Mechanistic studies of aquachlororhodium(III) catalysis in potassium iodate oxidation of 1,2-propanediol in acidic medium: A kinetic approach

Bharat Singh*, Aniruddh Kumar Singh & Anamika Singh

Chemical Kinetics Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211 002, India

Email: bschem_au@yahoo.com

The kinetics of homogeneously Rh(III) catalysed oxidation of 1, 2-propanediol by acidic solution of potassium iodate at constant ionic strength of the medium has been investigated at 308 K. The reaction follows complex kinetics, being first order in $[KIO_3]$, zero order in 1, 2-propanediol and inverse fractional order in both $[H^+]$ and $[Cl^-]$. The first order rate constant increases linearly with increase in [Rh(III)] in its lower concentration range but as the concentration of Rh(III) is increased towards the higher range, the rate constant becomes almost constant, indicating positive fractional order in [Rh(III)]. Variation of ionic strength of the medium and successive addition of mercuric acetate (used as I^- ions scavenger) has a positive effect on the rate of the reaction. IO_3^- and $[RhCl_5(H_2O)]^{-2}$ have been postulated as the reactive species of KIO_3 and Rh(III), respectively. Activation parameters for the slow and rate determining step of the proposed mechanism, which involves the formation of the most activated complex, $[Cl_5Rh(HO\rightarrow Hg)]^-$, prior to the slowest step, have been obtained from rate measurements at 30, 35, 40 and 45 °C. The rate law conforming to the observed kinetic results has been derived

as
$$-\frac{d[KIO_3]}{dt} = \frac{kK_1K_2[IO_3^-][Rh(III)]_T[Hg(II)]_T}{[H^+]([K_1+Cl^-])+K_1K_2([Rh(III)]_T+[Hg(II)]_T)}$$
. The main oxidation products have been identified as acetic acid and formic acid.

Keywords: Kinetics, Reaction mechanisms, Oxidation, Rhodium, Propanediol

The kinetics of the redox processes involving transition metals ions, viz., osmium(VIII)[1] ruthenium(III)[2], ruthenium(VIII)[3], iridium(III)[4] and palladium(II)[5] as homogeneous catalyst has been extensively investigated. Such studies has helped industrial growth as well as understanding of the biological properties of transition metal complexes. Rhodium, like other platinum group metals, also forms a variety of complexes with oxidation states ranging from +1 to +6 of which its +3 oxidation states is comparatively more stable than the other oxidation states of the metal. Antibacterial and antitumor activities[6,7] of Rh(III) complexes with nitrogen donor ligands, viz., ethylene diamine, pyridine, 2, 2'-bipyridine, 1,10-phenanthroline etc., attachment of DNA to the metal rhodium in its octahedral complex[8] and their catalytic functions with potential industrial applications have generated enormous and continued interest[9-11], particularly in studies on biological properties of rhodium(III) complexes along with other transition metal complexes[12]. Rh(III) is reported to form a variety of complexes such as $[RhCl_2]^+$, $[RhCl_3]$, $[RhCl_4]^-$, $[RhCl_5]^{2-}$ and $[RhCl_6]^{3-}$ in the presence of HCl with its varying concentration[13].

The 1,2-diol functionality has been found in a series of synthetic intermediates. 1,2-Propanediol is non-toxic antifreeze in breweries and dairies and finds importance in several applications[14,15] such as in production of unsaturated polyester resins, as an additive in nutrition products, non-ionic detergent, cosmetics, brake fluid or hydraulic fluid, as de-icing agent, etc. 1,2-Propanediol derivatives have recently found use as centrally acting skeletal muscle relaxant. Therefore, it was of interest to study the oxidation kinetics of 1,2-prpanediol. Potassium iodate is an irritant and toxic causing damage to the central nervous system, structural composition of blood as well as kidneys. It can also cause explosion with flammable materials or powdered metals. It also serves as nuclear protector agent during nuclear disaster. Despite the diverse properties of potassium iodate[16-18] and importance of 1,2-propanediol and its derivatives, relatively less information is available in the literature about their kinetic studies in the presence of transition metal ions as catalyst. A survey of the existing literature reveals little work on Rh(III) catalysed oxidation of diols by potassium iodate[19,20]. In view of biological importance of Rh(III)

complexes, potassium iodate and 1,2-propanediol and also in view of the lack of information on the role of the chloro complex of Rh(III) as homogenous catalyst in oxidation of diols, an attempt has been made to study the kinetics and mechanism of Rh(III) catalysed oxidation of 1,2-propanediol by potassium iodate in acidic medium in presence of the iodide ions scavenger, mercuric acetate[21]. The main objectives of the present study are to ascertain (i) the reactive species of potassium iodate in acidic medium, (ii) the actual catalytic species of rhodium(III) chloride in acidic medium, (iii) the role of chloride ions in deciding the reactive catalytic species of Rh(III), (iv) the role of mercuric acetate, in addition to its role as iodide ion scavenger, and finally (v) to elucidate the mechanistic steps on whose basis rate law consistent with observed kinetic data is derived.

Materials and Methods

The reagents used in the present study were potassium iodate (BDH), 1,2-propanediol (BDH), rhodium(III) chloride (Sigma), perchloric acid (E. Merck, 70 %) and mercuric acetate (E. Merck). All other reagents used were of (AR) grade. All the solutions were prepared in doubly distilled water.

The solution of rhodium(III) chloride was prepared by dissolving its 1 g sample in HCl (3.6 mol dm^{-3}). The concentrations of rhodium(III) chloride and HCl were noted in the final solution which was stored in black coated bottles to prevent any photochemical decomposition. The solution of potassium iodate was prepared by dissolving its weighed amount in known volume of distilled water. The solution of 1,2-propanediol was prepared by dissolving its known amount in desired volume of distilled water. Sodium perchlorate and perchloric acid were used to maintain the required ionic strength and acidity, respectively. A standard solution of mercuric acetate was acidified with 20 % (*v/v*) acetic acid and solutions of all other reagents, viz., KCl, sodium thiosulphate of E. Merck grade were prepared by dissolving their weighed samples in known volume of distilled water.

Kinetic procedure

All the kinetic measurements were carried out at constant temperature 35 °C (±0.1 °C). Appropriate volumes of all the reactants, i.e., KIO$_3$, Rh(III), Hg(OAc)$_2$, KCl and NaClO$_4$ were taken in a reaction bottle (Jena glass). The requisite volume of doubly distilled water was added to the reaction mixture so that total volume of the reaction mixture was 100 ml

after addition of 1,2-propanediol solution. The bottle containing the reaction mixture was placed in an electrically operated thermostat (maintained at 35 °C) for thermal equilibrium. Appropriate volume of solution of 1,2-propanediol, also equilibrated at 35 °C, was rapidly poured into the reaction mixture to initiate the reaction. The progress of the reaction was followed by estimating the amount of unconsumed [KIO$_3$] iodometrically in aliquots (5 ml) withdrawn from the reaction mixture at regular time intervals for about 75 % of the reaction.

The rate of the reaction (*-dc/dt*) in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of potassium iodate which is written as [KIO$_3$]*. The order of the reaction with respect to each reactant was determined by the relation between initial rate, i.e., (*-dc/dt*) and initial [reactant].

Stoichiometry and product analysis

Varying [KIO$_3$]:[1,2-propanediol] ratios were equilibrated at 35 °C for 72 h under the condition, [KIO$_3$] >> [1,2-propanediol]. Estimation of residual [KIO$_3$] in different experimental sets showed that one mole of diol consumed one mole of KIO$_3$. Accordingly, the following stoichiometric equation can be formulated:
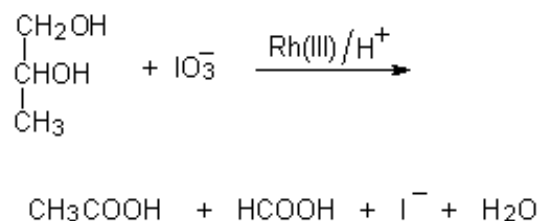
The main products of oxidation of 1, 2-propanediol are acetic acid and formic acid. The appearance of a black colour in the spot test[22] identified the formic acid in the reaction mixture. The presence of acetic acid in the reaction mixture was confirmed by TLC[23], using *n*-butanol-diethylamine-water in the ratio of 85:1:14 as the developing solvent. The R_f value was found to be 0.44, which is very close to the reported R_f value, (0.45) for acetic acid in the aforesaid solvent system.

Results and Discussion

The oxidation kinetics was carried out at different initial concentrations of reactants at 308 K. The rate of the reaction (*-dc/dt*) increases in direct

proportionality with increase in the initial [KIO$_3$], showing first order kinetics with respect to [KIO$_3$]. This is also obvious from the fair degree of closeness in k_{obs} value obtained from slope of the linear plot between (-dc/dt) and [KIO$_3$] (slope = 3.08 × 10^{-4}) and average value of k_{obs} obtained from the formula, k_{obs} = (-dc/dt)/[KIO$_3$]* at different initial [KIO$_3$]. At constant [KIO$_3$], [HClO$_4$], [Rh(III)], [Hg(OAc)$_2$], ionic strength and temperature, the first order rate constant, k_{obs} remains practically constant (Table 1)

on varying five-fold initial [1,2-propanediol], indicating zero order dependence of the reaction on [1,2-propanediol].

The reaction rate (-dc/dt) and first order rate constant (k_{obs}) both increase with increase in [Rh(III)] under constant solution conditions. A plot of log k_{obs} versus log [Rh (III)] was linear with fractional slope (0.34), confirming fractional order dependence on [Rh(III)]. Addition of Cl$^-$ ions in the form of KCl (0.5 × 10^{-3} to 2.5 × 10^{-3} mol dm^{-3}) under constant solution conditions decreases -dc/dt (Table 2) and a plot of log k_{obs} versus log [Cl$^-$] was linear with slope of − 0.62, indicating negative effect of [Cl$^-$] on the rate of the reaction.

Under constant solution conditions, increase in perchloric acid concentration decreases the rate and k_{obs}, indicating negative effect of [H$^+$]. A log-log plot between k_{obs} and [H$^+$] gives negative fractional order of − 0.59. In the case of mercuric acetate, k_{obs} value increases linearly without any correlation with increase in [Hg(OAc)$_2$] (Table 3), indicating positive effect of [Hg(OAc)$_2$] on the reaction rate.

The effect of ionic strength was studied by varying NaClO$_4$ concentration in the reaction. The ionic strength of the reaction medium was varied from 1.95 ×10^{-2} to 7.50 × 10^{-2} mol dm^{-3} at constant experimental conditions. It was found that the rate constant increased with increase in ionic strength, indicating positive effect of ionic strength of the medium on the rate of the reaction.

Table 1—Effect of variation of [KIO$_3$] and [1,2-propanediol] on the rate constants at 35 °C. {Cond.: [Rh(III)] = 15.20 × 10^{-7} mol dm^{-3}; [HClO$_4$] = 10.00 ×10^{-3} mol dm^{-3}; [KCl] = 1.00 ×10^{-3} mol dm^{-3}; [Hg(OAc)$_2$] = 2.50 ×10^{-3} mol dm^{-3}; I = 2.10 ×10^{-2} mol dm^{-3} (varying [KIO$_3$]); 1.95×10^{-2} mol dm^{-3} (varying [1,2-propanediol])}

[KIO$_3$]×10^4 (mol dm^{-3})	[1,2-propanediol] ×10^2 (mol dm^{-3})	(-dc/dt) ×10^7 (mol dm^{-3}s^{-1})	k_{obs}×10^4 (s^{-1})
5.00	2.00	1.46	3.50
6.67	2.00	1.88	3.60
8.00	2.00	2.18	3.56
10.00	2.00	2.94	3.62
13.33	2.00	3.76	3.54
20.00	2.00	6.04	3.60
25.00	2.00	7.34	3.52
10.00	1.00	2.55	3.18
10.00	1.34	2.60	3.20
10.00	2.00	2.54	3.18
10.00	2.50	2.42	3.04
10.00	3.34	2.52	3.14
10.00	4.00	2.46	3.08
10.00	5.00	2.60	3.20

Table 2—Comparison of observed and calculated rate constants on varying [Rh(III)] and [Cl$^-$] at 35 °C. {Cond.: [KIO$_3$] = 10.00 × 10^{-4} mol dm^{-3}; [1,2-propanediol] = 2.00 × 10^{-2} mol dm^{-3}; [HClO$_4$] = 10.00 ×10^{-3} mol dm^{-3}; [Hg (OAc)$_2$] = 2.50 ×10^{-3} mol dm^{-3}; I = 1.95 ×10^{-2} mol dm^{-3} (varying [Rh(III)]); 2.10 ×10^{-2} mol dm^{-3} (varying [Cl$^-$])}

[Rh(III)] ×10^7 (mol dm^{-3})	[Cl$^-$] ×10^3 (mol dm^{-3})	(-dc/dt) ×10^7 (mol dm^{-3} s^{-1})		k_{obs} × 10^4 (s^{-1})	
		Obs.	Calc.[a]	Obs.	Calc.[b]
1.52	1.00	1.18	1.10	1.48	1.38
3.04	1.00	1.50	1.44	1.88	1.80
4.56	1.00	1.76	1.70	2.20	2.12
6.08	1.00	2.00	1.96	2.50	2.46
15.20	1.00	2.54	2.50	3.18	3.12
22.80	1.00	2.84	2.80	3.56	3.50
30.40	1.00	3.04	2.98	3.80	3.72
38.00	1.00	3.16	3.10	3.95	3.88
15.20	0.50	4.20	3.96	5.26	4.96
15.20	0.66	3.50	3.12	4.38	3.90
15.20	0.80	3.30	3.00	4.14	3.75
15.20	1.00	2.94	2.50	3.64	3.12
15.20	1.34	2.54	2.16	3.18	2.70
15.20	2.00	1.85	1.48	2.32	1.85
15.20	2.50	1.52	1.24	1.90	1.56

[a]Calculated on the basis of rate law (12).
[b]Calculated as k_{obs} = (-dc/dt)^a / [KIO$_3$]*.

The reaction was performed at four different temperatures (303, 308, 313 and 318 K), keeping other experimental conditions constant. The activation energy (E_a) was calculated from the linear Arrhenius plot of log k_{obs} versus $1/T$. Thermodynamic activation parameters such as enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), Gibbs free energy of activation ($\Delta G^{\#}$) and Arrhenius factor (A) were calculated using specific rate constant (k_r) at 35 °C (Table 4).

Table 3—Effect of varying [HClO₄], [Hg(OAc)₂] and ionic strength of the medium (I) on the rate constants at 35 °C. {Cond.: [KIO₃] = 10.00×10^{-4} mol dm⁻³; [1,2-propanediol] = 2.00×10^{-2} mol dm⁻³; [KCl] = 1.00×10^{-3} mol dm⁻³; [Rh(III)] = 15.20×10^{-7} mol dm⁻³}

[HClO₄] $\times 10^3$ (mol dm⁻³)	[Hg(OAc)₂] $\times 10^3$ (mol dm⁻³)	$(I) \times 10^2$ (mol dm⁻³)	$k_{obs} \times 10^4$ (s⁻¹)
4.00	2.50	2.95	6.60
5.00	2.50	2.95	5.76
6.67	2.50	2.95	4.90
8.00	2.50	2.95	4.46
10.00	2.50	2.95	3.88
14.28	2.50	2.95	3.14
20.00	2.50	2.95	2.50
10.00	1.00	2.70	2.00
10.00	1.25	2.70	2.34
10.00	1.66	2.70	2.64
10.00	2.00	2.70	3.04
10.00	2.50	2.70	3.74
10.00	3.34	2.70	4.44
10.00	5.00	2.70	5.82
10.00	2.50	1.95	3.18
10.00	2.50	3.50	4.26
10.00	2.50	4.30	4.84
10.00	2.50	5.00	5.44
10.00	2.50	6.00	6.26
10.00	2.50	7.50	7.80

Table 4—Effect of temperature on k_{obs} and values of activation parameters for the oxidation of 1,2-propanediol by KIO₃ in the presence of Rh(III) catalyst in acidic medium. {Cond.: [KIO₃] = 10.00×10^{-4} mol dm⁻³; [1,2-propanediol] = 2.00×10^{-2} mol dm⁻³; [HClO₄] = 10.00×10^{-3} mol dm⁻³; [Rh(III)] = 15.20×10^{-7} mol dm⁻³; [KCl] = 1.00×10^{-3} mol dm⁻³; [Hg(OAc)₂] = 2.50×10^{-3} mol dm⁻³; $I = 1.95 \times 10^{-2}$ mol dm⁻³}

Temp. (K)	$k_{obs} \times 10^4$ (s⁻¹)
303	2.34
308	3.18
313	4.70
318	6.40
$k_r \times 10^4$ (s⁻¹)	11.62
E_a (kJ mol⁻¹)	51.08
$\Delta H^{\#}$ (kJ mol⁻¹)	48.50
$\Delta G^{\#}$ (kJ mol⁻¹)	92.72
$\Delta S^{\#}$ (J K⁻¹ mol⁻¹)	- 143.56
$A \times 10^{-5}$ (s⁻¹)	05.44

The addition of the reaction mixture to aqueous acrylamide monomer solution in dark did not initiate polymerization, indicating the absence of formation of free radical species in the reaction sequence. The control experiments were also performed under the same reaction conditions.

Oxidative species of potassium iodate in acidic medium

It has been earlier reported[24,25] that IO_3^- is the reactive species of KIO₃ in alkaline and acidic media in oxidation of xylose, maltose, pyruvic acid, 1,3-dihydrobenzene, α-hydroxy acids and aminoiminomethanesulfinic acid etc. and this conclusion has also been confirmed by spectral studies[24]. Therefore, in the present investigation also IO_3^- has been assumed to be the reactive species of KIO₃ in acidic medium.

Catalytic species of Rh(III) chloride in acidic medium

It has been reported[26] that in acid solution the anionic chlororhodate(III) complex is the only effective catalyst and activity of the species decreases with decreasing number of chloride ligands attached to the metal ion in the following manner: $[RhCl_6]^{-3} > [RhCl_5(H_2O)]^{-2} > [RhCl_4(H_2O)_2]^{-1}$.

It has been also reported[27] that the complex species $[RhCl]^{+2}$, $[RhCl_2]^{+1}$, $[RhCl_3]$, $[RhCl_4]^{-1}$, $[RhCl_5]^{-2}$ and $[RhCl_6]^{-3}$ exist with change in HCl concentration from 0.01 to 2.00 *M*. The cationic species are reported[28] to be completely inactive and the activity increases with increase in number of chloride ions up to a maximum of five. Hexachloro-complex is thus reported to be inactive. In view of earlier reports and observed negative effect of added Cl⁻ ions on the rate of reaction, it can be concluded that $[RhCl_5(H_2O)]^{-2}$ is the reactive species of Rh(III) chloride in acidic medium in the present studies and dissociation of Cl⁻ ions from $[RhCl_6]^{-3}$ is favoured according to the equilibrium:

$$[RhCl_6]^{-3} + H_2O \rightleftharpoons [RhCl_5(H_2O)]^{-2} + Cl^-$$

The species $[RhCl_5(H_2O)]^{-2}$ as the real reactive species is also supported and verified by spectral studies (Fig. 1). It is quite clear from the Fig. 1 that with increase in [HCl] there is increase in absorbance at the same wavelength, i. e., at λ_{max} = 230 nm. This indicates that rhodium(III) chloride in acid solution remains as $[RhCl_5(H_2O)]^{-2}$ only. The single peak observed for all the three solutions with varying [HCl] is strong evidence for the existence of $[RhCl_5(H_2O)]^{2-}$ as predominant species in HCl solution.

[Rh(III)] = 1.90 x 10^{-4} mol dm^{-3}
[H^+] = 1: 0.1 mol dm^{-3}
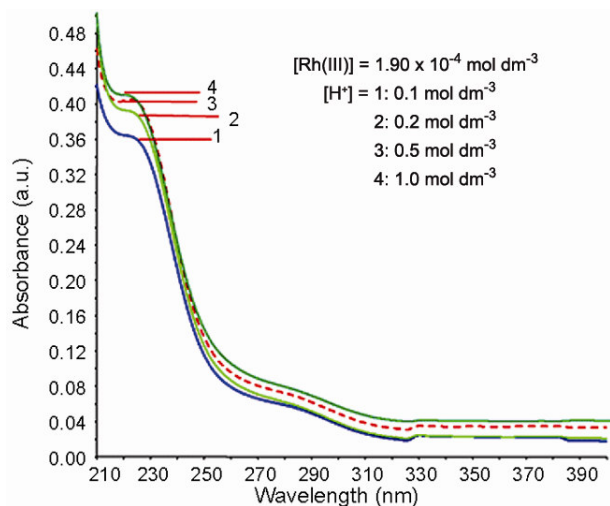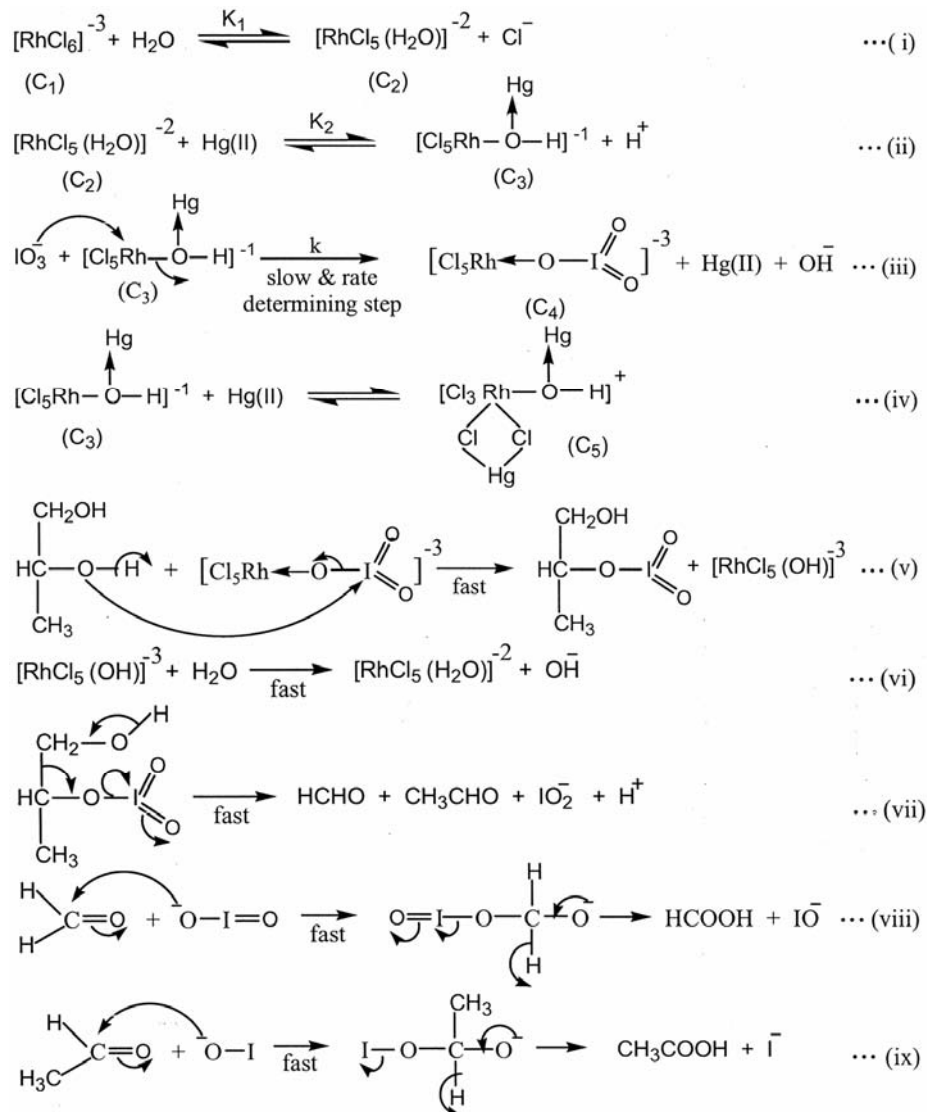2: 0.2 mol dm^{-3}
3: 0.5 mol dm^{-3}
4: 1.0 mol dm^{-3}

Fig. 1—UV-vis spectra recorded at room temperature.

Role of mercuric acetate in present investigation

In the absence of mercuric acetate in the reaction mixture, iodide ions (reduction product of KIO_3) interact with KIO_3 to form I_2 which induces parallel oxidation of the substrate and thus creates complications in KIO_3 oxidation. In order to prevent parallel I_2 oxidation of the substrate, mercuric acetate has been used as iodide ions scavenger. Formation of the complex, $[HgI_4]^{-2}$, ensures pure potassium iodate oxidation of 1,2-propanediol. Earlier, also it has been reported that Hg(II) acts as an oxidant[29] as well as co-catalyst[30]. Therefore, the role of $Hg(OAc)_2$ as oxidant and co-catalyst needs to be ascertained in the present investigation in addition to its role as I^- ions scavenger. In preliminary experiments, it has been observed that in the absence of KIO_3 at

$$[RhCl_6]^{-3} + H_2O \xrightleftharpoons{K_1} [RhCl_5(H_2O)]^{-2} + Cl^- \quad \cdots(i)$$
$$(C_1) \qquad\qquad\qquad (C_2)$$

$$[RhCl_5(H_2O)]^{-2} + Hg(II) \xrightleftharpoons{K_2} [Cl_5Rh-\overset{\overset{Hg}{\uparrow}}{O}-H]^{-1} + H^+ \quad \cdots(ii)$$
$$(C_2) \qquad\qquad\qquad\qquad (C_3)$$

$$IO_3^- + [Cl_5Rh-\overset{\overset{Hg}{\uparrow}}{O}-H]^{-1} \xrightarrow[\substack{slow\ \&\ rate \\ determining\ step}]{k} [Cl_5Rh\leftarrow O-IO_2]^{-3} + Hg(II) + OH^- \quad \cdots(iii)$$
$$(C_3) \qquad\qquad\qquad\qquad\qquad (C_4)$$

$$[Cl_5Rh-\overset{\overset{Hg}{\uparrow}}{O}-H]^{-1} + Hg(II) \rightleftharpoons [Cl_3Rh-\overset{\overset{Hg}{\uparrow}}{O}-H]^{+} \quad \cdots(iv)$$
$$(C_3) \qquad\qquad\qquad\qquad\qquad (C_5)$$

$$\underset{\substack{| \\ HC-O-H \\ | \\ CH_3}}{CH_2OH} + [Cl_5Rh\leftarrow O-IO_2]^{-3} \xrightarrow{fast} \underset{\substack{| \\ HC-O-IO_2 \\ | \\ CH_3}}{CH_2OH} + [RhCl_5(OH)]^{-3} \quad \cdots(v)$$

$$[RhCl_5(OH)]^{-3} + H_2O \xrightarrow{fast} [RhCl_5(H_2O)]^{-2} + OH^- \quad \cdots(vi)$$

$$\underset{\substack{| \\ HC-O-IO_2 \\ | \\ CH_3}}{CH_2-O-H} \xrightarrow{fast} HCHO + CH_3CHO + IO_2^- + H^+ \quad \cdots(vii)$$

$$\underset{H}{\overset{H}{>}}C=O + O-I=O \xrightarrow{fast} O=I-O-C<\overset{O}{\underset{H}{}} \rightarrow HCOOH + IO^- \quad \cdots(viii)$$

$$\underset{H_3C}{\overset{H}{>}}C=O + O-I \xrightarrow{fast} I-O-C<\overset{CH_3}{\underset{H}{}}O \rightarrow CH_3COOH + I^- \quad \cdots(ix)$$

Scheme 1

constant concentration of all other reagents, e.g., 1,2-propanediol, Hg(OAc)$_2$, HClO$_4$, Rh(III), KCl and NaClO$_4$ (used for maintaining constant ionic strength), the reaction did not proceed at all, indicating non-involvement of Hg(OAc)$_2$ as oxidant. Further, in another experiments with KIO$_3$ used as oxidant and at constant concentration of all other reagents, the rate of the reaction was found to increase with increase in [Hg(OAc)$_2$], showing thus the role of mercuric acetate in the reaction as co-catalyst. These observations indicate that Hg(II) is involved in the reaction as (i) I$^-$ ion scavenger, and, (ii) co-catalyst, and rules out its role as oxidant.

Reaction mechanism and derivation of rate law

In view of the above conclusion regarding the role of Hg(OAc)$_2$ in the reaction and in the light of reactive species of KIO$_3$ and Rh(III) in acid solution as IO$_3^-$ and [RhCl$_5$(H$_2$O)]$^{-2}$, respectively as well as other kinetic results, the following reaction mechanism is suggested (Scheme 1).

The rate of the reaction may be written in terms of rate of loss of [KIO$_3$] in the light of aforesaid Scheme 1.

$$\text{rate} = -\frac{d[KIO_3]}{dt} = k[IO_3^-]\,C_3 \qquad \cdots (1)$$

From step (i) we have

$$C_2 = \frac{K_1 C_1}{[Cl^-]} \qquad \cdots (2)$$

From step (ii) we have

$$C_3 = \frac{K_2 C_2 [Hg(II)]_F}{[H^+]} \qquad \cdots (3)$$

Considering Eqs (2) and (3) we have

$$C_3 = \frac{K_1 K_2 C_1 [Hg(II)]_F}{[H^+][Cl^-]} \qquad \cdots (4)$$

Total concentration of Rh(III), i.e., [Rh(III)]$_T$ may be written on the basis of steps (i) and (ii) as Eq. (5)

$$[Rh(III)]_T = C_1 + C_2 + C_3 \qquad \cdots (5)$$

Considering Eqs (2), (4), (5) we have

$$C_1 = \frac{[H^+][Cl^-][Rh(III)]_T}{[H^+][Cl^-] + K_1[H^+] + K_1 K_2[Hg(II)]_f} \qquad \cdots (6)$$

On substituting the value of C_1 from Eq. (6) in Eq. (4) we have

$$C_3 = \frac{[H^+][Cl^-][Rh(III)]_T}{([H^+][Cl^-] + K_1[H^+] + K_1 K_2 [Hg(II)]_f)} \times \frac{K_1 K_2 [Hg(II)]_f}{[H^+][Cl^-]}$$

$$or \quad C_3 = \frac{K_1 K_2 [Hg(II)]_f [Rh(III)]_T}{[H^+]([Cl^-] + K_1) + K_1 K_2 [Hg(II)]_f)} \qquad \cdots (7)$$

Further, total [Hg(II)], i.e., [Hg(II)]$_T$ may be written as Eq. (8)

$$[Hg(II)]_T = [Hg(II)]_f + C_3 \qquad \cdots (8)$$

Considering Eqs (3) and (8) we have Eq. (9)

$$[Hg(II)]_T = [Hg(II)]_f + \frac{K_2 C_2 [Hg(II)]_f}{[H^+]} \qquad \cdots (9)$$

On solving Eq. (9) for [Hg(II)]$_f$ we have

$$[Hg(II)]_f = \frac{[H^+][Hg(II)]_T}{([H^+] + K_2 C_2)} \qquad \cdots (10)$$

Considering Eqs (7) and (10) and on further solving, we have

$$C_3 = \frac{K_1 K_2 [Hg(II)]_T [Rh(III)]_T [H^+]}{\{[H^+]([Cl^-] + K_1) + \frac{K_1 K_2 [Hg(II)]_T [H^+]}{([H^+] + K_2 C_2)}\}} \times \frac{1}{([H^+] + K_2 C_2)}$$

$$or \quad C_3 = \frac{K_1 K_2 [Hg(II)]_T [Rh(III)]_T}{\{([Cl^-] + K_1)([H^+] + K_2 C_2) + K_1 K_2 [Hg(II)]_T\}}$$

Further, on assuming $K_1 [H^+] \gg K_2 C_2 [Cl^-]$, we have

$$C_3 = \frac{K_1 K_2 [Hg(II)]_T [Rh(III)]_T}{\{K_1 K_2 (C_2 + [Hg(II)]_T) + [H^+]([Cl^-] + K_1)\}} \qquad \cdots (11)$$

On substituting the value of C_3 from Eq. (11) in Eq. (1), we get final rate law (12)

$$-\frac{d[KIO_3]}{dt} = \frac{k K_1 K_2 [IO_3^-][Hg(II)]_T [Rh(III)]_T}{\{K_1 K_2 ([Rh(III)]_T + [Hg(II)]_T) + [H^+]([Cl^-] + K_1)\}} \qquad \cdots (12)$$

The rate law (12) fully conforms to all the observed kinetic results. Interaction between similarly charged species (step iii) confirms positive effect of ionic strength. At low [Hg(II)], the rate law should show first order in [Hg(II)], but due to the formation of inactive species (C_5) in step iv the rate does not increase in direct proportionality with increase in [Hg(II)] in its lower concentration range, showing predominance of reactive species (C_3) over inactive species (C_5).

Further verification of the above rate law can be achieved on re-arranging the Eq. (12),

$$\frac{\text{rate}}{[\text{IO}_3^-]} = k_{obs} = \frac{kK_1K_2[\text{Hg(II)}]_T[\text{Rh(III)}]_T}{\{K_1K_2([Rh(III)]_T + [\text{Hg(II)}]_T) + [\text{H}^+]([\text{Cl}^-] + K_1)\}}$$

$$\frac{1}{k_{obs}} = \frac{[\text{H}^+]}{kK_2[\text{Hg(II)}]_T[\text{Rh(III)}]_T} + \frac{1}{k[\text{Rh(III)}]_T}$$
$$+ \frac{[\text{H}^+][\text{Cl}^-]}{kK_1K_2[\text{Hg(II)}]_T[\text{Rh(III)}]_T} + \frac{1}{k[\text{Hg(II)}]_T}$$

$$or\ \frac{1}{k_{obs}} = \frac{1}{k[\text{Hg(II)}]_T} + \frac{1}{[\text{Rh(III)}]_T}$$
$$\times \left\{ \frac{1}{k} + \frac{[\text{H}^+]}{kK_2[\text{Hg(II)}]_T} + \frac{[\text{H}^+][\text{Cl}^-]}{kK_1K_2[\text{Hg(II)}]_T} \right\} \cdots (13)$$

Further on re-arranging Eq. (13) we get Eq. (14)

$$\frac{1}{k_{obs}} = [\text{Cl}^-]\left\{ \frac{[\text{H}^+]}{kK_1K_2[\text{Hg(II)}]_T[\text{Rh(III)}]_T} \right\}$$
$$+ \left\{ \frac{[\text{H}^+]}{kK_2[\text{Hg(II)}]_T[\text{Rh(III)}]_T} + \frac{1}{k[\text{Rh(III)}]_T} + \frac{1}{k[\text{Hg(II)}]_T} \right\}$$
$$\cdots (14)$$

According to Eqs (13) and (14), when $1/k_{obs}$ versus $1/[\text{Rh(III)}]$ and $1/k_{obs}$ versus $[\text{Cl}^-]$ were plotted, straight lines having positive intercept on y-axis were obtained (slopes, 9.33×10^{-4} and 16.57×10^5). This not only proves the validity of rate law (12) but also gives support to the proposed reaction scheme (Scheme 1). From the intercept of straight line of the former and intercept and slope of straight line of the latter, the values of k, K_1 and K_2 have been calculated and found as 22.00×10^{-2} s^{-1} mol^{-1} dm^3, 4.83×10^{-4} mol dm^{-3} and 19.74×10^3, respectively for the oxidation of 1,2-propanediol. Utilizing these values of k, K_1 and K_2, the reaction rates ($-dc/dt$) for the variation of

[Rh(III)] and [Cl$^-$] in the Rh(III)-catalysed oxidation of 1,2-propanediol have been calculated with the help of rate law (12) and found very close to the rate observed experimentally (Table 2). The close resemblance between the calculated and the observed rate further proves the validity of the rate law (12) and hence the proposed Scheme 1.

It is well known[31] that solvation in general increases with the charge on the ion. In case of reaction between two ions of opposite charge, it will result in a lowering of the net charge and due to this some frozen solvent molecules will be released with an increase of entropy. However, on the other hand when reaction takes place between two similarly charged ions, transition state will be a more highly charged ion and due to this more solvent molecules will be required than for the separate ions, leading to a decrease in entropy. In the present study of oxidation of 1,2-propanediol by KIO_3 in presence of Rh(III) catalyst in acidic medium, the observed high negative entropy of activation ($\Delta S^{\#} = -143.56$ J K^{-1} mol^{-1}) can be considered as due to the reaction between two similarly charged species, IO_3^- and $[\text{RhCl}_5(\text{HO}{\rightarrow}\text{Hg})]^{-1}$ leading to the formation of a highly charged complex, $[\text{RhCl}_5(\text{IO}_3)]^{-3}$ in the slow and rate determining step (iii).

Conclusions

On the basis of the present study on Rh(III) catalysed oxidation of 1,2-propanediol by KIO_3 in the presence of $HClO_4$, the following may be concluded: IO_3^- is the reactive species of KIO_3 while $[\text{RhCl}_5(\text{H}_2\text{O})]^{-2}$ is the reactive species of Rh(III) chloride in acidic medium. In the rate determining step, the highly charged complex, $[\text{RhCl}_5(\text{IO}_3)]^{-3}$ is formed by the interaction of IO_3^- and $[\text{RhCl}_5(\text{HO}{\rightarrow}\text{Hg})]^{-1}$ in acidic medium. The high negative value of $\Delta S^{\#}$ suggests that the two ionic species combine in the rate determining step to give one intermediate complex which is more ordered than the reactants. A high positive value of $\Delta G^{\#}$ (92.72 kJ mol^{-1}) indicates that the transition state is highly solvated. Hg(II) plays the role of promoter as well as inhibitor (step iv) in addition to its role as I$^-$ ion scavenger in the present investigation. Acetic acid and formic acid have been identified as the main oxidation products of the reaction. It can be concluded that Rh(III) acts as an efficient catalyst in the oxidation of 1,2-propanediol by KIO_3 in aqueous perchloric acid.

Acknowledgement

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