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Kinetics and Mechanism of Rhodium(III) Catalyzed Oxidation of Ethylene Glycol by Acidified Sodium Periodate

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The kinetics of the Rh(III) catalyzed oxidation of ethylene glycol in an acidified solution of $NaIO_4$ in the presence of $Hg(OAc)_2$ as a scavenger, have been studied in the temperature range 30-45 ºC. The rate shows first order kinetics in $[IO_4^-]$ and [Rh(III)]. The order of reaction with respect to the substrate is zero. Increase in $[H^+]$ and $[Cl^-]$ show no effect. Negligible effects of mercuric acetate $[Hg(OAc)_2]$ and ionic strength of the medium were observed. The effect of varying percentage of AcOH on the reaction rate was also observed. A suitable mechanism in conformity with the kinetic observations has been proposed. Various activation parameters were calculated from rate measurement and the rate law is derived on the basis of obtained data.

Key Words: Kinetics, Rh(IIII), Oxidation, Ethylene glycol, Acidic sodium periodate.

INTRODUCTION

Potassium bromate[1-8] and $[NaIO_4]$[9] have been used as an oxidant for various compounds in acidic medium. N-bromoacetamide[10-13], N-bromosuccinimide[14,15] have been earlier used in oxidation of a number of compounds in presence of catalyst. A little attention has been paid to reactivity of sodium periodate[16-18] as an oxidant in various catalyzed reaction. The work on kinetics and mechanism of Rh(III) catalyzed oxidation of 1,2-glycols[19] and polyhydric alcohols by acidic $KBrO_3$[20] has also been reported. No investigation has so far been reported on the catalytic role of rhodium(III) chloride with $NaIO_4$ as an oxidant.

In this paper, the oxidation of ethylene glycol by acidified $NaIO_4$ in the presence of Rh(III) chloride as a catalyst and $Hg(OAc)_2$ as a scavenger for iodide ion (I^-) is reported.

EXPERIMENTAL

An aqueous solution of ethylene glycol (E. Merck), sodium periodate (SD Fine Chemicals, AR), $NaClO_4$ and $Hg(OAc)_2$ (E. Merck), were prepared by dissolving the weighed amount of samples in triple distilled water, perchloric acid (60 %, E. Merck) was used as a source of hydrogen ions. A $RhCl_3$ (Sigma) solution was prepared in HCl of known strength (0.018 N). Other reagents were of analytical grade. Reaction vessels were painted black to prevent photochemical decomposition.

Kinetics: The requisite volume of all reagents, including substrate, were thermostated at 35 ± 0.1 ºC to attain equilibrium. A measured volume of $NaIO_4$ solution maintained separately at the same temperature was rapidly poured into the reaction vessel. Progress of the reaction was followed by assaying aliquots of the reaction mixture for $NaIO_4$, iodometrically using starch as an indicator after suitable time intervals.

Stoichiometry and product analysis: The stoichiometry of the reaction was determined by equilibrating varying ratios of $[NaIO_4]$ to ethylene glycol separately at 35 ºC for 48 h under kinetic conditions. Estimation of unconsumed $NaIO_4$ revealed that, one mole of ethylene glycol consumes two moles of periodate according to eqn. 1:

$$RCH_2OH + 2HIO_4 \longrightarrow RCOOH + 2HIO_3 + H_2O \qquad (1)$$

where R = CH_2OH for ethylene glycol whose oxidation product *i.e.*, glycollic acid was detected by measuring its melting point of amide derivative as follows[21].

Kept the reaction mixture for 48 h under kinetic conditions and then added PCl_5 to it. Refluxed till a clear solution was obtained. Cooled and added 4-5 mL of concentrated ammonia solution to this acid chloride. Heated it on water bath for 4-5 min, cooled it and filtered the precipitated solid, washed with water and recrystallized (m.p. 120 ºC).

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$RCOCl + NH_4OH \longrightarrow RCONH_2 + HCl + H_2O$$

RESULTS AND DISCUSSION

In order to propose a probable reaction mechanism for Rh(III) catalyzed oxidation of ethylene glycol by acidic sodium periodate, it is necessary to study the effect of variation in concentration of different reactants on the rate of reaction.

The kinetics of oxidation of ethylene glycol was investigated at several initial reactant concentrations (Table-1). First order kinetics was observed with respect to the catalyst *i.e.*, Rh(III) while positive effect in case of substrate was found.

A plot of (-dc/dt) *versus* [Rh(III)] (Fig. 1) gives a slope = $1.0 \times 10^{-2}\ s^{-1}$ for ethylene glycol which is close to the average value of first order rate constants *i.e.*, $k_1 = 1.1 \times 10^{-2}\ s^{-1}$ for ethylene glycol at 35 ºC. The graphically obtained values of (-dc/dt)/[Rh(III)] clearly confirm the first order dependence on [Rh(III)]. This has also been confirmed by the least square method (Fig. 2).

TABLE-1
EFFECT OF REACTANTS ON THE REACTION RATE AT 35 ºC

$[S] \times 10^2$ (M)	$[Rh(III)] \times 10^6$ (M)	$[IO_4^-] \times 10^3$ (M)	$(-dc/dt) \times 10^7$ (ML^{-1} s^{-1})
0.33	12.00	1.00	0.96
0.40	12.00	1.00	1.00
0.50	12.00	1.00	1.13
0.66	12.00	1.00	1.32
1.00	12.00	1.00	1.23
2.00	12.00	1.00	1.66
2.00	3.00	1.00	0.41
2.00	6.00	1.00	0.72
2.00	9.00	1.00	1.24
2.00	12.00	1.00	1.66
2.00	15.00	1.00	2.07
2.00	18.00	1.00	2.38
2.00	12.00	0.83	1.81
2.00	12.00	1.00	1.66
2.00	12.00	1.25	2.00
2.00	12.00	1.67	2.25
2.00	12.00	2.50	2.66
2.00	12.00	5.00	4.40

$[KCl] = 1.00 \times 10^{-3}$ (M), $[HClO_4] = 1.00 \times 10^{-3}$ (M)
$[Hg(OAc)_2] = 1.25 \times 10^{-3}$ (M)

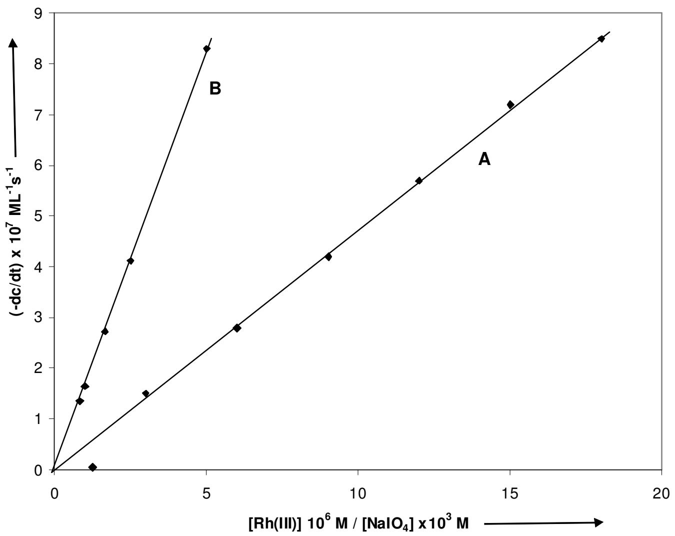

Fig. 1. Plot between [Rh(III)] (A)/$[NaIO_4]$ (B) *vs.* (-dc/dt) for oxidation of ethylene glycol at 35 ºC

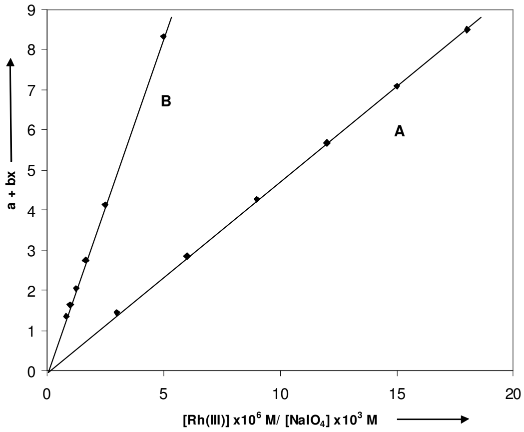

Fig. 2. Plot between [Rh(III)] (A)/[NaIO4] (B) *vs.* (a + bx) for oxidation of ethylene glycol at 35 ºC

It is also clear from the (Table-1) that an increase in concentration of substrate shows positive effect because as we increase the concentration of (-dc/dt) values increases. Constant k_1 values are obtained in case of Rh(III) chloride catalyst and oxidant $NaIO_4$ which further show first order kinetics with respect to catalyst and oxidant ($NaIO_4$), respectively. An insignificant effect of [Cl^-], [H^+] and [$Hg(OAc)_2$] variation were also observed (Table-2).

The rate measurement were taken in the temperature range 30-45 ºC and the specific rate constants were used to draw a plot of log k *vs.* 1/T (Fig. 3) which was linear and various activation parameters has been calculated (Table-3).

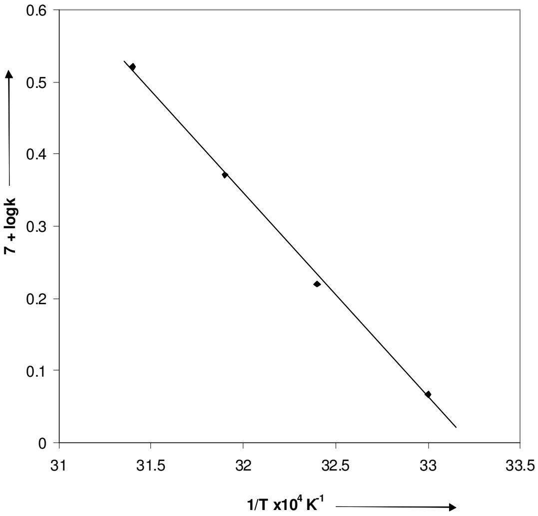

Fig. 3. Plot between log k *vs.* 1/T for oxidation of ethylene glycol at 35 ºC

TABLE-2
EFFECT OF VARIATION OF PERCLORIC ACID, KCl, MERCURIC ACETATE AND IONIC STRENGTH ON THE REACTION RATE AT 35 ºC

$[HClO_4] \times 10^{-3}$ (M)	$[KCl] \times 10^{-3}$ (M)	$[Hg(OAc)_2] \times 10^{-3}$ (M)	$[NaClO_4] \times 10^{-3}$ (M)	$(-dc/dt) \times 10^7$ $ML^{-1}s^{-1}$
0.83	1.00	1.25	–	1.80
1.00	1.00	1.25	–	1.66
1.25	1.00	1.25	–	2.22
1.67	1.00	1.25	–	2.30
2.25	1.00	1.25	–	2. 50
5.00	1.00	1.25	–	2.50
1.00	0.83	1.25	–	1.69
1.00	1.00	1.25	–	1.66
1.00	1.25	1.25	–	1.80
1.00	1.67	1.25	–	2.00
1.00	2.50	1.25	–	1.80
1.00	5.00	1.25	–	2.00
1.00	1.00	0.83	–	1.14
1.00	1.00	1.00	–	1.40
1.00	1.00	1.25	–	1.66
1.00	1.00	1.67	–	1.33
1.00	1.00	2.50	–	1.27
1.00	1.00	5.00	–	1.00
1.00	1.00	1.25	0.83	2.50
1.00	1.00	1.25	1.00	2.57
1.00	1.00	1.25	1.25	2.20
1.00	1.00	1.25	1.67	1.80
1.00	1.00	1.25	2.50	2.50
1.00	1.00	1.25	5.00	2.60

$[Rh(III)] = 12.00 \times 10^{-6}$ (M), $[S] = 2.00 \times 10^{-2}$ (M), $[IO_4^-] = 1.00 \times 10^{-3}$ (M)

TABLE-3
ACTIVATION PARAMETERS FOR ACID IODATE OXIDATION OF ETHYLENE GLYCOL

Activation parameters	Temp. (ºC)	Ethylene glycol
$K_r \times 10^4\ s^{-1}$	30	1.15
$K_r \times 10^4\ s^{-1}$	35	1.66
$K_r \times 10^4\ s^{-1}$	40	2.35
$K_r \times 10^4\ s^{-1}$	45	3.32
log A	–	1.09
ΔE^* (kJ mol^{-1})	–	51.70
ΔG^* (kJ mol^{-1})	35	75.01
ΔH^* (kJ mol^{-1})	35	58.37
ΔS^* (J $K^{-1}mol^{-1}$)	35	-7.35

Reaction mechanism and rate law derivation: The reaction scheme is proposed as follows:

$$\underset{}{Rh^{3+} + IO_4^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{[C_1]}{[Rh{-}{-}{-}{-}IO_4]^{2+}}$$

$$\underset{[C_1]}{[Rh{-}{-}{-}{-}IO_4]^{2+}} \xrightarrow[k_2]{Slow} \underset{[C_2]}{[Rh{—}O]^+} + IO_3^-$$

$$[Rh{—}O]^+ + RCH_2OH \longrightarrow [Rh{—}OH]^{2+} + R^+CHOH$$

$$R^+CHOH + H_2O \longrightarrow RCHO + H_3O^+$$

$$[Rh{—}OH]^{2+} + RCHO + IO_4^- + H_3O^+ \longrightarrow Rh^{3+} + RCOOH + IO_3^- + 2H_1O$$

Considering the above steps and applying steady state approximation to the complex, the rate of reaction in terms of loss of IO_4^- may be written as:

$$\frac{-d[IO_4^-]}{dt} = \frac{k_2K_1[Rh(III)][IO_4^-]}{1 + K_1[IO_4^-]}$$

Conclusion

The experimental results revealed that the reaction rate doubles when the concentration of catalyst is doubled. The rate law equation is in conformity with all kinetic observations and the proposed mechanistic steps are supported by the negligible effect of ionic strength. The high positive value of free energy of activation (ΔG^*) indicates highly solvated transition state, while negative value of entropy of activation (ΔS^*) suggest the formation of an activated complex with reduction in the degree of freedom of molecules. From the present investigation, it is concluded that IO_4^- and Rh^{3+} are the reactive species of the oxidant and catalyst in acidic medium for ethylene glycol.

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