Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry
2017, 6 (5): 923-933
(International Peer Reviewed Journal)

Kinetic Studies of Rh (III)-Catalysed Oxidation of Mannose by N-Bromoacetamide in Alkaline Medium

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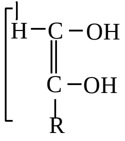
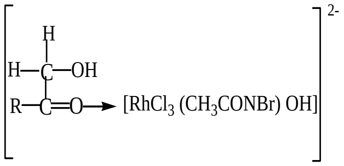
Accepted on 7th September 2017, Published online on 27th September 2017

ABSTRACT

The kinetics of oxidation of mannose by N-bromoacetamide (NBA) in alkaline medium using Rh (III) as homogeneous catalyst have been studied at 40^0*C. The reaction exhibits first order kinetics with respect to [NBA], [Mannose] and [Rh (III)]. The rate of reaction is fractional positive order with respect to* $[OH^-]$*. The reaction remains unaffected by the change in ionic strength,* $[Cl^-]$ *and dielectric constant of the medium.There are no effects of [NHA] and* $[Hg(OAc)_2]$ *on rate of reaction. Various activation parameters such as* E_a, $\Delta S^\#$, $\Delta H^\#$, $\Delta G^\#$ *and Arrhenius frequency factor (A) have been calculated for the reaction under investigation. The species* $[RhCl_3(H_2O)_2(OH)]^-$ *and* $[CH_3CONBr^-]$ *have been considered as the reactive species of Rh(III) chloride and NBA in alkaline medium respectively. On the basis of observed kinetic data, spectral information and activation parameters; a suitable mechanism for the oxidation of mannose has been proposed.*

Graphical Abstract

Kinetics of oxidation of mannose by N-bromoacetamide (NBA) in alkaline medium using Rh(III) as homogeneous catalyst have been studied at 40^0C. In the present study, the species $[RhCl_3(H_2O)_2(OH)]^-$ and $[CH_3CONBr^-]$ have been considered as the reactive species of Rh(III) chloride and NBA in alkaline medium for the oxidation of mannose and also it was observed that the positive entropy of activation which clearly supports the interaction between the species, $[RhCl_3(H_2O)(CH_3CONBr)OH]^{2-}$ and neutral form of sugar  , leading to the formation of most reactive activated complex(C_4),  , in the proposed reaction mechanism.

Keywords: Kinetics, N-bromoacetamide, Mannose, Rh(III), Alkaline medium.

INTRODUCTION

Carbohydrates are the most abundant class of organic compounds found in living organisms and a biologically important substance whose microbiological and physiological activities depend largely on their redox behaviour [1-2]. The literature revels that the oxidation of sugars has been carried out in acidic and alkaline medium by different oxidants using transition metal ions such as Ruthenium(III) [3], Manganese(II) [4], Osmium(VIII) [5], Palladium(II) [6], Iridium(III) [7], Lanthanum(III) [8] as homogeneous catalyst. Interest on the co-ordination chemistry of rhodium continues to be in accelerating pace due to interesting chemical reactivity such as antitumor activity, electronic structure, and catalytic functions of its complexes with potential industrial applications [9]. The complexes of rhodium are versatile catalysts, which can be used for several oxidation reactions by Cu(II) [10] and NBS [11]. There are many N-haloimides which have been used as analytical reagents. N- bromoacetamide is a brominating and oxidizing agent that is used as source for bromine in radical reactions and various electrophilic additions. Recently, N-halo compounds have extensively been used as oxidizing agents for the catalysed reaction [12-14]. In view of the biological importance of rhodium, NBA, mannose and also in view of the fact that no report is available on Rh(III) catalysed oxidation of mannose by NBA in alkaline medium, the present study has been undertaken.

The main objectives of the present study are to ascertain:

1. The oxidative behaviour of NBA in alkaline medium in the oxidation of mannose.
2. Role of reducing sugar as reductant in the presence of Rh(III) as catalyst in alkaline medium.
3. The reactive species of NBA, sugar and Rh(III) choride in alkaline medium.
4. The possibility of formation of complex or complexes during the course of reaction.
5. Activation parameters like E_a, $\Delta S^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$ and A are calculated for Rh(III)-catalysed oxidation of mannose by NBA in alkaline medium.
6. Catalytic potential of rhodium (III) in the oxidation of mannose by NBA.

MATERIALS AND METHODS

Chemicals and measurements: All the solutions were prepared in doubly distilled water. N-bromoacetamide (Sigma Chem.) solution was prepared a fresh daily by weighing and dissolving it in doubly distilled water. The solution was standardized iodometrically against standard sodium thiosulphate solution using starch as an indicator. Reducing substrate i.e. mannose (Loba Chem.) solution was prepared daily by weighing and dissolving it in doubly distilled water. Stock solution of Rh (III) chloride (Loba Chem.) was prepared by dissolving its sample in HCl of known strength. The concentration of Rh(III) chloride was 3.79×10^{-3} M. All other reagents, $Hg(OAc)_2$, $NaClO_4$, $HClO_4$, acetamide (NHA) and KCl were prepared from samples obtained from E. Merck and all of the standard solutions were prepared with double distilled water.

The reaction mixture was prepared in a black-coated conical flask (Jena) to prevent photochemical reaction. Each kinetic run was performed at constant temperature 40ºC. In a black coated conical flask all the reactants except reducing sugar were mixed in required quantity and hanged in thermostat bath. A measured amount of sugar solution, equilibrated at the same temperature, was rapidly added to the reaction mixture. The progress of the reaction was monitored by estimating the amount of remaining NBA at regular time intervals iodometrically.

Stoichiometry of Rh (III)-catalyzed oxidation of mannose by NBA: The stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBA over mannose at room temperature for 48 h. Under the condition of NBA >> mannose, the estimation of unconsumed NBA showed that the two mole of NBA was consumed to oxidize one mole of mannose. Accordingly, the following stoichiometric equation can be suggested as

$$\underset{\text{NBA}}{2CH_3CONHBr} + \underset{\text{Mannose}}{C_6H_{12}O_6} + 2NaOH \xrightarrow{Rh(III)} \underset{\text{NHA}}{2CH_3CONH_2} + \underset{\text{Sodium salt of arabinonic acid}}{C_5H_9O_6Na} + \underset{\text{Sodium salt of formic acid}}{HCOONa} + 2HBr$$

RESULTS AND DISCUSSION

The kinetics of oxidation of mannose by NBA have been investigated in the presence of alkaline solutions of Rh (III) chloride at different concentrations of each reactant. The initial rate i.e. (-dc/dt) of reaction in each kinetic run was calculated by the slope of the tangent drawn at fixed concentration of NBA. The pseudo first-order rate constant (k_1) was calculated as, k_1= (-dc/dt)/ [NBA]

A uniform first-order rate constant (k_1) value for NBA shows that order with respect to [NBA] is unity (Table-1). When the effect of [sugar] was studied on the rate of reaction at constant concentrations of all other reactants, first-order kinetics with respect to [Mannose] was observed throughout its variation (Table-1). There is a direct proportionality between k_1 and [Rh (III)], suggesting a first-order dependence of reactions on [Rh(III)] (Table-1). The reaction follows fractional positive order in [OH^-] (Table-1). Nil effects of the [Hg (II)], [NHA] or [Cl^-] on the rate of oxidation of mannose were noted. Similarly, dielectric constant and ionic strength of the medium do not influence the rate. The reaction has been studied at four different temperatures i.e. 35, 40, 45 and 50°C and observed k_1 values were utilized to calculate various activation parameters such as energy of activation (E_a), entropy of activation ($\Delta S^\#$), enthalpy of activation ($\Delta H^\#$), Gibbs free energy of activation ($\Delta G^\#$) and Arrhenius frequency factor(A) (Table -2).

Table 1: Calculated values of first order rate constants (k_1) and composite rate constants (k') for the variations of [NBA], [Mannose], [OH^-] and [Rh(III)] in the Rh(III)-catalysed oxidation of mannose at 40^0C

[NBA]×10^3 M	**[Mannose]×10^2M**	**[NaOH]×10^2 M**	**[Rh(III)]×10^9 M**	**k_1 × 10^4 (s^{-1})**	**k' × 10^{-8} (s^{-1})**
0.50	2.00	4.00	1.52	5.72	4.70
1.00	2.00	4.00	1.52	5.83	4.79
2.00	2.00	4.00	1.52	5.66	4.65
3.00	2.00	4.00	1.52	5.55	4.56
4.00	2.00	4.00	1.52	5.66	4.66
5.00	2.00	4.00	1.52	5.73	4.71
1.00	1.00	4.00	1.52	2.72	4.47
1.00	2.00	4.00	1.52	5.55	4.56
1.00	4.00	4.00	1.52	10.8	4.44
1.00	6.00	4.00	1.52	16.66	4.56
1.00	8.00	4.00	1.52	21.11	4.34
1.00	10.00	4.00	1.52	27.70	4.55
1.00	2.00	2.00	1.52	2.93	4.81
1.00	2.00	4.00	1.52	5.33	4.38
1.00	2.00	8.00	1.52	11.33	4.65
1.00	2.00	12.00	1.52	17.22	4.72
1.00	2.00	16.00	1.52	21.33	4.38
1.00	2.00	20.00	1.52	28.66	4.71

1.00	2.00	4.00	0.76	2.92	4.80
1.00	2.00	4.00	1.52	5.33	4.38
1.00	2.00	4.00	3.04	10.66	4.38
1.00	2.00	4.00	4.56	16.00	4.69
1.00	2.00	4.00	6.08	23.33	4.79
1.00	2.00	4.00	7.60	26.66	4.39

Reaction condition $[Cl^-] = 1.00 \times 10^{-5}$ M, $\mu = 5.00 \times 10^{-2}$ M.

Table 2: Thermodynamic activation parameters for Rh(III)-catalysed oxidation of mannose by NBA in alkaline medium at 40^0 C

Compound	Ea (kJ mol^{-1})	$k_r \times 10^8$ ($mol^{-3}L^3s^{-1}$)	$\Delta H^\#$ (kJ mol^{-1})	$\Delta G^\#$ (kJ mol^{-1})	A ($mol^{-3} L^3 s^{-1}$)
Mannose	76.18	5.75	73.56	24.32	4.60×10^{23}

Reactive species of N-Bromoacetamide in alkaline medium: It has been reported [15] that NBA exists in the following equilibria in alkaline medium:

$$\underset{NBA}{CH_3CONHBr} + OH^- \rightleftharpoons \underset{NBA^-}{CH_3CONBr^-} + H_2O \qquad (1)$$

$$CH_3CONHBr + OH^- \rightleftharpoons CH_3CONH_2 + OBr^- \qquad (2)$$

Or

$$CH_3CONHBr + H_2O \rightleftharpoons CH_3CONH_2 + HOBr \qquad (3)$$

$$HOBr + OH^- \rightleftharpoons H_2O + OBr^- \qquad (4)$$

It appears from the above two sets of equilibria that there can be four reactive species of NBA. These are NBA itself, NBA^-, OBr^- or HOBr. Hypobromous acid exists exclusively as hypobromite ion even at the lowest concentration of the alkali used [15]. Hence HOBr cannot play a dominant role in the reactions. In present study the effect of OH^- shows fractional positive order and nil effect of acetamide on the rate of reaction. Now the only choice is CH_3CONBr^- which can be taken as the reactive species of NBA in alkaline medium for the oxidation of mannose in presence of Rh (III)-catalysed.

Reactive species of Rh (III) chloride in alkaline medium: It is also reported [16] that on boiling aqueous solution of the trichloride, $[Rh(H_2O)_6]^{3+}$ is formed and with excess HCl, the rose pink hexachlororhodate ion $[RhCl_6]^{3-}$ is obtained . Rh(III) is reported [17] to form a variety of complexes such as $[Rh\ Cl]^{2+}$, $[RhCl]^+$, $RhCl_3$, $[RhCl_4]^-$, $[RhCl_4]^{2-}$ and $[RhCl_6]^{3-}$ in the presence of HCl. In view of the literature reported [18, 19], between these two species there are clearly several intermediates. The solution of Rh(III)chloride was prepared in 3M HCl solution and its concentration was determined as 3.79×10^{-3} M . This original solution was further diluted with the help of double distilled water and the concentration of the catalyst Rh(III)chloride in each kinetic run was fixed in the order of 10^{-9}. In view of the observed kinetic data and the reported literature, it is reasonable to assume that the starting species of Rh(III) chloride is $[RhCl_3(H_2O)_3]$. On the basis of observed kinetic order with respect to $[OH^-]$ and also on the basis of spectra observed for $[RhCl_3(H_2O)_3]$ solution alone and for $[RhCl_3(H_2O)_3]$ solutions with two different concentrations of OH− where an increase in absorbance from 0.21 to 0.27 and 0.41(Fig-1(2),(3) and (4)) and was noted, it can be assumed that the following equilibrium exists in the reaction under investigation.

$$Rh\ Cl_3(H_2O)_3 + OH^- \rightleftharpoons [RhCl_3(H_2O)_2(OH)]^- + H_2O$$

Out of the two species $[RhCl_3(H_2O)_3]$ and $[RhCl_3(H_2O)_2(OH)]^-$, the species $[RhCl_3(H_2O)_2(OH)]^-$ can be considered as the reactive species of Rh(III) chloride in alkaline medium because only with this reactive species fractional positive order in $[OH^-]$ can very well be explained and a suitable rate law can be derived.

Reactive form of sugar in alkaline medium: Reported [20-22] are available in the presence of alkali reducing sugars undergo a tautomeric change resulting in the formation of an enediol anion, $[RC(OH)CHO^-]$ and an enediol, [RC(OH)CHOH]. Out of these two which one is the reactive species of reducing sugar in alkaline medium it has been decided on the basis of effect of $[OH^-]$ on the rate of oxidation. In the case of kinetic order being fractional positive for the variation of OH^- ions, it can be assumed that it is the enediol form which is actually taking part in the reaction.

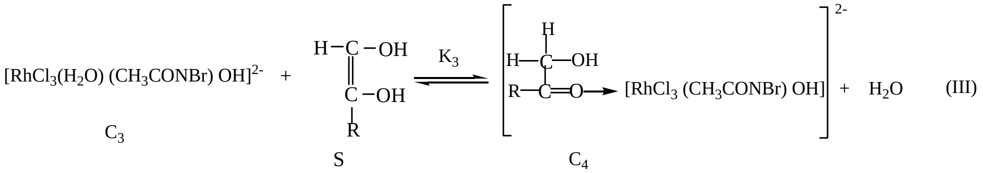
Spectral information for the verification of complexes: On the basis of observed kinetic data and spectral information, efforts were made to ascertain possible formation of complexes between different reactive species during the course of reaction with the help of VARIAN CARY WIN UV–VIS spectrophotometer. The spectra of various solutions of NBA, OH^-, Rh(III) and sugar were collected. It was found that when spectra for the solutions of Rh(III) chloride alone and for the solutions of Rh(III) chloride with two different concentration of OH^-, there is substantial increase in absorbance from 0.21 to 0.27 and 0.41 with the increase in $[OH^-]$ (Fig-1(2),(3) and(4)) at wavelength 221nm which indicates the existence of following equilibrium in the reaction under investigation.

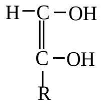
$$\underset{C_1}{[RhCl_3(H_2O)_3]} + [OH]^- \overset{K_1}{\rightleftharpoons} \underset{C_2}{[RhCl_3(H_2O)_2OH]^-} + H_2O \qquad (I)$$

When spectra for the solutions of Rh(III) chloride and OH^- with varying concentration of NBA were collected (Fig-1(4),(5) and(6)).It was found that there was an increase in absorbance from 0.41 to 0.45 and 0.52 at wavelength 221nm. This increase in absorbance with the increase in [NBA] clearly indicates that there is a formation of complex species, $[RhCl_3(H_2O)\ OBr\ OH]^{2-}$, according to the following equilibrium

$$\underset{C_2}{[RhCl_3(H_2O)_2OH]^-} + \underset{(NBA^-)}{CH_3CONBr^-} \overset{K_2}{\rightleftharpoons} \underset{C_3}{[RhCl_3(H_2O)\ (CH_3CONBr)\ OH]^{2-}} + H_2O \qquad (II)$$

Further when five different concentrations of sugar were added to the solution of Rh(III), OH^- and NBA, it was found that there is an increase in absorbance from 0.52 to 0.57, 0.69, 0.71, 0.77 and 0.98 with a slight at shift in λ_{max} value towards longer wavelength from 222 to 223 nm. (Fig-1(6)-(11), this increase in absorbance with the increase in sugar concentration might be assumed as due to more and more formation of the complex formed between C_3 and S.



When a Job's plot (1/ΔA vs. 1/ [S]) was made, a straight line with positive intercept on y-axis was obtained (Fig-2) which clearly supports the formation of 1:1 complex between C_3 and  .

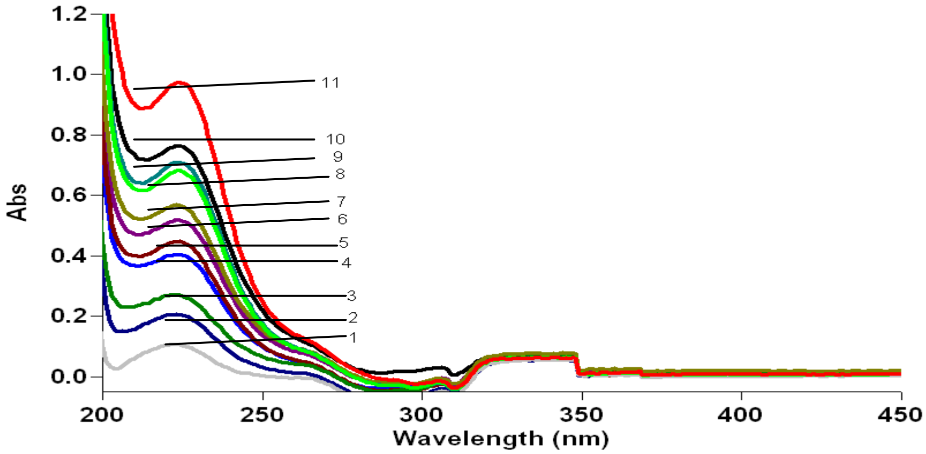


Figure 1: Spectra of various solutions containing Rh(III), OH^-, NBA and Mannose at room temperature

(1) [Rh(III)] = 3.80×10^{-6} M,

(2) [Rh(III)] = 15.20×10^{-6} M,

(3) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 1.00×10^{-3} M,

(4) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,

(5) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,
[NBA] = 1.00×10^{-4} M,

(6) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,
[NBA] = 4.00×10^{-4} M,

(7) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,
[NBA] = 4.00×10^{-4} M,
[Mannose] = 1.00×10^{-2} M,

(8) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,
[NBA] = 4.00×10^{-4} M,
[Mannose] = 2.00×10^{-2} M,

(9) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,
[NBA] = 4.00×10^{-4} M,
[Mannose] = 4.00×10^{-2} M,

(10) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,
[NBA] = 4.00×10^{-4} M,
[Mannose] = 6.00×10^{-2} M,

(11) [Rh(III)] = 15.20×10^{-6} M,
[OH^-] = 4.00×10^{-3} M,
[NBA] = 4.00×10^{-4} M,
[Mannose] = 8.00×10^{-2} M.

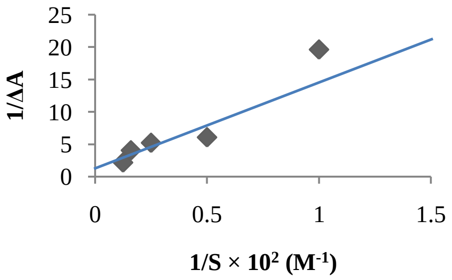
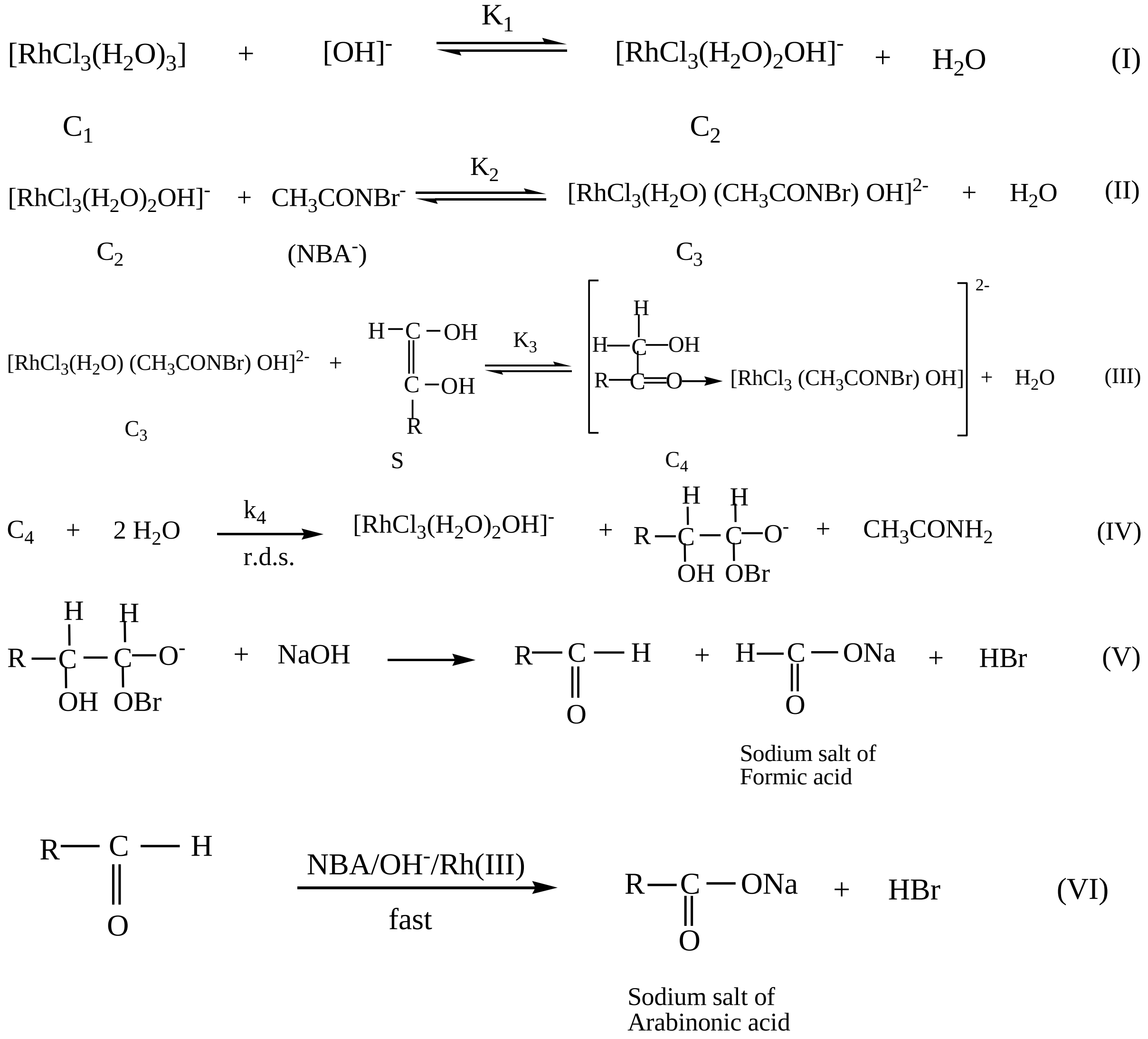


Figure 2: Plot between 1/ΔA and 1/ [S] at 40 ^{0}C

Mechanism and the derivation of rate law: On the basis of observed kinetic order with respect to each reactants involved in the reaction, spectral information collected for the probable formation of complex or complexes in the reaction and taking into consideration the observed value of activation parameters, a reaction Scheme 1 for the reaction under investigation can be proposed in following way.



Scheme 1

On the basis of reaction scheme-1and also on the basis of stoichiometric equation given for the oxidation of mannose, the rate in terms of decrease in concentration of NBA can be expressed as

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = 2\,k_4\,[C_4] \qquad (1)$$

On applying the law of chemical equilibrium to steps(I)-(IV) and taking total concentration of Rh(III) chloride at any moment in the reaction as $[\text{Rh(III)}]_T = [C_1] + [C_2]$, the rate in terms of disappearance of [NBA] can be shown as

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{2\,k_4\,K_1\;K_2\;K_3\,[CH_3CONBr^-]\,[S]\,[\text{Rh(III)}]_T\,[OH^-]}{1 + K_1[OH^-]} \qquad (2)$$

Where ‘S’ stands for D(+)Mannose ($C_6H_{12}O_5$),Eq. (2) is the final rate law which clearly supports the first order kinetics with respect to [NBA], [S] [Rh(III)] and fractional positive order with respect to$[OH^-]$. Under our experimental conditions, the inequality 1>> K_1 $[OH^-]$ can be assumed as valid one and Eq.(2) will be reduced to Eq.(3)

$$\text{rate} \quad = \quad -\frac{d[NBA]}{dt} \quad = \quad 2\ k_4 K_1\ K_2\ K_3 [CH_3CONBr^-] [S] [Rh(III)]_T [OH^-] \qquad (3)$$

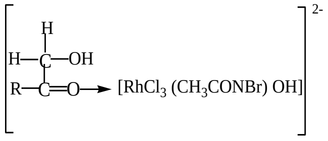
$$\text{rate} \quad = \quad -\frac{d[NBA]}{dt} \quad = \quad k' [CH_3CONBr^-] [S] [Rh(III)]_T [OH^-] \qquad (4)$$

Where k' is the composite rate constant = $2k_4K_1K_2K_3$

Equation (4) is then the rate law applicable for the conditions used for the determination of kinetic order in this study. On the other hand, when K_1 $[OH^-]$>>1 is assumed as valid one, Eq. (2) reduces to Eq.(5).

$$\text{rate} \quad = \quad -\frac{d[NBA]}{dt} \quad = \quad 2\ k_4\ \ K_2\ K_3 [CH_3CONBr^-] [S] [Rh(III)]_T \qquad (5)$$

This rate law will be valid at high concentration of OH^-. Since the present study was not made under such condition, the limiting rate law (5) is not observed. The values of the composite rate constant (k') were calculated from Eq.4 for the variations of [NBA], [Sugar], [Rh (III)] and [NaOH] in the Rh(III)-catalyzed oxidation of mannose (Table-1).

It is well know [23] that when reactions occur between ions of unlike sign, there is generally an entropy increase in going from reactants to the activated complex, whereas reaction between ions of like sign, gives an entropy decrease. It is also reported [24] that when reaction occurs between an ion and a neutral molecule, the transition state becomes less polar than the initial state, because in the transition state the same charge is dispersed over a greater volume. In the present study of oxidation of mannose by alkaline solution of NBA in presence of Rh (III) chloride as homogeneous catalyst, the positive entropy of activation was observed which clearly supports the interaction between the species, $[RhCl_3(H_2O)(CH_3CONBr)OH]^{2-}$ and neutral form of sugar, leading to the formation of most reactive activated complex(C_4), 

, in the proposed reaction mechanism.

Comparative studies: The results of the present study of the Rh(III)-catalyzed oxidation of mannose by NBA can be compared with the results for the Ir(III)-catalyzed [25] and Pd(II)-catalyzed [26] oxidations of reducing sugars by NBA in acidic medium. The first-order kinetics observed in [NBA] in the present study are different from the other two studies where first- to zero-order kinetics with respect to NBA were observed. The reactive species CH_3CONBr^- of NBA suggested by our kinetic data and spectroscopic evidence is different from the reactive species HOBr reported for the Ir (III) [25] and Pd (II) [26]-catalyzed oxidations. First order kinetics with respect to [sugar] on one hand shows similarity with the reported Pd(II) [26]-catalyzed oxidation; and on the other hand, differs from the Ir(III) [25]-catalyzed oxidation where the order with respect to sugar was found to be zero. The fractional positive order in $[OH^-]$ in the present study differs from the fractional negative order in $[H^+]$ in the Ir(III)[25] and Pd(II) [26]-catalyzed oxidations. The order with respect to Hg (II) in the Ir(III)[25]-catalyzed oxidation varies from 2 to 1; and in the Pd(II) [26]-catalyzed oxidation, it is fractional and positive. Nil effect of [Hg (II)] on the rate of oxidation distinguishes the present study from the other two studies. The composition proposed for the activated complex in the Ir(III) [25] and Pd(II) [26] catalyzed oxidations is different from the activated complex, $[RhCl_3(CH_3CONBr)(OH)S]^-$ assumed for the Rh(III)-catalyzed oxidation of mannose. From these distinguishing features, it is clear that the differences in behaviour of the three transition metal catalysts are due to variations in their catalytic functions and coordination chemistry.

CONCLUSIONS

On the basis of the observed kinetic data and spectral information, the following conclusions for the oxidation of mannose by NBA using chloro complex of Rh (III) as catalyst in alkaline medium were derived

(1) The main reactive species of NBA is CH_3CONBr^- in alkaline medium in the present investigation

(2) $[Rh\,Cl_3(H_2O)_2(OH)]^-$ is the reactive species of Rh (III) chloride in alkaline medium.

(3) There is formation of a most reactive activated complex, $[Rh\,Cl_3\,(H_2O)(CH_3CONBr)OH]^{2-}$, between reactive species of Rh(III)chloride and reactive species of NBA in alkaline medium.

(4) In step (III), the interaction between a charged species, $[Rh\,Cl_3(H_2O)(CH_3CONBr)OH]^{2-}$ and a enediol form of sugar molecule is well supported by the observed positive entropy of activation.

(5) The reaction rate is unaffected by the change in the concentration of [NHA], [KCl], μ and $[Hg\,(OAc)_2]$.

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