3-diol has a spectrum of applications as a monomer in the production of different polymers like polyethers, polytrimethylene terephthalate, polyurethanes and polyesters [17,18]. It is also used as protective agent/antifreeze agent and solvent [19,20]. Oxidation of vicinal diols in presence of ruthenium catalyst was extensively studied and mechanistic pathways

were explored. But, the reaction pattern was not studied completely in departed hydroxyl groups of diols. Singh *et al.* [21] studied the kinetics of oxidation of 1,3-propanediol by alkaline *N*-bromoacetamide in presence of Os(VIII). Silver(I) catalyzed oxidation was studied by Singh *et al.* [22] using peroxodiphosphate as an oxidant in acetate buffers to form 3-hydroxy propanol. Agrawal *et al.* [23] carried out the Ru(III) catalyzed oxidation of diols by ceric sulphate in aqueous sulphuric acid medium. As the oxidation studies on non-vicinal diols are scanty, the present study is aimed at understanding the mechanism involved in ruthenium(III) catalyzed oxidation of propane-1,3-diol by periodate in aqueous perchloric acidic medium.

## EXPERIMENTAL

All the chemicals used in the present study were of analytical grade. Double distilled water was used to prepare the solutions. Kinetics of Ru(III) catalyzed oxidation of propane-1,3-diol by periodate in aqueous perchloric acid medium was followed by iodometry. The reaction took place till the conversion of periodate to iodate. A separate test was conducted where  $\text{KIO}_3$  didn't oxidize propane-1,3-diol. However, Singh *et al.* [24] reported aquachloro-rhodium(III) catalysis in oxidation of diol (1,2-propanediol) by potassium iodate in acidic medium.

**General procedure:** The catalyst was maintained on oxidant side before mixing of oxidant and substrate. Both the oxidant and substrate solutions (maintained along with desired acid concentration and solvent composition) were kept in thermostat at the required constant temperature for 1 h. Both of them were mixed and then drawn at regular intervals of time. The kinetics experiments were repeated in triplicate and the results were reproducible within  $\pm 4\%$ .

**Detection method:** The formed product in the present study was converted to concerned phenylhydrazone by using acidic 2,4-DNP (2,4-dinitrophenylhydrazine). Then the hydrazone was characterized by melting point and spectral studies.

## RESULTS AND DISCUSSION

In the present study, an attempt is made to study the kinetics of uncatalyzed and Ru(III) catalyzed oxidation of non-vicinal diol (propane-1,3-diol) and vicinal diols (glycol, glycerol, propane-1,2-diol) in aqueous perchloric acid medium. It is observed that uncatalyzed oxidation of vicinal diols (glycol, glycerol, propane-1,2-diol) by periodate in aqueous perchloric acid medium was completed instantaneously. Whereas, the uncatalyzed oxidation of propane-1,3-diol under similar conditions was infinitesimally slow and Ru(III) catalyzed oxidation of non-vicinal diol (propane-1,3-diol) by periodate is a slow reaction with observable kinetics. The difference in the reactivity of propane-1,3-diol from vicinal diols can be understood from the fact that propane-1,3-diol is a simple acyclic molecule and won't display any sort of steric strain. Hence, kinetics of Ru(III) catalyzed oxidation of non-vicinal diol (propane-1,3-diol) by periodate is carried out in the present study. Effect of variation and hence reaction orders with respect to various reactants are discussed below.

**Variation of [periodate]:** While keeping the concentrations of other reactants at constant concentrations, [periodate] was

varied in the range 0.00025 to 0.002 M. Constructed the pseudo first order plots *i.e.*  $\log(a-x)$  against time (Fig. 1). Linearity of plots was observed upto completion of 85% of total reaction. In addition, it was found that values of pseudo-first-order constants ( $k_1$ ) were independent of the initial [oxidant] (Table-1).

TABLE-1 RATE CONSTANTS IN Ru(III) CATALYZED OXIDATION OF 1,3-PROPANE-DIOL BY POTASSIUM PERIODATE IN AN ACID MEDIUM General conditions: $[\text{KIO}_4] = 0.0005 \text{ M}$ ; $[\text{Substrate}] = 0.025 \text{ M}$ ; $[\text{Ru(III)}] = 2 \times 10^{-7} \text{ M}$ ; $[\text{H}^+] = 0.1 \text{ M}$ ; Temperature = 308 K		
Variant	Conc. of variant (M)	$k_1 \times 10^4 \text{ min}^{-1}$
[Periodate]	0.00025	46.52
	0.00050	46.53
	0.00100	47.63
	0.00200	49.63
[Substrate]	0.01250	52.33
	0.02500	46.53
	0.05000	28.42
	0.10000	18.02
[Acid]	0.025	65.56
	0.050	56.11
	0.100	46.53
	0.200	25.25
	0.500	18.97
Salt	0	46.53
	KCl (0.1 M)	10.74
	KBr (0.1 M)	8.85
	KI (0.1 M)	No reaction
	$\text{KNO}_3$ (0.1 M)	44.88
[Catalyst]	0 M	Infinitesimally slow
	$0.25 \times 10^{-7}$	2.94
	$0.50 \times 10^{-7}$	7.42
	$1.0 \times 10^{-7}$	22.58
	$2.0 \times 10^{-7}$	46.53
	$4.0 \times 10^{-7}$	82.83
	$8.0 \times 10^{-7}$	172.49
[Boric acid]	0	46.53
	0.01	51.32
	0.025	51.67
	0.05	53.58
Temperature (K)	308	46.53
	313	54.96
	318	64.23
	323	96.49
	333	183.37
Acetic acid:water (v/v)	0:100	46.53
	05:95	26.16
	20:80	18.78
	40:60	15.34
	60:40	14.15

**Variation of [substrate]:** Substrate inhibition is observed in the present case *i.e.* an increase in concentration of propane-1,3-diol from 0.0125 to 0.1 M has resulted in a decrease of rate constant from  $52.33 \times 10^{-4}$  to  $18.02 \times 10^{-4} \text{ min}^{-1}$  (Table-1). The plot of  $\log k_1$  vs.  $\log[\text{propane-1,3-diol}]$  shows a slope of -0.532 (Fig. 2), which indicates the inverse fractional order in [substrate]. Literature [25,26] shows that substrate inhibition

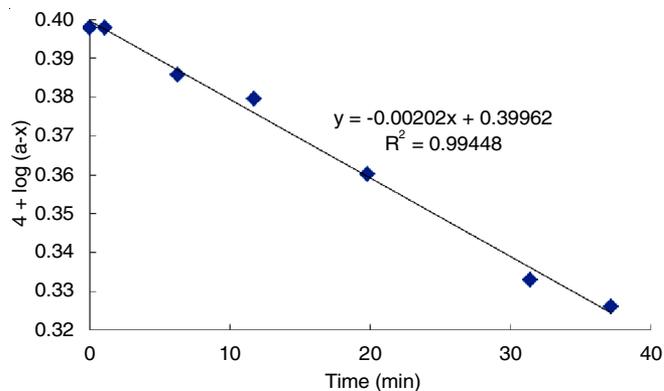


Fig. 1. Plot of  $\log(a-x)$  versus time at  $[\text{KIO}_4] = 0.0025 \text{ M}$ ,  $[\text{1,3-diol}] = 0.025 \text{ M}$ ,  $[\text{Ru(III)}] = 2 \times 10^{-7} \text{ M}$ ,  $[\text{H}^+] = 0.1 \text{ M}$  and Temperature = 308 K

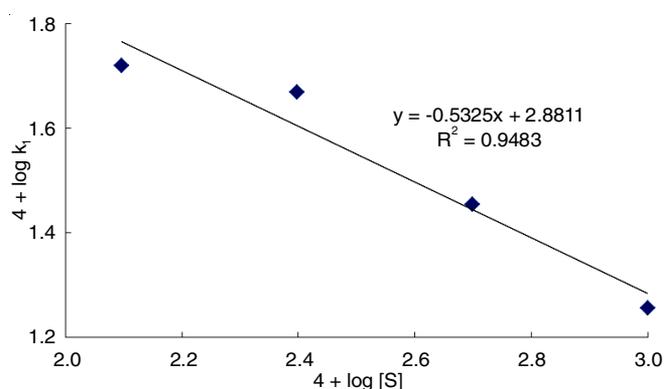


Fig. 2. Effect of substrate concentration on oxidation of propane-1,3-diol by  $\text{KIO}_4$

was reported in the oxidation of different sugar alcohols by periodate in alkaline medium, which was assigned to the formation of periodate substrate complex which resists oxidation. In the present case, an increase in substrate concentration increases the chances of forming an activated complex between substrate and the catalyst. At the same time, the increased number of substrate molecules improves their complexation possibility with the oxidant. And hence, decreases the availability of oxidant to attack the substrate-catalyst complex. However, independence of substrate concentration was reported in the periodate oxidation of polyethylene glycols (PEGs) in alkaline medium [27,28] which can be explained based on the fact that PEGs possess high hydroxyl values [29].

**Variation of [acid] and [catalyst]:** A decrease of rate constant was resulted from  $65.56 \times 10^{-4}$  to  $18.97 \times 10^{-4} \text{ min}^{-1}$  by increasing the concentration of perchloric acid concentration from 0.025 to 0.50 M (Table-1). An inverse fractional order in  $[\text{H}^+]$  was noticed as the slope is -0.444 in the plot of  $\log k_1$  vs.  $\log[\text{perchloric acid}]$  (Fig. 3). Literature survey shows contrary results regarding acid effect on kinetics of oxidation of propane-1,3-diol. Inverse order in acid concentration was reported by Singh *et al.* [22,24] in phosphotungstic acid catalyzed *N*-chlorosaccharin oxidation and silver ions catalyzed peroxydisulphate oxidation. However, an increase in rate constants with increase in hydrogen ion concentration was noticed in the oxidation of terminal hydroxyl compounds by chromium(VI)

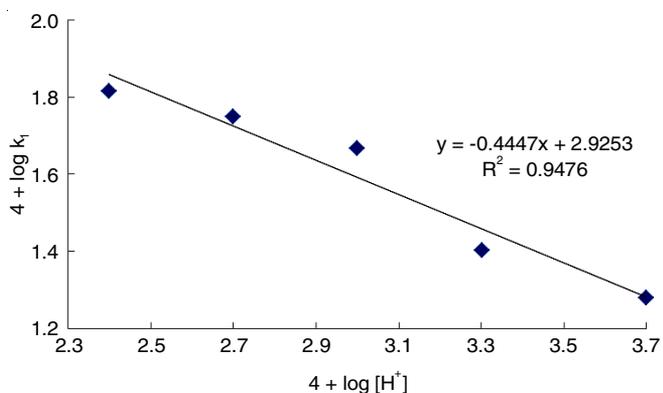
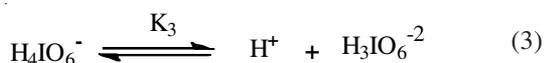
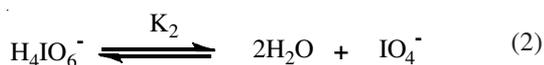
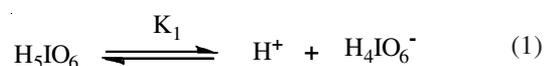


Fig. 3. Effect of acid concentration on oxidation of propane-1,3-diol by periodate

[30,31]. In addition, present observation is contrary to that of Bhamare *et al.* [32], who noticed an increase in rate of reaction with an increase in acidity. In perchloric acid medium, potassium periodate predominantly exists as potassium metaperiodate ( $\text{KIO}_4$ ) and paraperiodic acid ( $\text{H}_5\text{IO}_6$ ) [33]. According to Martin *et al.* [33], in acidic medium, periodate exists in the following equilibria:



Increase in catalyst concentration has resulted in an increase in reaction rate. Unit order dependence on  $[\text{Ru(III)}]$  was observed from the slope value of the plot between  $\log k_1$  and  $\log [\text{Ru(III)}]$  (Fig. 4). It shows the active involvement of catalyst species in similar to the studies of Bhamare and Kulkarni [34].

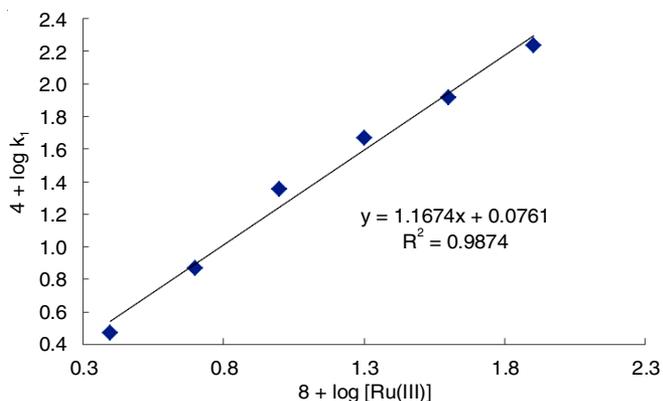


Fig. 4. Effect of concentration of catalyst on oxidation of propane-1,3-diol by  $\text{KIO}_4$

**Effect of addition of solvent acetic acid:** Acetic acid is a commonly used dipolar aprotic solvent, which possesses lower dielectric constant compared to water. In order to understand the influence of dielectric constant on the reaction rate in the present conditions, different compositions of acetic acid and water were used. A decrease in reaction rate with an addition of acetic was observed in this study (Table-1). A negative slope

was observed for the plot between  $\log k_1$  versus  $1/D$  (Fig. 5). It indicates the reaction between negative ion and dipole [35]. However, the rate constant value decreased marginally with an increase in percentage of acetic acid. It specifies the involvement of dipole-dipole reactions too. It indicates that  $\text{H}_5\text{IO}_6$  is also an active oxidant species in addition to  $\text{H}_4\text{IO}_6^-$  and  $\text{IO}_4^-$ . In the oxidation of propane-1,3-diol and butane-1,4-diol by *N*-chlorosaccharin, a decrease in rate constant with an increase in phosphoric acid was reported by Singh *et al.* [24], which corroborates with the present trend.

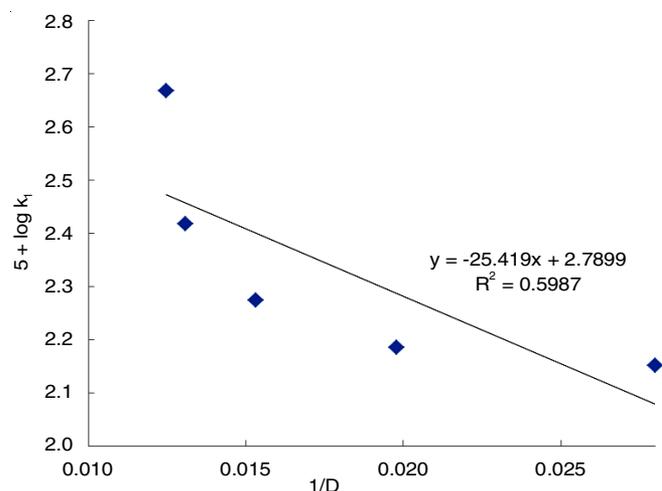


Fig. 5. Effect of solvent composition on oxidation of propane-1,3-diol by  $\text{KIO}_4$

**Temperature effect:** An increase in first order rate constants ( $k_1$ ) was observed with an increase in temperature (Table-1) and yielded a straight line in the plot of  $\ln k$  vs.  $1/T$  (Fig. 6). By using slope of the plot and Eyring equation, various activation parameters were calculated (Table-2). The transition state is highly solvated, in view of high positive values for  $\Delta G^\ddagger$ . Further, a reduction in the degree of freedom of molecule can be observed in the so formed activated complex, as  $\Delta S^\ddagger$  is negative.

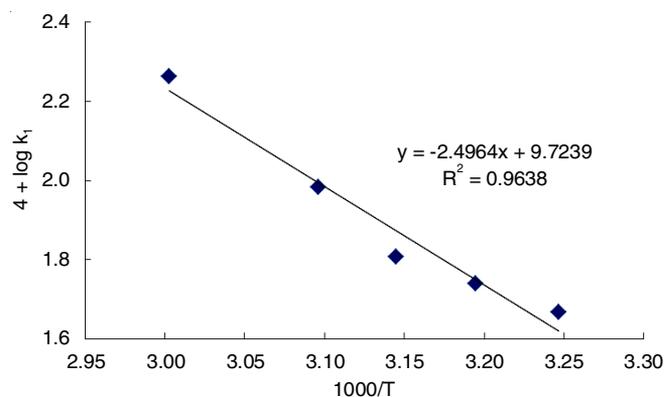
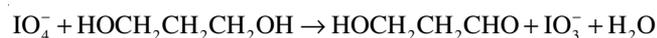


Fig. 6. Effect of temperature on oxidation of propane-1,3-diol by  $\text{KIO}_4$

TABLE-2 ARRHENIUS PARAMETERS AT 308 K				
$\Delta E^\ddagger$ (KJ/mol)	$\Delta H^\ddagger$ (KJ/mol)	$-\Delta S^\ddagger$ (JK <sup>-1</sup> /mol)	$\log_{10} P_z$	$\Delta G^\ddagger$ (KJ/mol)
47.79	45.23	177.07	3.99	99.77

**Effect of boric acid, salts and ionic strength:** A marginal increase in reaction rate was observed with an addition of boric acid. However, a substantial decrease in reaction rate with an addition of halide ions is observed. Such an inhibition by chloride ions was reported by Gupta *et al.* [30,36] in Cr(VI) oxidation of diols, which was explained based on the formation of less reactive  $\text{CrO}_3\text{Cl}^-$ . Chloride inhibition was taken as indirect evidence for the complexation between Cr(VI) and substrate. Ionic strength variation didn't effect the rate of reaction. The effect of salts on reaction rate was discussed by Kulkarni *et al.* [37] based on their studies about Ru(III) catalyzed oxidative degradation of azidothymidine by Mn(VII).

**Stoichiometry and product analysis:** The reaction was allowed to proceed under experimental conditions (*i.e.* [propane-1,3-diol]  $\gg$  [periodate]) for overnight in a thermostatted water bath in order to determine the reaction stoichiometry. Acidic solution of 2,4-DNP was added to the reaction mixture and maintained overnight at refrigerated temperature. Ice cold water was used to wash the corresponding 2,4-dinitrophenylhydrazone, which was separated by centrifugation of the above refrigerated mixture. The melting point of the air dried product was found to be 425 K, which is in agreement with the earlier reported values. IR and NMR spectral data confirmed the formation of phenylhydrazone of 3-hydroxypropanal. Hence, the corresponding reaction equation is shown below:



It indicates the attacking of single hydroxy group whereas the other hydroxyl group of the diol remain intact. It substantiates the above observed stoichiometry of the reaction.

Variation in the product was reported based on either with or without fission of C-C linkage in diols. Fission of C-C leading to the formation of acetaldehyde and formaldehyde were reported in the oxidation of propane-1,3-diol in presence of  $\text{Ag}^+$ /peroxydisulphate [38] and  $\text{F}^-$ /acid permanganate [39]. However, instead of C-C bond cleavage, one of the terminal hydroxyl groups oxidizes in acid medium to yield hydroxyaldehyde [30,36]. In alkaline medium, 3-hydroxypropanal was reported as the product in the oxidation of propane-1,3-diol in presence of different combinations of catalyst/oxidant *viz.* Os(VIII)/chloramine-T [40], Ru(III)/hexacyanoferrate(III) [41,42]. Same product was reported in acidic medium in presence of different catalyst/oxidant combinations *viz.* Ru(III)/Ce(IV) [23] and  $\text{Ag}^+$ /peroxodiphosphate [22]. In similar lines, 3-hydroxypropanal, 4-hydroxybutanal and 5-hydroxypentanal were the products in the oxidation of propane-1,3-diol, butane-1,4-diol and pentane-1,5-diol, respectively [24,43].

**Reaction mechanism:** In aqueous medium, a range of complexes  $[\text{Ru}(\text{H}_2\text{O})_x\text{Cl}_{6-x}]^{3-3}$  were formed by ruthenium(III) chloride [44] where  $x = 0$  to 6. Based on structural and electrochemical studies, it was confirmed that  $x$  value varies from 4 to 6 in acidic medium [45-47]. However, perchlorate ion of  $\text{HClO}_4$  has affinity towards ruthenium(III) to form a complex [44,48]. Based on the spectral study carried out on  $\text{RuCl}_3$  in acidic medium by Connick and Fine [49],  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$  is the principal species. Literature survey shows that Ru(III) involves in different mechanisms. In different acidic media (perchloric,

sulphuric, trifluoromethane sulphonic acid, trifluoro acetic acid and *p*-toluenesulphonic acid), 0.239 V was the redox potential [45] for  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}/[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ . Ruthenium(III) is considered to be a weak oxidant in moderate concentrations of perchloric acid as the potential is about 0.1 V. Hence, instead of trivalent ruthenium, octavalent ruthenium species is considered to be active species which forms by the oxidation of Ru(III) in acid medium [45,50]. For some of the substrates, ruthenium forms a complex with substrate which decomposes to form final products with recycling of catalyst [51-54]. In other reactions, Ru(III) is converted to Ru(V) by the oxidant and the activated catalyst participates in the reaction [55]. As per the previous investigation, it was reported that at the higher concentration of  $\text{H}^+$  or lower values of pH, catalyst Ru(III) is oxidized to its higher oxidized forms Ru(VI) and Ru(VII) due to the higher oxidation potential of oxidant. During the oxidation of Ru(III) to higher oxidized forms by oxidant species [56], Ru(VI) is found to be unstable species due to its rapid conversion into hydroxide of ruthenium *i.e.*  $\text{Ru}(\text{OH})_4$ .

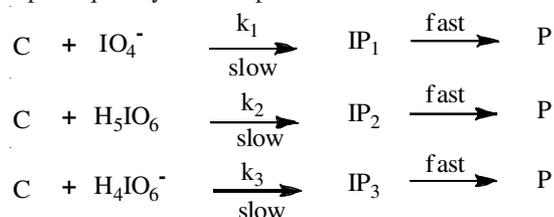
According to Menghani and Bakore *et al.* [38], propane-1,3-diol complexes with  $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  to form a complex in which one hydroxyl group coordinates with the active species. Singh *et al.* [41,57] reported the establishment of Ru(III)-alcohol complex in alkaline medium, where hydride ion present on the  $\alpha$ -carbon (of alcohol) is abstracted by the catalyst to form ruthenium ion and carbonium ion. A similar hydride abstraction from the  $\alpha$ -carbon of propane-1,3-diol was proposed in the Os(VIII) catalyzed oxidation by chloramine-T in alkaline medium [40]. In such a case, an electron transfer was proposed to the oxidant from the substrate *via* the catalyst.

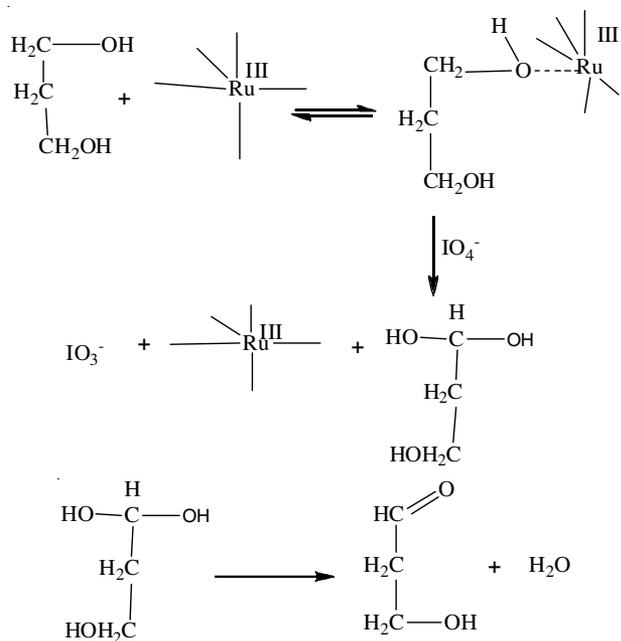
Ionic [58] and free radical [59] pathways were proposed in the Ru(III) catalyzed oxidations of alcohols. Free radical mechanism was also adopted in the oxidation of 1,3-propanediol in the presence of different catalysts like silver (I) [6]. However, involvement of ionic pathway is proposed in the present case taking into consideration of the above solvent effect on rate of reaction and non-formation of insoluble precipitate in free radical test by using acrylonitrile [56,60]. In addition, propane-1,3-diol forms a complex with  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ . In rate determining step, the complex reacts with periodate to form a geminal diol, which is unstable and hence undergoes loss of water molecule in a fast step to form the concerned aldehyde as a final product (**Scheme-I**).

**Rate law:** Propane 1,3-diol complexes with ruthenium(III) catalyst.

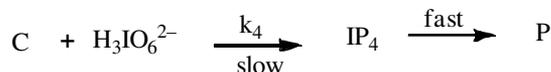


In rate determining steps, complex C reacts with different species of periodate to form intermediate complexes, which decompose quickly to final products.





**Scheme-I:** Mechanism of Ru(III) catalyzed oxidation of propane-1,3-diol by periodate



From eqn. 1:

$$[H_4IO_6^-] = \frac{K_1[H_5IO_6]}{[H^+]}$$

From eqn. 2:

$$[IO_4^-] = K_2[H_4IO_6^-] = \frac{K_1K_2[H_5IO_6]}{[H^+]}$$

From eqn. 3:

$$[H_3IO_6^{2-}] = \frac{K_3[H_4IO_6^-]}{[H^+]} = \frac{K_1K_3[H_5IO_6]}{[H^+]^2}$$

Total concentration of periodate  $[IO_4^-]_T$  is given by:

$$[IO_4^-]_T = [H_5IO_6] + [H_3IO_6^{2-}] + [H_4IO_6^-] + [IO_4^-]$$

From eqn. 3, it is clear that  $H_3IO_6^{2-}$  exists preferably at low concentrations of acid. As  $[H^+] \gg [IO_4^-]$ ,  $[H_3IO_6^{2-}]$  is negligible. Hence, the above equation can be rewritten as:

$$\begin{aligned} [IO_4^-]_T &= [H_5IO_6] + [H_4IO_6^-] + [IO_4^-] \\ &= [H_5IO_6] + \frac{K_1[H_5IO_6]}{[H^+]} + \frac{K_1K_2[H_5IO_6]}{[H^+]} \\ &= \frac{[H_5IO_6]}{[H^+]} \{ [H^+] + K_1 + K_1K_2 \} \end{aligned}$$

In perchloric acid medium, potassium periodate predominantly exists in potassium metaperiodate ( $KIO_4$ ) and paraperiodic acid ( $H_5IO_6$ ) [16]. By rearranging the above equation, we get:

$$[H_5IO_6] = \frac{[IO_4^-]_T [H^+]}{[H^+] + K_1 + K_1K_2}$$

Total concentration of catalyst  $[Catalyst]_T$  can be written as:

$$\begin{aligned} [Catalyst]_T &= [Catalyst] + [Complex] \\ &= [Catalyst] + K_4 [1,3\text{-diol}][Catalyst] \\ &= [Catalyst] \{ 1 + K_4 [1,3\text{-diol}] \} \end{aligned}$$

By rearranging the above equation:

$$[Catalyst] = \frac{[Catalyst]_T}{1 + K_4 [1,3\text{-diol}]}$$

$$\begin{aligned} \text{Rate} &= k_1 [Complex][IO_4^-] + k_2 [Complex][H_5IO_6] + \\ & \quad k_3 [Complex][H_4IO_6^-] \end{aligned}$$

$$= [Complex] \{ k_1 [IO_4^-] + k_2 [H_5IO_6] + k_3 [H_4IO_6^-] \}$$

$$= K_4 [1,3\text{-diol}][Catalyst] \left\{ k_1 \frac{K_1K_2[H_5IO_6]}{[H^+]} + k_2 [H_5IO_6] + k_3 \frac{K_1[H_5IO_6]}{[H^+]} \right\}$$

$$= \frac{K_4 [1,3\text{-diol}][Catalyst][H_5IO_6]}{[H^+]} \{ k_1 K_1 K_2 + k_2 [H^+] + k_3 K_1 \}$$

$$= \frac{K_4 [1,3\text{-diol}]}{[H^+]} \left\{ \frac{[Catalyst]_T}{1 + K_4 [1,3\text{-diol}]} \right\}$$

$$\left\{ \frac{[IO_4^-]_T [H^+]}{[H^+] + K_1 + K_1K_2} \right\} \{ k_1 K_1 K_2 + k_2 [H^+] + k_3 K_1 \}$$

$$= \frac{K_4 [1,3\text{-diol}][Catalyst]_T [IO_4^-]_T}{1 + K_4 [1,3\text{-diol}]} \left\{ \frac{k_1 K_1 K_2 + k_2 [H^+] + k_3 K_1}{[H^+] + K_1 + K_1K_2} \right\}$$

The above rate law explains the observed first order in oxidant and ruthenium(III) and inverse fractional order with the concentrations of acid and substrate.

## Conclusion

The observed substrate inhibition in the ruthenium(III) catalyzed periodate oxidation of propane-1,3-diol was explained based on the competitive formation of a complex between propane-1,3-diol and periodate. Based on the inverse acid dependence and solvent effect,  $H_5IO_6$ ,  $H_4IO_6^-$  and  $IO_4^-$  were the active periodate species. Formation of 3-hydroxypropanal as the final product indicates the attacking of single hydroxy group, whereas the other hydroxyl group of substrate remain intact.

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## CONFLICT OF INTEREST

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

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