Oxidation of some primary alcohols by N-bromoacetamide in acidic media by using chloro complex of Rh (III) as catalyst.

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Abstract

Kinetics of oxidation of two of primary alcohols by N-bromoacetamide (NBA) has been studied in acidic medium using chloro complex of Rh(III) as homogeneous catalyst. The reaction shows first order kinetics with respect to NBA and alcohols concentrations, The reaction also shows first order kinetics with respect to Rh(III) concentration and fractional order with respect to $[H^+]$. Invers fractional order with respect to [Acetamide] was obtained in Rh(III) catalysed oxidation of alcohols. Variation of ionic strength, dielectric constant and chloride ion of the medium has no effect on the rate of oxidation. H_2OBr^+ and $[Rh(H_2O) Cl_5]^2$ have been suggested to be the reactive species of NBA and Rh(III)chloride in acid medium. The rates were determined at four different temperatures and the activation parameters were evaluated. A mechanism involving formation of hypobromite ester in the rate determining step has been proposed. The main oxidation products of the reactions have been identified as aldehyde.

Introduction

The chemistry of organic halo-amines has received considerable attention as they are sources of haloniumcations, hypohalite species and N-anions which act both as bases and nucleophiles. The important members of this group are chloramine-T, chloramine-b, bromoamine-b, N-chorosuccinimide, N-bromosuccinimide [1-3]. N-bromoacetamide (NBA) has been used to be a better oxidizing and hydrogenating agent than chloro compound[4-7]. Rhodium complexes are reported as versatile catalyst , which can be used for several oxidation reaction [8-10]. The uses of chlorocomplex of Rh (III) as homogeneous catalyst has been reported for the oxidation of reducing sugars by NBA [11-13] in acid medium. The aim of present study is to investigate the reaction bath for the kinetics of oxidation primary alcohol viz, methanol and ethanol by NBA using chlorocomplex of Rh (III) as homogeneous catalyst in acid medium. It also aims to understand if the role of alcohol molecule in the presence of Rh (III) chloride as catalyst and as oxidant in acidic mediumis similar to the reported role of amino-acid oxidation in presence of Ru (III)[14].

Experimental Methods

NBA was prepared by the reported method[15] and its purity checked by iodometric titration of active bromine, the alcohols were purified by magnesium alkoxide method [16.] The solution of Rh (III) chloride was prepared by dissolving the sample in hydrochloric acid of 0.5M ionic strength. A standard solution of mercuric acetate was acidified with acetic acid. All other standardized solution of KCl, $NaClO_4$ and acetamide was prepared with doubly distilled water. Ethanol (0.01 mol) and NBA (0.01 mol) made up to 50 ml with perchloric acid (0.25M) were kept in the dark for 12 hr until completion of oxidation, then the solution was treated with an excess of (200 ml) of a freshly filtered saturated solution of 2,4-dinitrophenyl hydrazine in 2M hydrochloric acid. The precipitated 2,4-dinitrophenyl hydrazone was collected and filtration. Mixture melting point and mixture TLC of 2,4-dinitrophenyl hydrazone confirmed that the product was acetaldehyde. The stoichiometry was ascertained by treating ethanol (0.01 mol) with NBA (0.05 mol) in presence of perchloric acid (0.25M) and estimation of consumed NBA indicated that one mole of NBA was consumed to oxidize one mole of ethanol, the following stoichiometric equation was suggested

$$CH_3CH_2OH + CH_3CONHBr \leftrightarrow CH_3CHO + CH_3CONH_2 + Br^- + H^+$$

Results and Discussion

Kinetics of oxidation of methanol and ethanol in presence of chloro complex of Rh (III) have been studied at 35^oC. The reactions were followed up to 70% reaction, the reactions were carried out under pseudo-first order conditions by keeping an exess 10 times greater of the alcohol over NBA. The reaction was investigated at several initial concentrations of reactants. The pseudo first order rate constant, k_1 was computed from plots of log [NBA] against time. A slight induction period was noticed, but it disappeared at higher concentration. The pseudo first order rate constants are constant for varying the concentration of NBA and are given in **Table 1.** Value of rate constant increased when the concentration of alcohol increased, **Table 2.**

Table 1: Effect of [NBA] on the rate constant of oxidation of methanol and ethanol by NBA, [Meth.]=[Etha.]=0.8M, $[H^+]$= 0.5M, Rh(III) = 1.42×10^{-9}M, Temp.= $308K^o$

10^3 [NBA]/molL^{-1}	1.0	3.0	5
$10^2 k_1$/min^{-1} (methanol)	1.205	1.25	1.22
$10^2 k_1$/min^{-1} (Ethanol)	11.27	11.32	10.91

Table 2: Effect of [alcohols] on the rate constant of oxidation of methanol and ethanol by NBA, [NBA]= 3x10^{-3}, [H$^+$]= 0.5M, Rh(III) = 1.42x10^{-9}M, Temp.= 308K^o

[Methanol]= [ethanol]/M	0.8	1.2	1.6	2.0
10^2 k_1/min^{-1} (methanol)	1.25	1.37	1.44	1.49
10^2 k_1/min^{-1} (Ethanol)	11.32	18.71	25.09	31.58

Plots of (1/k) vs (1/substrate) are linear with intercept indicating the presence of an intermediate in appreciable concentration in the oxidation of alcohol by NBA, (**Figure 1**).
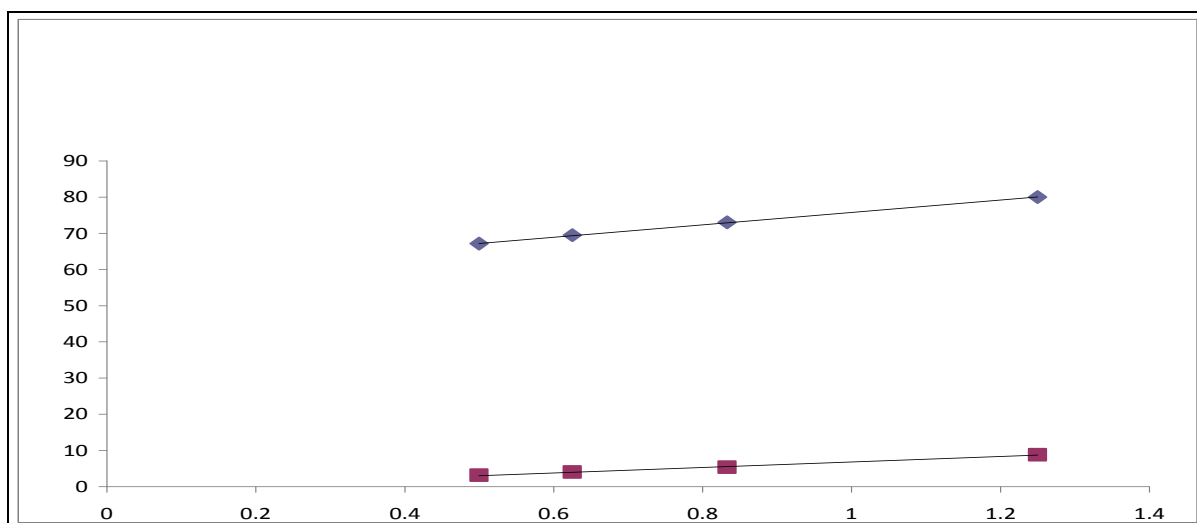

Fig. 1: shows the kinetic data for oxidation of alcohols by NBA at 308K, [H+]= 0.5M, Rh(III) 1.5x10^{-9}, [NBA]= 3x10^{-3}M

Variation in ionic strength and dielectric constant of the medium did not influence the oxidation rates. Various activation parameter have been calculated for the first order rate constants of the oxidation of alcohols by NBA at different four temperatures (Methanol, ΔH=9.846 kJ/mol, ΔS=-122.26J/mol, ΔG=47.5kJ/mol and ethanol, ΔH =7.676kJ/mol, ΔS=-185.119kJ/mol, ΔG=64.69kJ/mol Addition of acetamide decreases the rate of oxidation (**Table 3** and **Figure 2**).

Table 3: Effect of [acetamide] on the rate constant of oxidation of methanol and ethanol by NBA, [NBA]= 3x10^{-3}, [H$^+$]= 0.5M, Rh(III) = 1.42x10^{-9}M, Temp.= 308K^o
[Meth.]=[Etha.] = 0.8M

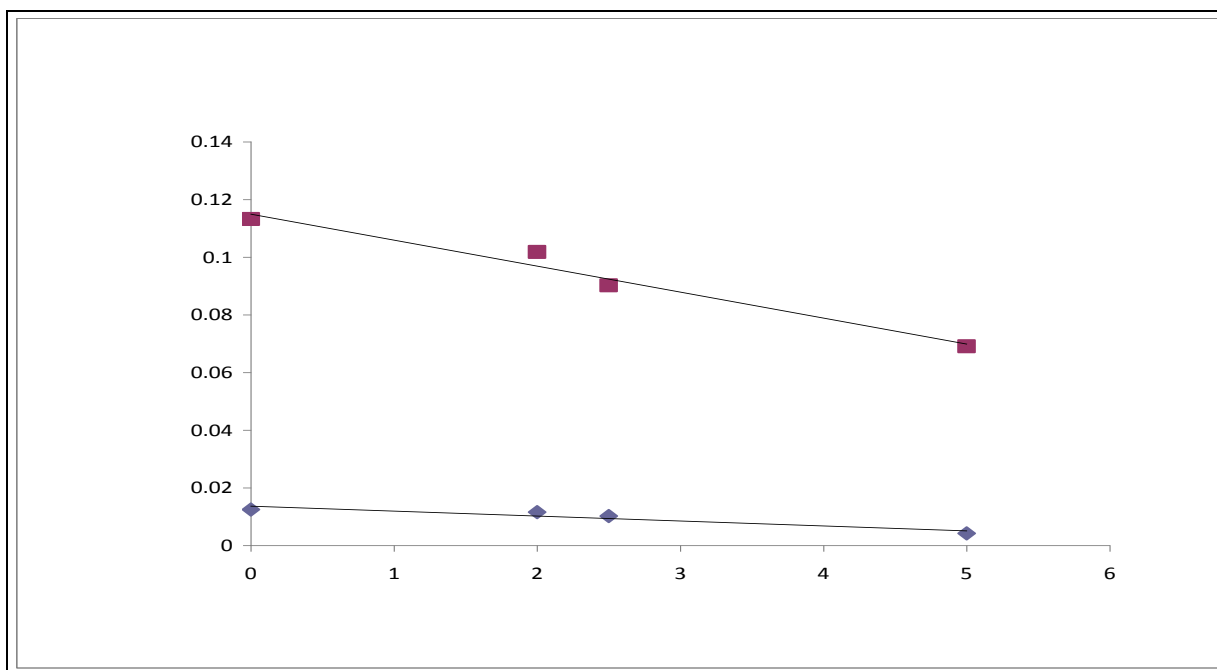| 10^3[Acetamide]/molL^{-1}	0.0	2.0	2.5	5.0
10^2 k_1/min^{-1} (methanol)	1.25	1.16	1.02	0.42
10^2 k_1/min^{-1} (Ethanol)	11.32	10.18	9.02	6.91

Fig. 2: Shows the effect of added acetamide on the rate of oxidation of alcohols by NBA at 308K, [NBA]=3x01-3 M ,[Rh(III)]=1.52x10-9 M, [H+]=0.5M, [alcohols]=0.8M

This retarding effect suggests that the pre-equilibrium step involves a process in which acetamide is one of the product[16].In the kinetic studies of chloro complexes of Rhodium as hydrogenation catalysts, the anionic complexes have been reported[17]such as $[RhCl_6]^{-3}$, $[Rh(H_2O)Cl_5]^{-2}$ and$[Rh(H_2O)_2Cl_4]^{-}$ activate molecular hydrogen for reduction of ferric ion in aqueous acid solution. Harrod and Helpern[18] have carried out studies with $RhCl_3$ in 3-5M HCl solutions and suggested that $[RhCl_6]^{-3}$ was the predominant species in solution. In the oxidation of phenyl acetylene, the authors have assumed $[Rh(H_2O)_3Cl_3]$as the reactive species of Rh(III)chloride in acidic medium.

In the this study the oxidation of alcohols by NBA in acidic medium Rh(III)chloride has been used as homogeneous catalyst and prepared in 3M HCl, and in the kinetic run Rhodium (III) chloride was used in the order of 10^{-9}, from the literature reported earlier it can be concluded that the original solution of Rhodium(III) chloride prepared in 3M HCl will contain the lone species $[Rh(H_2O) Cl_5]^{-2}$ .Considering the condition under which the original solution of Rh(III) chloride as well as very dilute solution of Rhodium (III) chloride used in various kinetic runs were prepared, it can be concluded that the lone species $[Rh(H_2O) Cl_5]^{-2}$, is the reactive species of Rhodium (III) chloride in the oxidation of alcohols by NBA in acidic

medium. Support to this assumption can be given by nil effect of [Cl⁻] on the rate of oxidation. First order kinetics with respect to [Rh (III)] is evident from the observed values of first order rate constant which show increase when the concentration of [Rh (III)] is increased (**Table 4, Figure 3**).

Table 4: Effect of [Rh(III)] on the rate constant of oxidation of methanol and ethanol by NBA, [NBA]= $3x10^{-3}$, [H⁺]= 0.5M, , Temp.= $308K^{o}$[Meth.]=[Etha.] = 0.8M

10^{9}[Rh(III)/molL^{-1}	1.52	3.0	5.0	7.0
10^{2} k_1/min^{-1} (methanol)	1.25	1.292	1.324	1.395
10^{2} k_1/min^{-1} (Ethanol)	11.32	17.01	22.03	28.00

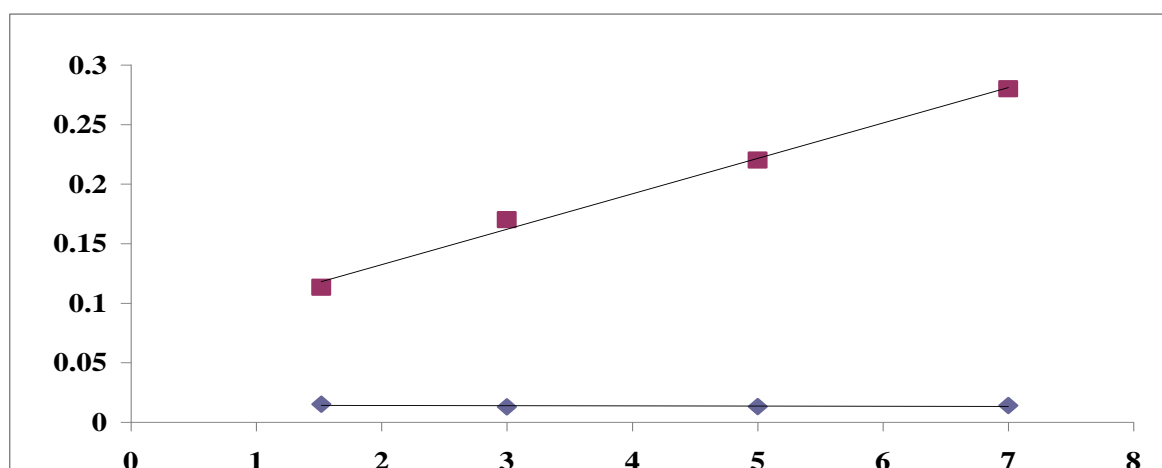**Fig. 3: Shows the effect of increasing the concentration of Rh(III) on the rate constant for the oxidation reaction , [H+]=0.5M, [alcohole]=0.8M, [NBA]=3x10-3 M, k1/min-1**

The observed effect of [H⁺] on the rate of oxidation may well be due to protonation of HOBr to give a cationic bromine species which is in agreement with literature[19], since an increases in acidity results an increase in the rate of the reaction (**Table 5 and Figure 4**), so it is likely that in the absence of mineral acid, the oxidation species will be the un protonated HOBr.

Table 5. Effect of [H⁺] on the rate constant of oxidation of methanol and ethanol by NBA, [NBA]= $3x10^{-3}$, [Rh(III)= $1.52x10^{-9}$M, Temp.= $308K^{o}$[Meth.]=[Etha.] = 0.8M

[H⁺]/molL^{-1}	0.1	0.3	0.5	0.7
10^{2} k_1/min^{-1} (Methanol)	0.79	1.01	1.25	1.47
10^{2} k_1/min^{-1} (Ethanol)	8.6	9.7	11.32	13.51

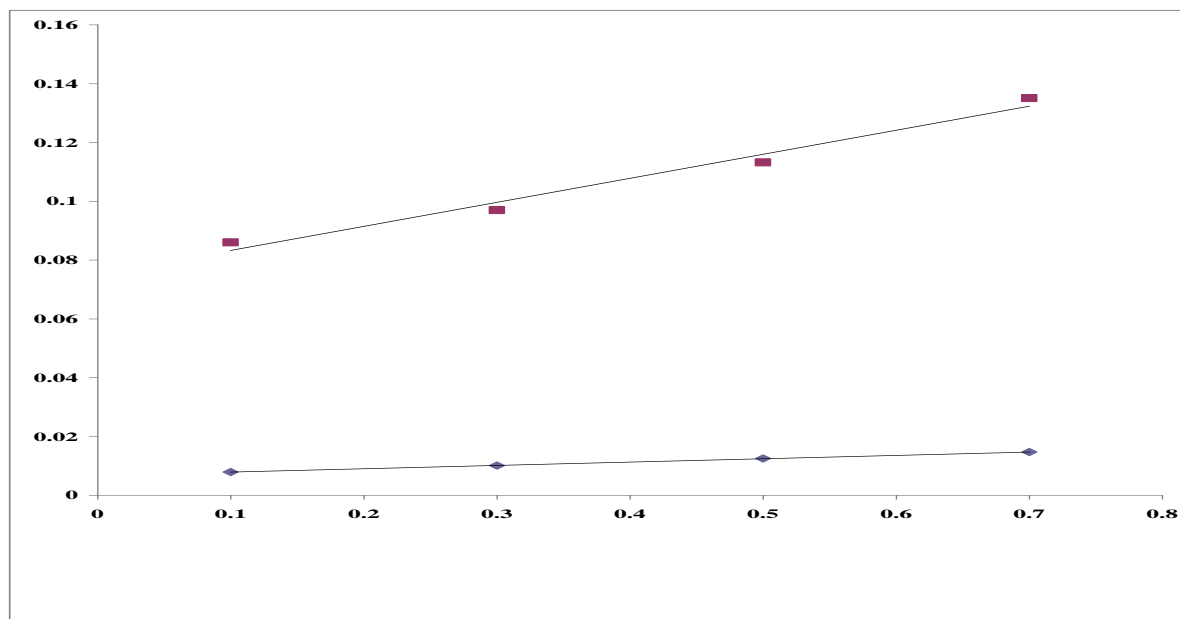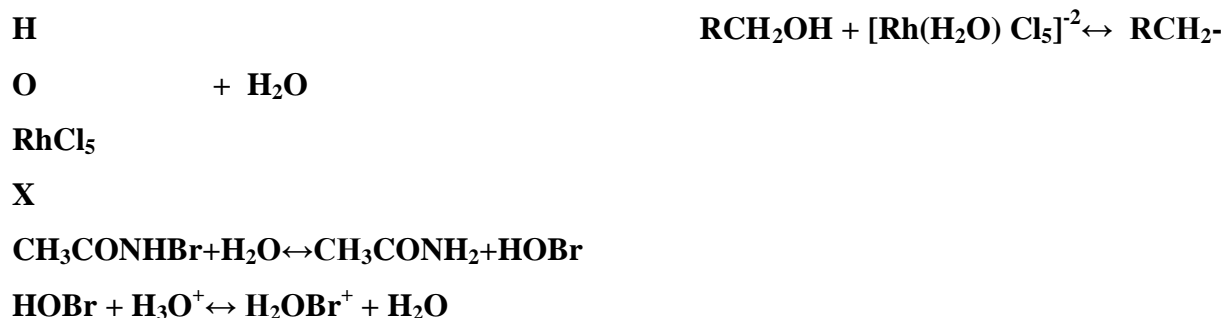**Fig. 4: Shows the effect of increasing the concentration of acid on the rate constant of the oxidation reaction, [NBA]=3x10-3 M, [Rh(III)]=1.5x10-9 M [alcohols]=0.8M k_1/min^{-1}**

The observed kinetic data show that addition of reaction product [Acetamide] to the reaction gives inverse effect on the rate of oxidation of alcohols (**Table 3 and Figure 2**). This is another indication of possibility of species HOBr to be protonated in present investigation. Absence of a primary kinetic isotope effect for the alcohol-NBS reaction [20], suggest that the C-H bond is not cleaved in the rate-determining step, this suggest that O-H bond rupture is involved in the rate determining step. Therefore it is proposed that the rate determining step involves formation of a hypobromite ester which then decompose to the aldehyde in a fast step. The hypohalite esters are known to decompose to carbonyl compounds (**Scheme 1**). The UV-Vis spectra of NBA and Rh(III) chloride or alcohols causes an increase in the absorbance, this confirm the existence of complex or complexes between various reactive species of the reactants have been investigated.

H $RCH_2OH + [Rh(H_2O) Cl_5]^{-2} \leftrightarrow RCH_2$-

O $+$ **H$_2$O**

RhCl$_5$

X

$CH_3CONHBr + H_2O \leftrightarrow CH_3CONH_2 + HOBr$

$HOBr + H_3O^+ \leftrightarrow H_2OBr^+ + H_2O$

H $H_2OBr^+ + RCH_2\text{-}O$

$\rightarrow RCH_2OBr + [RhH_2OCl_5]^{-2}$ **slow and R.D.S**

$RhCl_5$

$RCH_2OBr \rightarrow RCHO + H^+ + Br^-$ **fast**   **(Scheme 1)**

Numerate rate constant for the steps above from k_1 to k_7, The derived rate law can be followed:

$k_1 [RCH_2OH][Rh(H_2O) Cl_5]^{-2} = k_2 X$

$k_3[CH_3CONHBr][H_2O] - k_4[CH_3CONH_2][HOBr] = 0$

$k_5[HOBr] [H^+] - k_6[H_2OBr^+] - k_7 [X][H_2OBr^+] = 0$

Rate or reaction in slow step is

$R = k_7 [X][H_2OBr^+]$

Then R will be after substitution for $[H_2OBr^+]$ and [HOBr] is

$R = k_3k_5k_7 [CH_3CONHBr][H^+][X]/((k_6 + k_7 [X](k_4[CH_3CONH_2]))$

Substitute for[X]

$R = k_1k_3k_5k_7 [CH_3CONHBr][H^+] [RCH_2OH] [Rh(H_2O) Cl_5]^{-2}/k_2((k_6 + k_7 [X](k_4[CH_3CONH_2]))$

Consider[H^+] and] $[Rh(H_2O) Cl_5]^{-2}$ as catalysts the rate law will be

$R = k_1k_3k_5k_7 [CH_3CONHBr] [RCH_2OH] /k_2((k_6 + k_7 [X](k_4[CH_3CONH_2]))$

The rate law obey the experimental data obtained in this research in which the rate increases with increasing concentration of NBA, alcohols, catalyst and acidity and decreases with increasing concentration of Acetamide (reaction product)

In comparative studies, The results of present study were compared with the results reported Ru(III) and Pd(II) catalysed the oxidation of aminoacids in alkaline Medium [21-22]. The observed first order kinetics with respect to [alcohols] in Rh(III) catalysed oxidation is quite similar to the reported order in Ru(III) catalysed oxidation [21], but on other hand it is contrary to the zero order kinetics in Pd(II) catalysed oxidation. The involvement of formation reactive species of alcohols before the rate determining step in the present study and also in the reported Ru(III) catalysed oxidation is contrary to its participation after the rate determining step in basis of effect of $[H^+]$ on the rate of oxidation it was found that the fractional order in $[H^+]$ is entirely similar to the reported fractional positive order in $[OH^-]$ in

Ru(III)and Pd(II) catalysed oxidation. Kinetics and spectroscopicdata show that [Rh(H$_2$O) Cl$_5$]$^{-2}$ is the reactive species of Rh(III)chloride in our study whereas [Ru(H$_2$O) Cl$_5$]$^{-2}$ and[Pd(OH)Cl]were found as the reactive speciesof Ru(III) chloride and Pd(II)chloride in the earlier reported studies [16,21].

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