

**Rhodium (III) Catalyzed oxidation of ethyl diethylene glycol (EDG.) by N – bromoacetamide
: A kinetic and mechanistic study.**

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Abstract

The kinetics and mechanism of Rhodium (III) catalyzed oxidation of ethyl diethylene glycol (EDG) by acidic solution of N – bromoacetamide (NBA) in presence of mercuric acetate as bromide ion scavenger has been studied. The reaction follows first order kinetics in both NBA and Rh_{III} and zero order dependence on each of EDG and H^+ ions . Zero effect of ionic strength variation and chloride ion addition was observed while successive addition of acetamide showed negative effect on the rate. A suitable mechanism in agreement with kinetic observations has been proposed.

Keywords:

Ethyl diethylene glycol, N – bromoacetamide, Rhodium chloride, Oxidation Kinetics.

Introduction :

N-bromoacetamide is a mild and often selective but potent oxidant for many organic compounds¹⁻⁴ several papers have been devoted to the kinetics and mechanism of oxidation of unanalysed oxidation of alcohols⁵ , ketones ⁶⁻⁹ , Although some work has been reported involving Ru(III) , Ir (III), Pd (II) Chloride as homogenous catalyst involving N – Halogeno compounds¹⁰⁻¹³

AIM: This prompted us to undertake the present investigation which involves, the study of **Kinetic and mechanistic studies of Rh (III) catalyzed oxidation of Ethyl diethylene glycol. (EDG) by N – bromoacetamide in acidic medium.**

Materials and methods:

All the reagents used were highest purity available. NBA (S.Merck) solution was prepared afresh and its strength was checked by estimating its bromine iodometrically . All other reagents were of Analar R.Grade. Perchloric acid (E.merck) was used as H^+ ions. EDG (E.marck) solution was prepared by weighing its sample and dissolving it in double distilled water.The reaction was carried out under pseudo – first order conditions by keeping (EDG) ten times. Greater than that of NBA. The progress of the reaction was monitored by iodometric ,determination of unconsumed NBA at regular time intervals . The course of the reaction was studied for two -half lives.

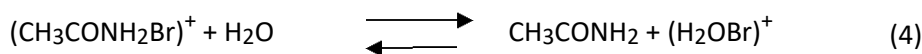
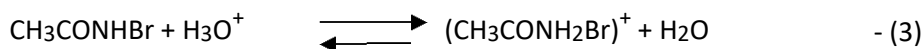
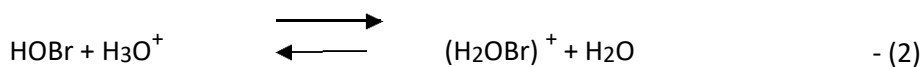
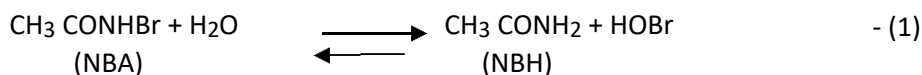
Result & Discussion:--

The Kinetics of Oxidation of Ethyl diethylene glycol. (EDG) BY NBA in presence of perchloric acid and Rh(III) was investigated at several initial concentrations of reactants (Table 1).At different concentrations of NBA the velocity constant for first order was nearly constant showing first order dependence on N-bromoacetamide. The first order velocity constant remained nearly constant at different initial concentration of EDG showing zero

order. Variation of perchloric acid did not bring about significant change in k_1 values establishing thus zero order with respect of H^+ ions. The reaction was markedly influenced by increase in $[Rh(III)]$ and a Linear relation between k_1 values and $[Rh(III)]$ was observed showing first order kinetics in $Rh(III)$. This is obvious from plot of k_1 vs $[Rh(III)]$ (Fig1) which yields a straight line passing through origin.

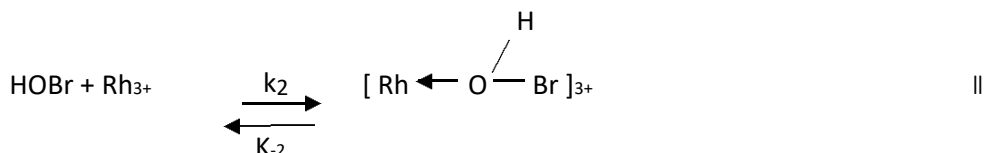
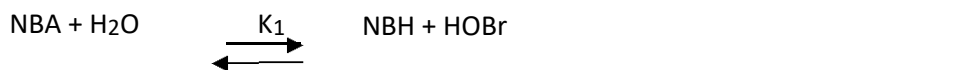
Further, the experimental data (not given) shows negligible effect of ionic strength of medium, zero effect of chloride ions and a negative effect of acetamide was observed. Negligible effect of mercuric acetate on the reaction rate rules out its participation in NBA oxidation and confirms its role as a scavengers for any Br^- formed in the reaction. The activation of energy was calculated from the rate measurements at 30, 35, and 40°C and was found to be 18.38 kcal mol⁻¹.

In acidic media NBA is known to exist¹⁻⁴ in the following equilibria.

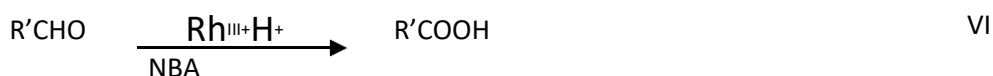
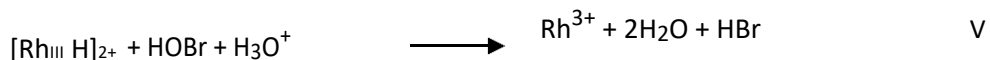
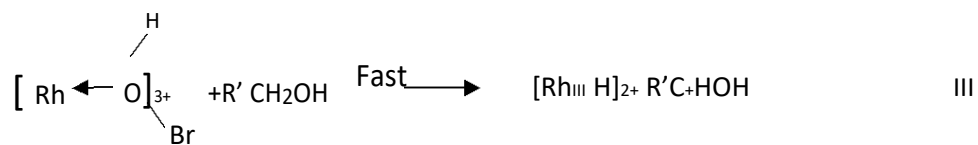


Thus in acidic solution, NBA as such as HOBr or $(NBAH)^+$ or $(H_2OBr)^+$ may be involved in oxidation as active species. Zero order in H^+ ion rules out the possibility of H_2OBr^+ and $NBAH^+$ as active species of NBA. and negative effect of acetamide will not allow us to assume NBA as oxidising species. Hence only choice left is HOBr which is involved in the reaction as reactive species.

On the basis of above discussions the following steps are suggested. Here Rh_{III} has been used for $RhCl_3$ for convenience.



Forward reaction is slow and rate determining step.



Where R' = -CH₂OCH₂CH₂OC₂H₅ and NBH is acetamide.

Considering the above steps the rate of the reaction in terms of rate of loss of [NBA] may be written as eq. (5).

$$\frac{-d[\text{NBA}]}{dt} = \frac{k_2 K_1 [\text{NBA}]_T [\text{Rh}^{\text{III}}]}{K_1 + [\text{NBH}]} \quad - (5)$$

which explains all the observed kinetics.

Table 1 – Effect of variation of [Reactants] on the reaction rates at 35o

[Rh^{III}] = 15.00X10⁻⁶ M , [KCl] = 5.00X10⁻²M [Hg(oAc)₂] = 3.34X10⁻³M

| [NBA]X10 ⁴ M | [EDG]X10 ² M | [Hclo ₄]X10 ² M | k ₁ X10 ⁵ s ⁻¹ |
|-------------------------|-------------------------|--|---|
| 8.00 | 5.00 | 10.00 | 8.68 |
| 10.00 | 5.00 | 10.00 | 9.87 |
| 12.50 | 5.00 | 10.00 | 8.82 |
| 16.66 | 5.00 | 10.00 | 8.18 |
| 20.00 | 5.00 | 10.00 | 9.62 |
| 25.00 | 5.00 | 10.00 | 10.36 |
| 10.00 | 1.00 | 10.00 | 8.98 |
| 10.00 | 1.33 | 10.00 | 8.62 |
| 10.00 | 2.00 | 10.00 | 9.50 |
| 10.00 | 5.00 | 10.00 | 10.25 |
| 10.00 | 10.00 | 10.00 | 10.81 |
| 10.00 | 13.33 | 10.00 | 9.84 |
| 10.00 | 5.00 | 2.50 | 8.88 |
| 10.00 | 5.00 | 5.00 | 9.25 |
| 10.00 | 5.00 | 20.00 | 9.50 |
| 10.00 | 5.00 | 30.00 | 9.15 |
| 10.00 | 5.00 | 50.00 | 9.68 |
| 10.00 | 5.00 | 100.00 | 9.72 |

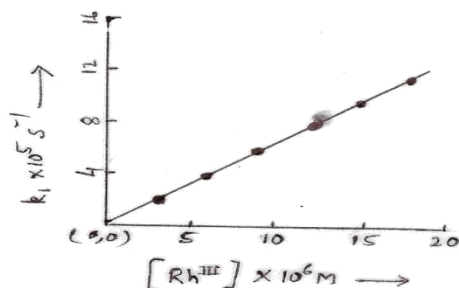


Fig. 1. Plots of k_1 vs $[Rh(III)]$; $[NBA] = 10.00 \times 10^{-4} M$,
 $[EDG] = 5.00 \times 10^{-2} M$, $[HClO_4] = 10.00 \times 10^{-2} M$,
 $[Hg(OAc)_2] = 3.34 \times 10^{-3} M$, $[KCl] = 5.00 \times 10^{-2} M$
 at 35° .

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