KINETIC AND MECHANISTIC STUDIES OF RU(III) CATALYSIS IN OXIDATION OF GLYCEROL BY ALKALINE SOLUTION OF N- BROMOACETAMIDE

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ABSTRACT

Kinetics of Ruthenium(III) catalysis in oxidation of glycerol(G) by alkaline solution of N-bromoacetamide have been studied in the temperature range of 30°C to 45°C using mercuric acetate as Br⁻ ions scavenger. The reaction follows zero order in [Glycerol] and first order with respect to both [Ru(III)] and [NBA]. Negligible effect of variation of both [OH⁻] and [Cl⁻] has been observed. A negative effect of acetamide is observed while mercuric acetate addition shows first order on the reaction velocity which shows that probably mercury(II) acts as co-catalyst. Variation of ionic strength of the medium shows insignificant effect. Various activation parameters have been computed and a suitable mechanism conforming to the observed kinetic data is proposed and discussed.

Keywords: Mechanism, Oxidation Kinetics, Glycerol, Ru(III) catalysis, NBA

NBA is a less familiar potent oxidant which is of special interest for studying mechanism as it behaves both as a halogenating and oxidizing agent. Although the oxidative capacity of this analytical reagent has been widely utilized for the quantitative direct and indirect estimation of a large number of compounds [I], only a few kinetic studies of the uncatalysed reactions have been made. Mechanism of oxidation of primary alcohols, dimethyl sulfoxide and a few ketones by acidic solution of N-bromoacetamide has been studied by Mukherjee and Banerjee [2], Radhakrishnamurthi and Sahu [3], and Singh and co-workers [4-7], respectively.

The use of transition metal ionssuch as ruthenium(VIII), osmium(VIII), iridium(III), ruthenium(III), palladium(II) and rhodium(III) as catalyst in various redox systems has been reported. This has attracted considerable interest due to their involvement in many industrial processes. Although the mechanism of catalyst depends upon the nature of substrates, oxidants and other experimental conditions, but it has been shown[8] that transition metal acts as catalyst by one of these different paths such as formation of reactive complex with reactants or oxidation of substrates itself or through the formation of free radicals. Although Ru(III) has long been used as catalyst in many redox reactions involving different oxidants but its catalytic activity in oxidation of ethylene glycol by NBA, especially in alkaline medium, is not known.This prompted us to report the kinetics of Ru(III)catalyzed oxidation of G by NBA in alkaline medium in the presence of mercuric acetate as scavenger as a part of our broad program on mechanistic studies of catalyzed reactions[9-11]with a

view to ascertain (i)the reactive species of Ru(III) in alkaline medium.(ii)the reactive species of NBA in alkaline medium ,(III)the role of OH⁻ ions in oxidation of

G in the presence of Ru(III) as catalyst.(IV)the role of Hg(OAc)₂in the present investigation in addition to its role as Br⁻ ions scavenger and(V)finally to elucidate the reaction mechanism and derive the related law.

EXPERIMENTAL
Materials

The reagents employed were glycerol(AR grade),ruthenium(III)chloride (Johnson&Matthey), NBA(G.R.S. Merck), NaClO₄ and NaOH (all of E. Merck).All other reagents used were of A.R. Grade. The stock solutions of all the reagents were prepared in doubly distilled water. Solution of G was prepared by weighing its sample and dissolving it in doubly distilled water.Ruthenium (III) chloride solution was prepared by dissolving its 1 g sample in hydrochloric acid of known strength. Perchloric acid (E. Merck) was used as a source of hydrogen ions; while the variation of ionic strength was affected by using appropriate amount of sodium perchlorate (E. Merck).All other reagents, namely potassium chloride and acetamide, were of Analar grade. Double distilled water was used throughout the course of the reaction and reaction bottles were opaque to light to avoid any photochemical effect.
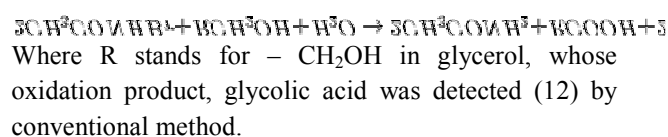
Kinetic Measurement

Appropriate volumes of glycerol, perchloric acid, ruthenium(III) chloride, potassium chloride, mercuric acetate and sodium perchlorate solutions and

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water taken in a reaction bottle (coated black from outside) wasthermostated at 35°C for thermal equilibrium.After half an hour when the reaction mixture attained the desired temperature a measured volume of NBA solution also thermostated at the same temperature was rapidly added to the reaction mixture to initiate the reaction. The progress of the reaction was monitored by iodometricestimationof unreacted NBA at regular time intervals. The course of the reaction was studied for two half lives of the reaction.

Stoichiometry and Product Analysis

Varying ratios of [NBA]:[G] were equilibrated at 35°C for 72 hours under [NBA]» [G] condition. Estimation of ridualNBA showed that one mole of G consumes two moles of NBA according to the stoichiometric equation (1):

$$3CH_3CONHBr+RCH_2OH+H_2O \rightarrow 3CH_3CONH_3+RCOOH+3$$

Where R stands for – CH_2OH in glycerol, whose oxidation product, glycolic acid was detected (12) by conventional method.

KINETIC RESULTS

When the concentration of the G is in excess over [NBA], the plot of unconsumed [NBA] versus time shows that the reaction is composed of two successive reactions. The initial slow reaction is followed by a faster reaction. Such observation has also been reported in N- bromosuccinimide oxidation (13) and the faster reaction has been attributed to bromine oxidation. We also observed a yellow color (perhaps due to liberation of bromine as a result of interaction between Br⁻ ion produced and NBA) in the reaction mixture after the reaction has proceeded to about 10 to 15%.The appearance of yellow color and the faster reaction were suppressed by the addition of 0.005 M mercury(II) acetate. This reaction, therefore, was carried out in the presence of mercury(II) acetateto scavenge the producedBr⁻ ions as $[Hg\ Br_4]^{2-}$complex.It was observed that the rate of reaction was nearly the same as the rate of slow initial reaction without Hg(II).

The kinetics of oxidation of the title reaction was investigated at several initial concentrations of all reactants (Table 1). Initial rates (-dc/dt) were measured while varying [NBA].The value of (-dc/dt)wasdetermined at fixed time in each kinetic run and first order rate constant (k_{obsd}) was calculated by the formula,k_{obsd} = (-dc/dt)/[NBA] . It was observed that there is linear relationship between (-dc/dt) and [NBA], indicating first order in [NBA].First order rate constant in NBA (k_{obs})

was evaluated also from the slope of the plot(Fig.)between (-dc/dt) and [NBA] .The graphical k_{obsd} was very close to the experimentally observed k_{obsd}(table1),confirming thus first order in [NBA].The rate of the reaction was not affected by increase in [G],showing zero order in [G].The rate of reaction is increased linearly with an increase in concentration of Ru(III), which was further confirmed by practically constant value of k_2 ($k_2 = k_{obs}$ / [Ru(III)]) of table 1. Plot of log (-dc/dt) against log [Ru(III)](Figurenot shown here) gave slope almost equal to k_2 value of table1 for the variation of [G] which indicates first order kinetics in [Ru(III)].

TABLE-1

Effect of [Reactants] on reaction rate at 35^0C under the conditions [NaOH] =1.00x10^{-2}M,

[KCl] = 1.00x10^{-3} M and [Hg(OAc)$_2$] = 2.50x10^{-3} M

[NBA] x 10^4 M	[G] x 10^2 M	[Ru(III)] x10^{6}M	k_{obsd} x 10^{4}s^{-1}
4.00	2.00	19.28	5.20
5.00	2.00	19.28	5.10
6.67	2.00	19.28	5.10
8.00	2.00	19.28	5.70
10.00	2.00	19.28	5.50
12.50	2.00	19.28	4.90
16.67	1.00	19.28	4.50
10.00	0.50*	19.28	1.90
10.00	1.00*	19.28	1.90
10.00	2.00*	19.28	2.00
10.00	3.33*	19.28	2.00
10.00	5.00*	19.28	2.00
10.00	10.00*	19.28	2.00
10.00	2.00	3.86	0.13
10.00	2.00	9.64	0.31
10.00	2.00	15.42	0.49
10.00	2.00	19.28	0.64
10.00	2.00	23.14	0.79
10.00	2.00	28.92	0.94

10.00	2.00	38.56	1.25

* $[Hg(OAc)_2] = 1.25 \times 10^{-3}$ M

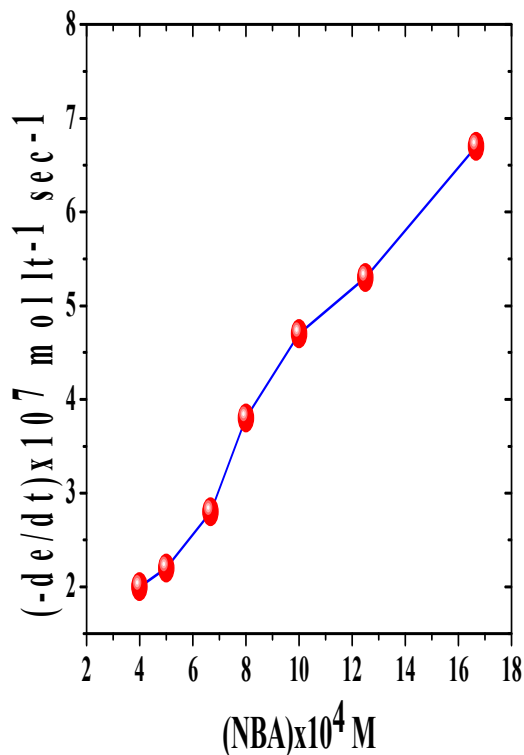$[Hg(OAC)_2] = 2.50 \times 10^{-3}$ M
AND TEMPERATURE 35^0 C

Table 2 contains the effect of variation of [OH⁻],[Hg(II)] and [acetamide] The effect of [OH⁻] on the rate of reaction was studied by taking into account the amount of NaOH already present in Ru(III)solution. On increasing [OH⁻] the rate of reaction remains unchanged which shows zero order in [OH⁻] .Variation of ionic strength from 0.58×10^{-2} M to 8.00×10^{-2}M did not affect the rate of the reaction ,indicating zero effect of ionic strength of the medium.Addition of acetamide(NBH) andKCldid not change the reaction rate significantly,showing zero effect of acetamide(NBH) and [Cl⁻] on the rate. Successive addition of mercuric acetate (used for Br⁻ion scavenger) showed linear relationship between Hg(II) concentration and first order rate constant(k_{obsd}), suggesting thus first order with respect to [Hg(II)].

Effect of variation of [NaOH], addition of mercuric acetate and Acetamide(NBH)on rate constant at 35^oC under the conditions of [NBA] = 10.00×10^{-4}M ,[G] = 2.00×10^{-2}M], and [Ru(III)] = 19.28×10^{-6}M

Fig: PLOT BETWEEN (-dc/dt) AND [NBA]*
[NaOH] =1.00×10^{-3}M [HCLO$_4$] = 1.00×10^{-2}M,

The effect of glycerol was studied in 30-45°C

[NaOH] x 10^3 M	[Hg(OAc)$_2$] x10^3 M	[NBH]x 10^{3}M	k_{obsd} x 10^4 s^{-1}
1.00	1.25	0.00	1.60
1.33	1.25	0.00	1.39
2.00	1.25	0.00	1.36
3.33	1.25	0.00	1.38
5.00	1.25	0.00	1.36
10.00	1.25	0.00	1.30
1.00	1.25	0.00	2.30
1.00	1.67	0.00	2.50
1.00	2.50	0.00	4.20
1.00	3.33	0.00	5.80
1.00	5.00	0.00	9.20
1.00	1.25	1.00	1.70
1.00	1.25	1.33	1.50
1.00	1.25	2.00	1.30
1.00	1.25	4.00	1.00

temperature range, keeping other experimental conditions constant. From the linear Arrhenius plot of log $_{kobsd}$ versus 1/T, values of activation parameters have been computed.

Activation parameters in oxidation of G by alkaline NBA solution catalyzed by Ru(III) at 35°C[NBA] = 1.00x10^{-3}M, [NaOH] = 1.00x10^{-3} M, [G] = 1.00x10^{-2} M, [Hg(OAc)$_2$] =1.25x10^{-3}M [KCl]= 1.00x10^{-3}Mand[Ru(III)] = 19.28x10^{-6} M. Energy of activation calculated, and it comes out to be 15.20 Ea. (kcal/mole)

Test of Free Radicals

Olifinic monomers such as acrylonitrite and freshly prepared 10%acrylamide solution under nitrogen atmosphere were added to the reaction mixture to indicate polymerization if free radicals were present. The lack of polymerization indicated the absence of free radicals in the reaction mixture. Proper control experiments were also run.
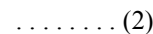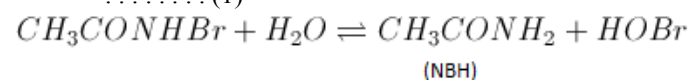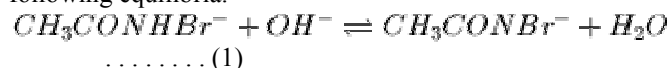
DISCUSSION

Ru(III) is reported[13] to exist in the following equilibrium in aqueous alkaline medium.

$[Ru(H_2O)_6]^{3+} + OH^- \rightleftharpoons [Ru(H_2O)_5OH]^{+2}$
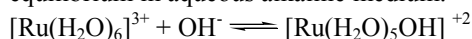
Since [OH$^-$] has negligible effect on the rate of the reaction, therefore Ru(H$_2$O)$_6$]$^{3+}$ can be safely assumed as the catalytic species of Ru(III) in alkaline medium. But Here for the sake of simplicity Ru(H$_2$O)$_6$]$^{3+}$ will be written as [RuCl$_6$]$^{3-}$as its solution was prepared in dilute solution of HCl.

In alkaline medium, the active species of N-bromoacetamide may be NBA or OBr$^-$ formed from the following equilibria.

$$CH_3CONHBr^- + OH^- \rightleftharpoons CH_3CONBr^- + H_2O$$

$$\ldots\ldots\ldots(1)$$

$$CH_3CONHBr + H_2O \rightleftharpoons CH_3CONH_2 + HOBr$$
(NBH)

$\ldots\ldots\ldots(2)$
$\ldots\ldots\ldots(3)$

$$HOBr + OH^- \rightleftharpoons OBr^- + H_2O$$

In alkaline medium, unlike in acid medium, there is a negative effect of added [acetamide] on the rate of the title reaction. If CH$_3$CONBr $^-$is taken as reactive species, the negative effect of added [Acetamide] on the rate is not explained. Hence involvement of CH$_3$CONBr $^-$ in the title reaction is ruled out.Further, it is well established [14] that even at the lower concentration of alkali used, HOBr exists exclusively as hypobromite ions. HOBr is formed from the hydrolysis of NBA [equilibrium 2]. Now if hypobromite ion is assumed to be actively involved in the reaction, the negative effect of acetamide is explained. Hence, under the experimental conditionsOBr$^-$is real oxidizing species.
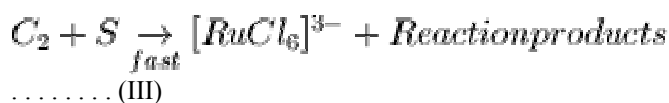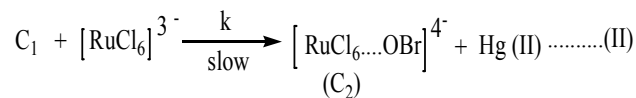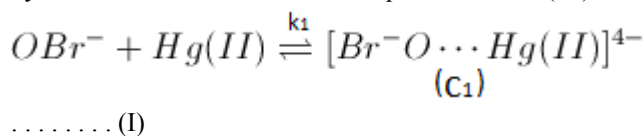
Role of Hg(II) in the present Investigation

It has been observed during kinetic investigation that after 10 to 15% progress of the reaction a yellow color is developed which causes all of a sudden increase in the rate of the reaction. This was ascribed due to the formation of molecular bromine as a result of interaction between NBA and Br$^-$ ions (which results in the reaction due to reduction of NBA). Therefore, in order to ensure pure NBA oxidation only, Hg(OAc)$_2$ was added initially to the reaction mixture. Hg(OAc)$_2$ traps Br$^-$ ions forming [HgBr$_4$]$^{2-}$ complex and thus Br$_2$ oxidation is obviated[15].

It has also been reported [16] earlier that Hg(II) acts as homogeneous catalyst, co-catalyst and oxidant[17]. In order to ascertain the real role of Hg(OAc)$_2$ in addition to its actionhere as Br– ions

scavenger, several experiments were carried out with different initial [Hg(OAc)$_2$], with and without the presence of NBA and RuCl$_3$(H$_2$O)$_3$ under similar experimental conditions.The kinetic observations in the presence of NBA but with and without RuCl$_3$ (H$_2$O)$_3$ showed that the rate of reaction increases with the increase in the concentration of Hg(OAc)$_2$, showing its role as co-catalyst in the reaction. The reaction also did not proceed without using NBA in the presence of mercuric acetate, indicating thus non-involvement of Hg(OAc)$_2$ as oxidant. Thus in view of aforesaid kinetic observations, Hg(OAc)$_2$ acts as co-catalyst and Br$^-$ ion scavenger due to formation of complex [HgBr$_4$]$^{2-}$. Therefore all the experiments were performed in the presence of Hg(OAc)$_2$.

Reaction Mechanism and Derivation of Rate law

Considering the reactive species of Ru(III) and NBA in alkaline medium and other kinetic results presented in tables 1, 2 and 3, the following reaction scheme is suggested for the oxidation of ethylene glycol by alkaline solution of NBA in the presence of Ru(III).

$$OBr^- + Hg(II) \overset{k_1}{\rightleftharpoons} [Br^-O \cdots Hg(II)]^{4-}$$
$$(C_1)$$

. . . . (I)

$$C_1 + [RuCl_6]^{3-} \xrightarrow[slow]{k} \left[RuCl_6....OBr\right]^{4-} + Hg(II) \cdots (II)$$
$$(C_2)$$

$$C_2 + S \xrightarrow[fast]{} [RuCl_6]^{3-} + Reaction products$$

. . . . (III)

Now the rate of reaction in terms of consumption of NBA may be written as eq. (1).

$-d$ [NBA]$/dt = k$ [C_1] [RuCl$_6$)]$^{3-}$. . . . . (1)

From step (I), we have:

[C_1] = K_1 [OBr$^-$] [Hg(II)] . . . . (2)

From eqn. (1) and (2), we have:

$-d$ [NBA]$/dt = kK_1$ [OBr$^-$][RuCl$_6$]$^{3-}$[Hg(II)]. . . . (3)

The final rate law (3) fully explains all the observed kinetic results.

CONCLUSION

The conclusions drawn from the observed kinetic data obtained for the Ru(III)- catalyzed oxidation of glyceroll by NBA in alkaline medium are as follows:

1.[RuCl$_6$]$^{3-}$ and OBr$^-$ have been found as the reactive species of Ru(III) and N-bromoacetamide,respectively in alkaline medium.

2. There is formation of a most reactive activated complex (C$_2$) between C$_1$ and reactive species of Ru(III) in alkaline medium where C$_2$ is [RuCl$_6$ . . . . . . OBr$^-$]$^{4-}$.

3. The existence of the reactive species of OBr$^-$ of NBA is due to negative effects of acetamide.

4. Hg(II) acts as co-catalyst as well as Br$^-$ ion scavenger due to the formation of complex [HgBr$_4$]$^{-2}$.

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