

Mechanistic studies of oxidation of maltose and lactose by $[\text{H}_2\text{OBr}]^+$ in presence of chloro-complex of Rh(III) as homogeneous catalyst

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Abstract

Kinetic studies in homogeneously Rh(III)-catalyzed oxidation of reducing sugars, i.e. maltose and lactose, by *N*-bromoacetamide (NBA) in the presence of perchloric acid have been made at 40 °C using mercuric acetate as Br^- ion scavenger. The results obtained for the oxidation of both reducing sugars show first-order dependence of the reactions on NBA at its low concentrations, which shifts towards zero-order at its higher concentrations. First-order kinetics in $[\text{Rh(III)}]$ and zero-order kinetics in $[\text{reducing sugar}]$ were observed. Positive effect of $[\text{Cl}^-]$ was observed in the oxidation of both maltose and lactose. Order of reaction was found to be one and half (1.5) throughout the variation of $[\text{H}^+]$ in the oxidation of both maltose and lactose. An increase in the rate of reaction with the decrease in $[\text{Hg}(\text{OAc})_2]$ and $[\text{NHA}]$ was observed for both the redox systems. The rate of oxidation is unaffected by the change in ionic strength (μ) of the medium. The main oxidation products of the reactions were identified as formic acid and arabinonic acid in the case of maltose and formic acid, arabinonic acid and lyxonic acid in the case of lactose. A common mechanism for the oxidation of both maltose and lactose, showing the formation of most reactive activated complex, $[\text{RhCl}_4(\text{H}_3\text{O})\text{H}_2\text{OBr}]^+$, and an unreactive complex, $[\text{RhCl}_4(\text{H}_2\text{O})(\text{H}_2\text{OBrHg})]^{2+}$, has been proposed. Various activation parameters have also been calculated and on the basis of these parameters, a suitable explanation for the reaction mechanism has been given.

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1. Introduction

Transition metal catalyzed reactions have created great interest [1] due to their involvement in many important industrial processes, such as hydrogenation, carbonylation reactions and low-pressure polymerization of ethylene and propene. Rhodium, which belongs to the group VIII, forms variety of complexes with different oxidation states ranging from +1 to +6 in which +3 oxidation state of rhodium is more stable than other oxidation states of the metal. It is reported [2] that the interest on the co-ordination chemistry of rhodium continues to be in accelerating pace due to

interesting chemical reactivity, antitumor activity, electronic structure and catalytic functions of its complexes with potential industrial applications. The octahedral rhodium complex, *cis*-dichloro bis(1,10 phenanthroline)rhodium(III) chloride (BISPHEM), is known [3] to form covalent linkages with DNA involving the attachment of the metal to a base. Catalysis by rhodium is so efficient that it has significantly displaced the previous technology based on less expensive cobalt catalysts. Antitumor activity [4] of cisplatin, *cis*[Pt(NH₃)₂Cl₂], was discovered by Rosenberg et al. and introduced an interest in the study of biological properties of transition metal complexes. Rhodium(III) forms complexes with nitrogen donor ligands viz. ethylene diamine, pyridine, 2-2' bipyridine, 1,10-phenanthroline, etc. which are reported [5] to have antibacterial activity. Rhodium(III) also forms [6] a variety of complexes such as $[\text{RhCl}]^{2+}$, $[\text{RhCl}_2]^+$, RhCl_3 , $[\text{RhCl}_4]^{1-}$, $[\text{RhCl}_5]^{2-}$ and

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$[\text{RhCl}_6]^{3-}$ when concentration of HCl was varied from 0.010 M to 2.00 M.

Carbohydrates are the most abundant class of organic compounds found in living organisms. Lactose, a disaccharide of galactose and glucose, often found in milk. Maltose is a dimer of glucose and obtained by careful acid hydrolysis of starch. Various oxidation products of the redox reactions having reducing sugars as reductant are reported to have industrial and biological significance. One of the products, formic acid, is used in the production of pharmaceuticals, dyes, flavors and perfume ingredients, textiles, leather and rubber. Vast literature [7] is available which illustrates the use of *N*-halo compounds in the reactions of biological and industrial interest viz: oxidation of psychotropic drugs, oxidative degradation of α -amino acids, in the study of peptide cleavage, in the fragmentation of high molecular weight peptides and proteins. Importance of *N*-halo compounds in the chemistry of many natural products is also reported. The kinetics of redox reactions have been investigated by using various homogeneous catalysts such as osmium(VIII) [8], ruthenium(III) [9], ruthenium(VIII) [10], palladium(II) [11] and iridium(III) [12,13] but there are very few reports available regarding studies in kinetics and mechanism of reactions using rhodium(III) chloride as homogeneous catalyst.

In view of the facts regarding chemical reactivity, anti-tumor activity, electronic structure and catalytic functions of Rh(III) complexes and also in view of biological and industrial importance of NBA, reducing sugars and their oxidation products, the present study, in the form of oxidation of maltose and lactose by acidic solution of NBA in presence of chloro-complex of Rh(III), has been undertaken. In this study our aim was to ascertain whether:

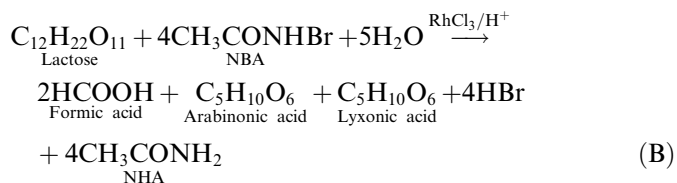
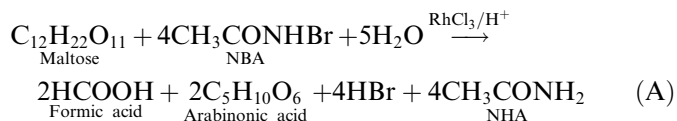
1. HOBr is the reactive species of NBA in acidic medium in the present investigation as is reported in Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation of reducing sugars by NBA in acidic medium or not?
2. There is formation of a complex between reactive species of Rh(III) chloride in acidic medium and a reducing sugar molecule before the rate determining step as is reported in Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation of reducing sugars or not?
3. There is a retarding effect of $[\text{H}^+]$ on rate of oxidation in the present investigation as is reported in Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation or not?
4. The Cl^- ions as one of the components of the reaction plays a significant role in deciding the reactive species of Rh(III) chloride as is reported in Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation or not?
5. The formation of most reactive activated complex takes place by the interaction of reactive species of Rh(III) chloride and reactive species of NBA in the present investigation contrary to the formation of most reactive activated complex in the reported Pd(II) [11]- or Ru(III) [25]-catalyzed oxidation involving interaction between reactive species of catalyst, reactive species of NBA, Hg(II) and a sugar molecule.
6. The role of Hg(II) is similar to its reported role as Br^- ion scavenger and as co-catalyst in Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation or not?
7. There is an enhancement in the catalytic activity of Rh(III) chloride in comparison to the catalytic activity of Pd(II) [11] or Ru(III) [25] in the oxidation of reducing sugars by NBA in acidic medium or not?

2. Experimental

The solution of rhodium(III) chloride (Loba) was prepared by dissolving 1 g of sample in hydrochloric acid (HCl) of known strength and the strength of rhodium(III) chloride ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) was found to be 3.80×10^{-3} M in which the strength of HCl was maintained at 3 M. The solution of *N*-bromoacetamide (Sigma chemicals) was prepared by dissolving weighed amount of NBA in double distilled water and stored in a black coated flask to prevent any photochemical deterioration. The strength of prepared NBA solution was checked for active bromine by standardizing it against sodium thiosulphate solution iodometrically. An aqueous solution of maltose and lactose was prepared a fresh everyday before use. An aqueous solution of perchloric acid, mercuric acetate, acetamide, sodium perchlorate, potassium chloride, sodium hydroxide, sodium thiosulphate and potassium iodide (all of E. Merck) were prepared in double distilled water. The reaction mixture containing the desired volume of all reactants i.e. NBA, HClO_4 , rhodium(III) chloride, mercuric acetate and water except reducing sugar was taken in blackened conical flask which kept in the thermostatic bath at constant temperature $40^\circ\text{C} \pm 0.1^\circ\text{C}$. The requisite volume of sugar solution was also placed within the same thermostatic bath at the same temperature. After 30 min, when the reaction mixture has attained the temperature of the bath, the required volume of sugar solution was sucked out by pipette and poured into reaction mixture to initiate the reaction. The actual progress of reaction was followed by estimating the amount of remaining NBA at regular time intervals iodometrically.

2.1. Stoichiometry of Rh(III)-catalyzed oxidation of maltose and lactose by NBA

Various sets of experiments were performed under the conditions $[\text{NBA}] \gg [\text{Sugar}]$ at room temperature for several days. The residual oxidant (NBA) was determined iodometrically. Estimation of residual [NBA] in different sets showed that 1 mol of each reducing sugar is oxidized by four mole of NBA. These information led us to propose the following stoichiometric equations for the oxidation of maltose and lactose.



Formic acid and arabinonic acid in the oxidation of maltose and formic acid, arabinonic acid and lyxonic acid in the oxidation of lactose were identified as the main oxidation products of the reactions by the help of equivalence, kinetics studies, spot tests and thin layer chromatography.

3. Results

Kinetics of oxidation of maltose and lactose by acidic solution of *N*-bromoacetamide in presence of Rh(III) chloride as homogeneous catalyst have been studied at constant temperature 40 °C. Order of reaction with respect to each reactant was determined by varying the concentrations of oxidant, reducing sugar, Rh(III) chloride, H⁺ ions, mercuric acetate, Cl⁻ ions and acetamide one by one in different sets keeping concentrations of all other reactants constant at constant temperature 40 °C. Considering NBA, reducing sugar, Rh(III) chloride and H⁺ ions as the main reactants of the reaction, the experimental rate law can be expressed as

$$\text{rate} = -\frac{d[\text{NBA}]}{dt}$$

$$= k[\text{NBA}]^{n_1} [\text{Reducing sugar}]^{n_2} [\text{Rh(III)}]^{n_3} [\text{H}^+]^{n_4} \quad (\text{i})$$

Since throughout the study, the concentrations of reducing sugar and H⁺ ions were taken in large excess of NBA and the role of Rh(III) in the reactions under investigation is as catalyst, hence under this condition Eq. (i) will take the shape of Eq. (ii)

$$\text{rate} = k_1[\text{NBA}]^{n_1} \quad (\text{ii})$$

where k_1 , the apparent rate constant = $k[\text{Reducing sugar}]^{n_2} [\text{Rh(III)}]^{n_3} [\text{H}^+]^{n_4}$

In the case of n_1 being equal to one, k_1 will be called as apparent first-order rate constant. In each kinetic run, the initial rate ($-dc/dt$) of the reaction was determined by the slope of the tangent drawn at a fixed concentration of NBA except for the NBA variation in which the slope of the tangent was drawn at fixed time. The first-order rate constant, k_1 , for the variations of all reactants were calculated as

$$k_1 = -\frac{(dc/dt)}{[\text{NBA}]^*}$$

where $[\text{NBA}]^*$ denotes the $[\text{NBA}]$ at which ($-dc/dt$) was determined.

For the determination of order of the reaction with respect to $[\text{NBA}]$, experiments with varying concentrations of NBA from $3.00 \times 10^{-4} \text{ mol dm}^{-3}$ to $28.00 \times 10^{-4} \text{ mol dm}^{-3}$ in the case of maltose and from $3.00 \times 10^{-4} \text{ mol dm}^{-3}$ to $27.00 \times 10^{-4} \text{ mol dm}^{-3}$ in the case of lactose have been performed at constant concentrations of all other reactants and at constant temperature 40 °C. The results thus obtained are presented in Fig. 1, which clearly shows that at low concentrations of NBA, there is direct proportionality between ($-dc/dt$) values and $[\text{NBA}]$, but at higher concentrations of NBA there is a deviation from the straight lines, indicating change in order from one to zero. After verifying the first-order dependence of the reactions at lower $[\text{NBA}]$ which tends to zero-order at its higher concentrations, efforts have been made to find out the order of reaction with respect to other reactants taking part in the reaction. Since throughout the study, the concentration of NBA has been fixed in its lower range, hence for the purpose of calculating pseudo first-order rate constant, k_1 , the order of reaction with respect to NBA has been taken as unity. The concentration of reducing sugar was varied from $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ to $10.00 \times 10^{-2} \text{ mol dm}^{-3}$ in the case of maltose and from $0.50 \times 10^{-2} \text{ mol dm}^{-3}$ to $5.00 \times 10^{-2} \text{ mol dm}^{-3}$ in the case of lactose at constant concentrations of all other reactants constant and at constant temperature 40 °C. On the basis of observed values of pseudo first-order rate constant, k_1 , for varying concentrations of reducing sugar, it has been concluded that order of reaction with respect to reducing sugar is zero (Tables 1 and 2). The order of reaction with respect to $[\text{Rh(III)}]$ is

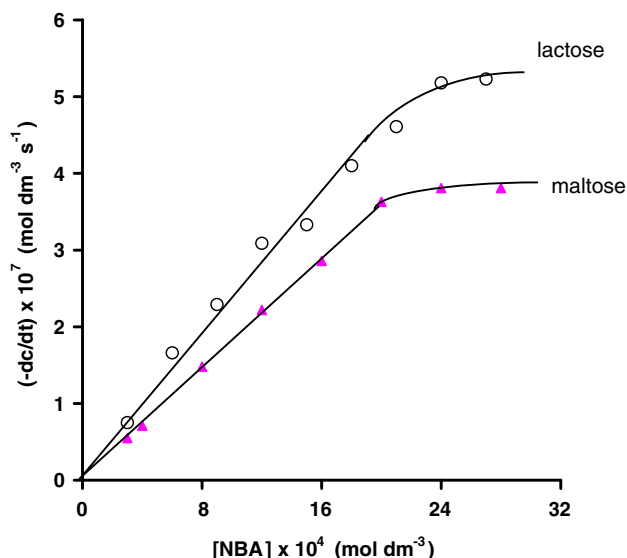


Fig. 1. Plots between ($-dc/dt$) and $[\text{NBA}]$ at 40 °C. $[\text{Sugar}] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Rh(III)}] = 3.79 \times 10^{-6} \text{ mol dm}^{-3}$ (maltose) and $2.28 \times 10^{-6} \text{ mol dm}^{-3}$ (lactose), $[\text{HClO}_4] = 10.00 \times 10^{-1} \text{ mol dm}^{-3}$ (maltose) and $20.00 \times 10^{-1} \text{ mol dm}^{-3}$ (lactose), $[\text{Hg(OAc)}_2] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ (maltose) and $1.80 \times 10^{-3} \text{ mol dm}^{-3}$ (lactose).

Table 1
Effect of $[H^+]$ and [Maltose] on the rate of reaction at 40 °C

$[H^+]$ (mol dm ⁻³)	[Maltose] × 10 ² (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)
0.50	2.00	3.50
1.00	2.00	6.47
2.00	2.00	14.57
2.50	2.00	17.81
3.50	2.00	31.58
4.00	2.00	40.24
1.00	1.00	6.12
1.00	1.66	6.29
1.00	2.00	6.12
1.00	3.33	6.53
1.00	5.00	6.53
1.00	6.00	6.12
1.00	8.00	6.53
1.00	10.00	6.73

Solution conditions:

For H^+ ions and maltose variation:

$$[NBA] = 6.66 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[Rh(III)] = 3.79 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[Hg(II)] = 7.14 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[Cl^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$$

Table 2
Effect of $[H^+]$ and [Lactose] on the rate of reaction at 40 °C

$[H^+]$ (mol dm ⁻³)	[Lactose] × 10 ² (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)
0.50	2.00	2.04
1.00	2.00	3.94
1.50	2.00	4.22
2.00	2.00	8.83
2.50	2.00	13.20
3.00	2.00	17.85
3.50	2.00	20.57
4.00	2.00	26.77
1.00	0.50	4.97
1.00	1.00	5.32
1.00	1.50	5.06
1.00	2.00	6.21
1.00	2.50	5.06
1.00	3.00	6.21
1.00	3.50	5.38
1.00	4.00	5.32
1.00	4.50	5.06
1.00	5.00	5.17

Solution conditions:

For H^+ ions variation:

$$[NBA] = 6.66 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[Rh(III)] = 1.52 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[Hg(II)] = 7.14 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[Cl^-] = 1.20 \times 10^{-3} \text{ mol dm}^{-3}$$

For lactose variation:

$$[NBA] = 6.66 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[Rh(III)] = 3.79 \times 10^{-6} \text{ mol dm}^{-3}$$

$$[Hg(II)] = 7.14 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[Cl^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$$

found to be unity throughout its variation as is evident from the plots of k_1 vs. $[Rh(III)]$, where straight lines passing through the origin have been obtained for the oxidation of both maltose and lactose (Fig. 2). In order to find out

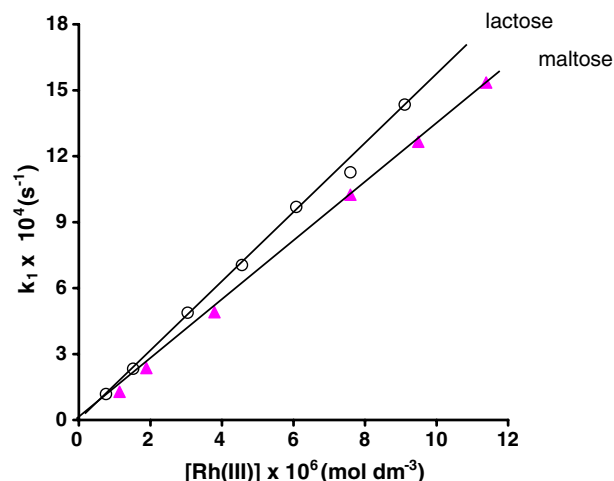


Fig. 2. Plots between k_1 and $[Rh(III)]$ at 40 °C. $[NBA] = 06.66 \times 10^{-4} \text{ mol dm}^{-3}$, $[Sugar] = 02.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[HClO_4] = 10.00 \times 10^{-1} \text{ mol dm}^{-3}$, $[Hg(OAc)_2] = 07.14 \times 10^{-4} \text{ mol dm}^{-3}$.

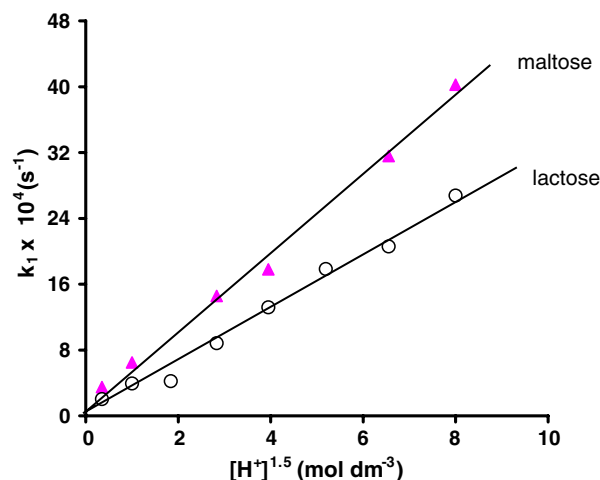


Fig. 3. Plots between k_1 and $[H^+]^{1.5}$ at 40 °C. $[NBA] = 6.66 \times 10^{-4} \text{ mol dm}^{-3}$, $[Sugar] = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[Rh(III)] = 3.79 \times 10^{-6} \text{ mol dm}^{-3}$ (maltose) and $1.52 \times 10^{-6} \text{ mol dm}^{-3}$ (lactose), $[Hg(OAc)_2] = 7.14 \times 10^{-4} \text{ mol dm}^{-3}$, $[Cl^-] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ (maltose) and $1.20 \times 10^{-3} \text{ mol dm}^{-3}$ (lactose).

the effect of $[H^+]$ on the rate of oxidation, its concentration has been varied from $5.00 \times 10^{-1} \text{ mol dm}^{-3}$ to $40.00 \times 10^{-1} \text{ mol dm}^{-3}$ at constant concentrations of all other reactants and at constant temperature 40 °C. The values of pseudo first-order rate constant, k_1 , thus obtained are presented in Tables 1 and 2 against varying concentrations of H^+ ions. When plots were made between k_1 vs. $[H^+]^{1.5}$ for both the redox systems under investigation, straight lines passing through the origin were obtained (Fig. 3). This clearly shows that order of reaction with respect to $[H^+]$ is 1.5. Fractional positive and fractional negative effects of $[Cl^-]$ and $[NHA]$ were observed respectively in the oxidation of both maltose and lactose (Tables 3–5). The decrease in pseudo first-order rate constant, k_1 , with the increase in $[Hg(II)]$ indicates that there is negative

Table 3
Effect of [Hg(II)] and [Cl⁻] on the rate of reaction in Rh(III)-catalyzed oxidation of maltose at 40 °C

[Hg(II)] × 10 ⁴ (mol dm ⁻³)	[Cl ⁻] × 10 ³ (mol dm ⁻³)	k ₁ × 10 ⁴ (s ⁻¹)
5.55	3.00	14.72
8.00	3.00	12.62
12.00	3.00	11.57
16.00	3.00	10.52
20.00	3.00	9.92
24.00	3.00	8.67
7.14	6.00	12.98
7.14	12.00	18.04
7.14	18.00	27.05
7.14	24.00	32.47

Solution conditions:

For Hg(II) ions variation:

$$\begin{aligned}
 [\text{NBA}] &= 5.00 \times 10^{-4} \text{ mol dm}^{-3} \\
 [\text{Maltose}] &= 2.00 \times 10^{-2} \text{ mol dm}^{-3} \\
 [\text{Rh(III)}] &= 3.79 \times 10^{-6} \text{ mol dm}^{-3} \\
 [\text{H}^+] &= 10.00 \times 10^{-1} \text{ mol dm}^{-3}
 \end{aligned}$$

For Cl⁻ ions variation:

$$\begin{aligned}
 [\text{NBA}] &= 6.66 \times 10^{-4} \text{ mol dm}^{-3} \\
 [\text{Rh(III)}] &= 3.79 \times 10^{-6} \text{ mol dm}^{-3} \\
 [\text{Maltose}] &= 2.00 \times 10^{-2} \text{ mol dm}^{-3} \\
 [\text{H}^+] &= 5.00 \times 10^{-1} \text{ mol dm}^{-3}
 \end{aligned}$$

Table 4
Effect of [Hg(II)] and [Cl⁻] on the rate of reaction in Rh(III)-catalyzed oxidation of lactose at 40 °C

[Hg(II)] × 10 ⁴ (mol dm ⁻³)	[Cl ⁻] × 10 ³ (mol dm ⁻³)	k ₁ × 10 ⁴ (s ⁻¹)
6.00	3.00	7.29
12.00	3.00	5.90
18.00	3.00	5.55
24.00	3.00	4.85
30.00	3.00	2.98
7.14	3.60	5.71
7.14	5.40	7.56
7.14	7.20	9.69
7.14	9.00	13.11
7.14	10.80	18.36

Solution conditions:

For Hg(II) ions variation:

$$\begin{aligned}
 [\text{NBA}] &= 5.00 \times 10^{-4} \text{ mol dm}^{-3} \\
 [\text{Maltose}] &= 2.00 \times 10^{-2} \text{ mol dm}^{-3} \\
 [\text{Rh(III)}] &= 3.79 \times 10^{-6} \text{ mol dm}^{-3} \\
 [\text{H}^+] &= 10.00 \times 10^{-1} \text{ mol dm}^{-3}
 \end{aligned}$$

For Cl⁻ ions variation:

$$\begin{aligned}
 [\text{NBA}] &= 6.66 \times 10^{-4} \text{ mol dm}^{-3} \\
 [\text{Rh(III)}] &= 2.28 \times 10^{-6} \text{ mol dm}^{-3} \\
 [\text{Sugar}] &= 2.00 \times 10^{-2} \text{ mol dm}^{-3} \\
 [\text{H}^+] &= 10.00 \times 10^{-1} \text{ mol dm}^{-3}
 \end{aligned}$$

effect of [Hg(II)] on the rate of oxidation of both the reducing sugars (Tables 3 and 4). The reaction rate is unaffected by the change in ionic strength (μ) of the medium. The reactions have also been studied at four different temperatures i.e 30, 35, 40 and 45 °C and observed k_1 values were utilized to calculate various activation parameters such as

Table 5

The rates calculated on the basis of rate law and the rates observed experimentally for the oxidation of maltose and lactose, respectively at 40 °C

[NHA] × 10 ⁴ (mol dm ⁻³)	-dc/dr × 10 ⁷ (mol dm ⁻³ s ⁻¹)			
	Maltose		Lactose	
	Experimental	Calculated	Experimental	Calculated
6.66	3.78	3.58	10.10	10.68
13.20	1.89	1.99	7.59	7.63
19.80	1.26	1.38	5.89	5.92
26.40	1.08	1.05	5.05	4.84
33.30	0.84	0.84	4.33	4.06

Solution conditions:

$$\begin{aligned}
 [\text{NBA}] &= 6.66 \times 10^{-4} \text{ mol dm}^{-3} \\
 [\text{Sugar}] &= 2.00 \times 10^{-2} \text{ mol dm}^{-3} \\
 [\text{Rh(III)}] &= 3.79 \times 10^{-6} \text{ mol dm}^{-3} \\
 [\text{H}^+] &= 10.00 \times 10^{-1} \text{ mol dm}^{-3} \\
 [\text{Hg(II)}] &= 7.14 \times 10^{-4} \text{ mol dm}^{-3} \\
 [\text{Cl}^-] &= 3.00 \times 10^{-3} \text{ mol dm}^{-3}
 \end{aligned}$$

energy of activation (E_a), entropy of activation (ΔS^\ddagger), free energy of activation (ΔG^\ddagger), and Arrhenius frequency factor (A) (Table 6).

On the basis of above experimental findings, the rate laws for the oxidation of maltose and lactose at low concentrations of NBA can be proposed in the form of Eqs. (iii) and (iv) respectively

$$k_1 = k[\text{Rh(III)}][\text{H}^+]^{1.5}[\text{Hg(II)}]^{-0.38}[\text{Cl}^-]^{0.75}[\text{NHA}]^{-0.77} \quad (\text{iii})$$

and

$$k_1 = k[\text{Rh(III)}][\text{H}^+]^{1.5}[\text{Hg(II)}]^{-0.33}[\text{Cl}^-]^{0.80}[\text{NHA}]^{-0.70} \quad (\text{iv})$$

where $k_1 = -\frac{dc}{dt} \cdot \frac{1}{[\text{NBA}]}$.

4. Discussion

4.1. Reactive species of rhodium(III) chloride in acidic medium

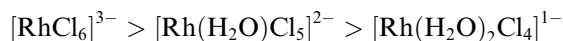
Wolsey et al. [6] have reported that the colour of aqueous solutions of rhodium(III) chloride varies from yellow to various shades of red depending upon the nature and history of the solution. They have also reported that a solution of hydrous rhodium(III) oxide in dilute hydrochloric acid is yellow; on heating to boiling, the solution becomes cherry red. Dissolution of hydrated rhodium(III) chloride in water yields a red brown solution, which turns yellow on boiling [14,15] or red if an excess of hydrochloric acid is present during the heating process. Wolsey et al. [6] have described the preparation of various complexes formed between rhodium(III) and chloride ion in dilute hydrochloric acid solution, and the isolation and characterization of these complexes by the ion exchange technique. In addition, the spectra of these complexes in aqueous solution have been determined and utilized for the calculation of successive formation constants by the aforesaid workers. For the determination of the formation constants of the

Table 6
Activation parameters of Rh(III)- catalyzed oxidation of maltose and lactose by NBA in acidic medium at 40 °C

Reducing sugars	E_a (kJ mol ⁻¹)	k_r (mol ⁻³ dm ⁹ s ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	A (mol ⁻³ dm ⁹ s ⁻¹)
Maltose	87.40	3.54×10^2	84.77	61.44	74.57	4.73×10^{17}
Lactose	76.49	31.44×10^2	73.86	55.76	57.85	0.65×10^{17}

complexes in the rhodium(III) chloride system, 40 solutions were prepared which were 0.01 M in rhodium(III) perchlorate and contained sufficient hydrochloric acid and perchloric acid to give a total ionic strength of 6.0 M. In these solutions the chloride ion content varied from 0.002 M to 6.0 M. The spectra of the solutions have been collected which showed shifts of the absorption maxima towards longer wavelengths with increasing chloride concentration. At 0.2 M HCl solution, the predominant species was found as $[\text{RhCl}_5]^{2-}$ and at 2 M and above the predominant species was found as $[\text{RhCl}_6]^{3-}$.

In the year 1966, an attempt has been made by James and Remple [16] to find out a correlation between catalytic activity and the nature of the rhodium(III) chloride species present in Rh(III)/H₂/Fe(III) system whose kinetics were studied by them over a wide range of chloride concentrations. They observed that the anionic complexes $[\text{RhCl}_6]^{3-}$, $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$, and $[\text{Rh}(\text{H}_2\text{O})_2\text{Cl}_4]^{1-}$ activate molecular hydrogen for the reduction of ferric ion in aqueous acid solution and the catalytic activity increases with increasing number of chloride ligands present. They have performed experiments with the complexes prepared from the $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ solution and reported that the activities of the anionic complexes decrease in the following order:



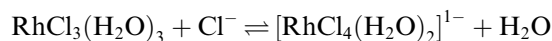
These workers have found that RhCl_3 in 3–5 M HCl solutions exists mainly in the form of $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$. Their findings are contrary to the results reported by Harrod and Halpern [17], who had observed that $[\text{RhCl}_6]^{3-}$ is the predominant species of RhCl_3 in 3–5 M HCl solutions.

In the study regarding hydration of acetylenes catalyzed by rhodium(III) chloride complexes, James and Remple [18] have observed that the activity of the $[\text{Rh}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ species in 0.2 M HCl–5.80 M HClO_4 is about twice that in the 3 M HCl media and this is likely due to an increase in the C_2H_2 solubility by about 2. According to them, the cationic species show no reactivity and neutral $[\text{RhCl}_3(\text{H}_2\text{O})_3]$ species shows reactivity and this reactivity increases to a maximum for a solution containing 5:1 chlorospecies. They have further observed that the hexachloro complex is very much less active. It is also reported [19] that on boiling aqueous solutions of the trichloride, $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ is formed and with excess HCl, the rose pink hexachlororhodate ion, $[\text{RhCl}_6]^{3-}$ is obtained. Between these two species there are clearly several intermediates. On aqution, $[\text{RhCl}_6]^{3-}$ produces $[\text{RhCl}_5(\text{H}_2\text{O})]^{2-}$, *cis* $[\text{RhCl}_4(\text{H}_2\text{O})_2]^{1-}$ and *fac* $\text{RhCl}_3(\text{H}_2\text{O})_3$.

The structural behaviour of the anionic chloro-complexes of Rh(III) and Ir(III) are very similar [20,21]. Since,

there is a similarity between anionic chloro-complexes of Rh(III) and Ir(III), hence before arriving at the reactive species of Rh(III) chloride in the oxidation of maltose and lactose by NBA in acidic medium, it is necessary to describe briefly the various chloro-complexes of Ir(III) formed with varying concentrations of HCl. du Preez et al. [22] have studied the effect of HCl concentration and temperature on Ir(III) speciation at equilibrium. They have observed that at 0.1 M HCl, Ir(III) chloride at room temperature exists in the form of $[\text{IrCl}_3(\text{H}_2\text{O})_3]$, whereas at 8 M HCl, it exists in the form of $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$. In between 0.1 M and 8 M HCl i.e. at 1.4 M, 4.0 M and 6.0 M HCl, the species $[\text{IrCl}_3(\text{H}_2\text{O})_3]$, $[\text{IrCl}_4(\text{H}_2\text{O})]^-$ and $[\text{IrCl}_4(\text{H}_2\text{O})]^-$ are reported to exist at room temperature respectively.

In the present paper, rhodium(III) chloride has been used as homogeneous catalyst in the oxidation of the reducing sugars i.e. maltose and lactose by NBA in presence of perchloric acid. The solution of rhodium(III) chloride was prepared in hydrochloric acid where its concentration was maintained at 3 M. Throughout the study Rh(III) chloride concentration, in which Cl^- ions was maintained at $1.2\text{--}24.0 \times 10^{-3}$ M, was fixed in the order of 10^{-6} . When spectrum for Rh(III) chloride solution containing Cl^- ions as 0.3 M was collected with the help of UV–vis spectrophotometer, it was found that there is a single peak at 250 nm indicating the presence of lone species of Rh(III) chloride in the solution (Fig. 4(1)). In view of reported literature quoted above specially the work [22] describing various chloro-complexes of Ir(III) formed with varying concentrations of HCl and also in view of the spectrum collected for Rh(III) chloride solution containing 0.3 M Cl^- ions, it is reasonable to assume that the starting species of Rh(III) chloride in the reactions under investigation is $[\text{RhCl}_3(\text{H}_2\text{O})_3]$. Observed positive effect of $[\text{Cl}^-]$ on the rate of oxidation on one hand indicates the existence of the following equilibrium in the reaction



and on the other hand it forced us to conclude that $[\text{RhCl}_4(\text{H}_2\text{O})_2]^{1-}$ is the reactive species of rhodium(III) chloride in the oxidation of maltose and lactose by NBA in acidic medium.

4.2. Reactive species of *N*-bromoacetamide in acidic medium

In order to propose a reaction mechanism for the oxidation of reducing sugars by NBA in presence of rhodium(III) chloride as homogeneous catalyst and perchloric acid as the medium, it is necessary to know

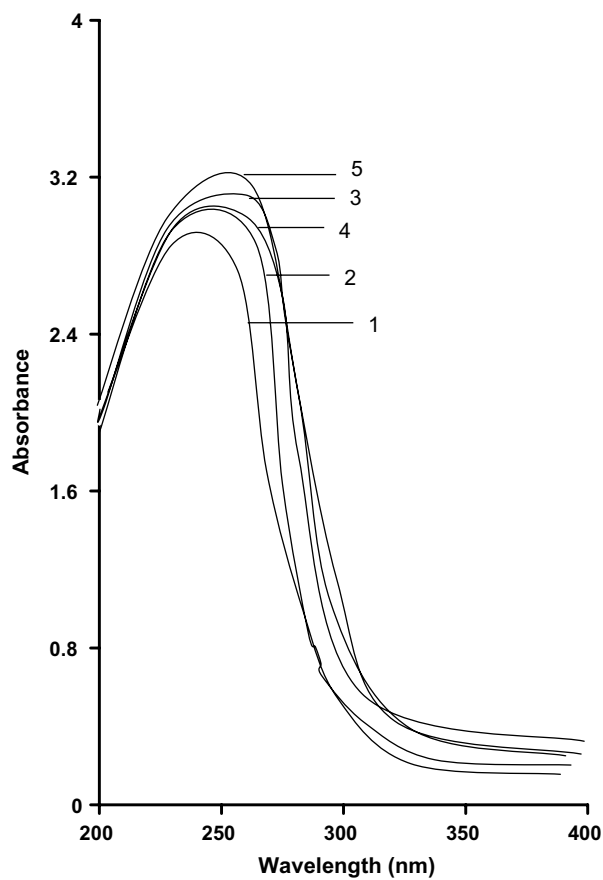
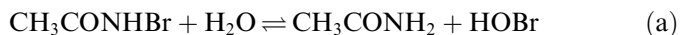
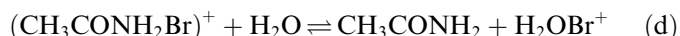
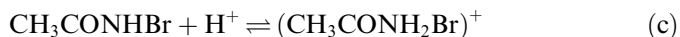


Fig. 4. Spectra for various solutions containing Rh(III), H^+ , Cl^- , NBA and Hg(II) at room temperature. (1) $[Rh(III)] = 3.79 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 1.00 \text{ mol dm}^{-3}$, $[Cl^-] = 0.30 \text{ mol dm}^{-3}$. (2) $[Rh(III)] = 3.79 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 1.00 \text{ mol dm}^{-3}$, $[Cl^-] = 0.30 \text{ mol dm}^{-3}$, $[NBA] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$. (3) $[Rh(III)] = 3.79 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 1.00 \text{ mol dm}^{-3}$, $[Cl^-] = 0.30 \text{ mol dm}^{-3}$, $[NBA] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$. (4) $[Rh(III)] = 3.79 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 1.00 \text{ mol dm}^{-3}$, $[Cl^-] = 0.30 \text{ mol dm}^{-3}$, $[NBA] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[Hg(II)] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$. (5) $[Rh(III)] = 3.79 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] = 1.00 \text{ mol dm}^{-3}$, $[Cl^-] = 0.30 \text{ mol dm}^{-3}$, $[NBA] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[Hg(II)] = 3.33 \times 10^{-3} \text{ mol dm}^{-3}$.

the reactive species of NBA in acidic medium. It is reported [23–25,11,12] that NBA in acidic medium exists in the following equilibria



or



From two sets of equilibria (a & b) and (c & d) as indicated above, it is clear that there are four possible reactive species of NBA in acidic medium. These species are NBA, HOBr, protonated NBA i.e. $(CH_3CONH_2Br)^+$ and cationic bromine i.e. $(H_2OBr)^+$. Now on the basis of kinetic data, it is to decide that which of the reactive species of NBA is taking part in the oxidation of reducing sugars

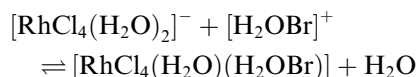
in acidic medium? If it is assumed that NBA as such takes part in the reaction then the rate law derived on this basis will fail to explain the observed negative effect of acetamide concentration. On the other hand, if $(CH_3CONH_2Br)^+$ is taken as reactive species of NBA in the present investigation then the observed positive effect of $[H^+]$ on the rate of reaction will be explained but the negative effect of [NHA] cannot be explained. By taking HOBr as the reactive species of NBA in the reaction, the negative effect of NHA concentration on the rate of reaction can be explained but it will not be possible to explain positive effect of H^+ concentration on the rate of reaction. The only option left to us was to assume $(H_2OBr)^+$ as the reactive species of NBA in acidic medium because by taking $(H_2OBr)^+$ as the reactive species of NBA in the present investigation, not only the observed negative effect of [NHA] on the rate of oxidation will be explained but also the positive effect of $[H^+]$ will also be explained.

4.3. Role of mercuric acetate in the present investigation

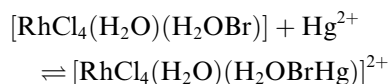
Earlier in Pd(II) [11]-, and Ir(III) [12]- and Ru(III) [24,25]-catalyzed oxidation of reducing sugars by NBA in acidic medium, $Hg(OAc)_2$ has been used as scavenger to eliminate Br^- ions which could have produced bromine in the reaction. In the absence of mercuric acetate, the bromine thus produced sets another parallel oxidation and creates complications in NBA oxidation. The presence of mercuric acetate thus ensures that the oxidation proceeds solely through NBA. Earlier it is also reported [26,27] that mercury(II) acts as an oxidant for certain reactions leading to the oxidation of reducing sugars. In the present investigation, before going through the oxidation of reducing sugars by NBA in presence of rhodium(III) and perchloric acid, efforts have also been made to ascertain whether in the absence of NBA and in the presence of mercury(II), the oxidation of reducing sugars in presence of rhodium(III) and perchloric acid is possible or not? It is observed that the oxidation of reducing sugars by mercury(II) under our experimental conditions is not at all possible. Thus in the present investigation, the function of mercury(II), is just to eliminate bromine produced during the course of reaction and to ensure oxidation of reducing sugars by NBA alone throughout the course of reaction. In addition to this, it is also observed that with the increase in mercury(II) concentration there is decrease in the rate of reaction. This decrease in the rate of reaction with the increase in mercury(II) concentration might be assumed as due to formation of unreactive complex between a part of the reactive complex, $[RhCl_4(H_2O)(H_2OBr)]$, and mercury(II) in the reactions under investigation. On the basis of these experimental findings, it can very easily be inferred that the role of mercury(II) is not limited only up to Br^- ion scavenger but it also acts as inhibitor by making an unreactive complex with a part of the complex indicated above.

4.4. Spectral information in support of complexes formed during the course of reaction

After ascertaining the reactive species of Rh(III) chloride and NBA in acidic medium as $[\text{RhCl}_4(\text{H}_2\text{O})_2]^{1-}$ and $(\text{H}_2\text{OBr})^+$ respectively, efforts have been made to verify the possible formation of complex or complexes in the reaction by obtaining the spectra of solutions containing Rh(III), H^+ and Cl^- , Rh(III), H^+ , Cl^- and NBA and Rh(III), H^+ , Cl^- , NBA and Hg(II) (Fig. 4). When spectrum of solution containing Rh(III), H^+ and Cl^- was compared with the spectra of solutions contain Rh(III), H^+ and Cl^- with two different concentrations of NBA, it was found that with the increase in concentration of NBA, there is an increase in absorbance from 2.92 to 3.04 and 3.12 with a shift in λ_{max} towards longer wave length from 250 nm to 266 nm (Fig. 4). This increase in absorbance with the increase in [NBA] is due to more and more formation of a complex between reactive species of Rh(III) chloride i.e. $[\text{RhCl}_4(\text{H}_2\text{O})_2]^{1-}$ and reactive species of NBA i.e. $(\text{H}_2\text{OBr})^+$ according to the following equilibrium



Further, when two different solutions of Hg(II) ($1.25 \times 10^{-3} \text{ mol dm}^{-3}$ and $3.33 \times 10^{-3} \text{ mol dm}^{-3}$) were added to the solution of Rh(III), H^+ , Cl^- and NBA, it was found that there is an increase in absorbance from 3.04 to 3.08 and 3.22 with a shift in λ_{max} towards longer wave length (Fig. 4). This increase in absorbance with the increase in [Hg(II)] can be considered as due to the formation of an unreactive complex of the type $[\text{RhCl}_4(\text{H}_2\text{O})(\text{H}_2\text{OBrHg})]^{2+}$ between a part of the complex and Hg^{2+} ions according to the equilibrium indicated below

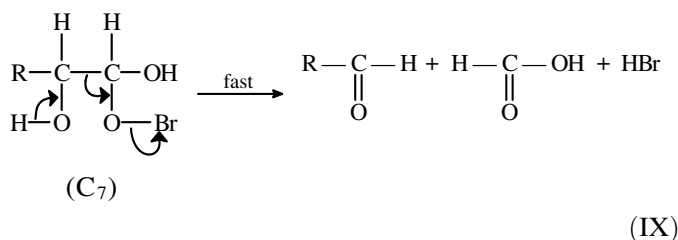
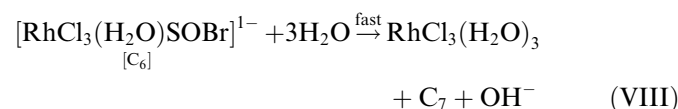
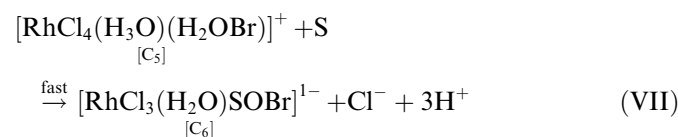
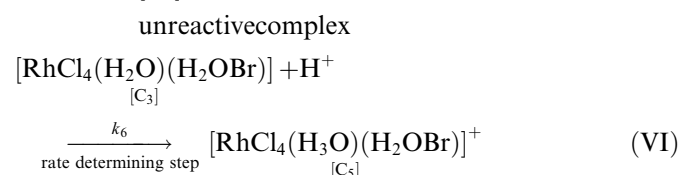
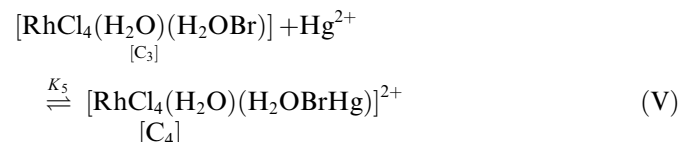
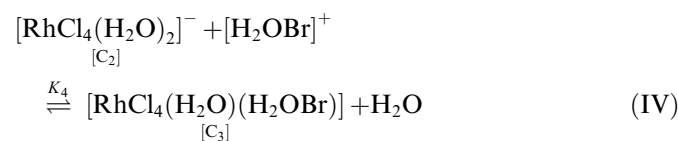
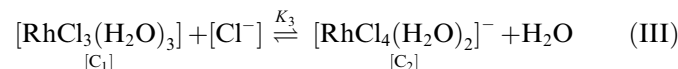
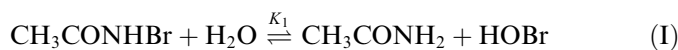


The observed shift in λ_{max} towards longer wave length is due to the combination of a chromophore (Hg(II)) with an auxochrome (Cl^-) to give rise to another chromophore, $[\text{RhCl}_4(\text{H}_2\text{O})(\text{H}_2\text{OBrHg})]^{2+}$.

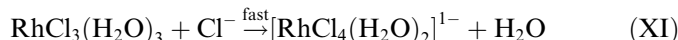
4.5. Mechanism and the derivation of rate law

On the basis of (1) kinetic order with respect to each reactant taking part in the reaction, (2) spectral information collected for the probable formation of complex or complexes in the reaction and (3) taking into consideration the observed values of activation parameters, a reaction Scheme 1 for the reactions under investigation can be proposed in the following way:

Scheme 1



where R is $\text{C}_4\text{H}_9\text{O}_4$ for maltose and lactose.



On the basis of reaction Scheme 1 and also on the basis of stoichiometric equations given for the oxidation of maltose and lactose, the rate in terms of decrease in concentration of NBA can be expressed as

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = 4k_6[\text{C}_3][\text{H}^+] \quad (1)$$

On applying the law of chemical equilibrium to steps Eqs. (I), (II), (III), (IV), and (V), we have Eqs. (2)–(6) respectively.

$$[\text{HOBr}] = \frac{K_1[\text{NBA}]}{[\text{NHA}]} \quad (2)$$

$$[\text{H}_2\text{OBr}]^+ = \frac{K_1 K_2 [\text{NBA}][\text{H}^+]}{[\text{NHA}]} \quad (3)$$

$$[\text{C}_2] = K_3 [\text{Cl}^-] \text{C}_1 \quad (4)$$

$$[\text{C}_3] = \frac{K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+][\text{Cl}^-][\text{C}_1]}{[\text{NHA}]} \quad (5)$$

and

$$[\text{C}_4] = \frac{K_1 K_2 K_3 K_4 K_5 [\text{NBA}][\text{H}^+][\text{Cl}^-][\text{C}_1][\text{Hg}(\text{II})]}{[\text{NHA}]} \quad (6)$$

On substituting the value of $[\text{C}_3]$ from Eq. (5) to Eq. (1), we get

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{4k_6 K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+]^2 [\text{C}_1][\text{Cl}^-]}{[\text{NHA}]} \quad (7)$$

At any moment in the reaction, the total concentration of Rh(III) chloride i.e. $[\text{Rh}(\text{III})]_{\text{T}}$ can be expressed as

$$[\text{Rh}(\text{III})]_{\text{T}} = [\text{C}_1] + [\text{C}_2] + [\text{C}_3] + [\text{C}_4] \quad (8)$$

On substituting the values of $[\text{C}_2]$, $[\text{C}_3]$ and $[\text{C}_4]$ from Eqs. (4)–(6) respectively to Eq. (8), we have Eq. (9)

$$[\text{C}_1] = \frac{[\text{Rh}(\text{III})]_{\text{T}} [\text{NHA}]}{[\text{NHA}] + K_3 [\text{Cl}^-] [\text{NHA}] + K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+][\text{Cl}^-] + K_1 K_2 K_3 K_4 K_5 [\text{NBA}][\text{H}^+][\text{Cl}^-][\text{Hg}(\text{II})]} \quad (9)$$

On substituting the value of $[\text{C}_1]$ from Eq. (9) to Eq. (7), we obtain Eq. (10)

$$\text{rate} = \frac{d[\text{NBA}]}{dt} = \frac{4k_6 K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+]^2 [\text{Rh}(\text{III})]_{\text{T}} [\text{Cl}^-]}{[\text{NHA}] + K_3 [\text{Cl}^-] [\text{NHA}] + K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+][\text{Cl}^-] + K_1 K_2 K_3 K_4 K_5 [\text{NBA}][\text{H}^+][\text{Cl}^-][\text{Hg}(\text{II})]} \quad (10)$$

Eq. (10) is the rate law which clearly supports the first-order kinetics with respect to $[\text{Rh}(\text{III})]$, less than first order with respect to $[\text{NBA}]$, less than second order with respect to $[\text{H}^+]$, fractional positive order with respect to $[\text{Cl}^-]$ and fractional negative order with respect to $[\text{NHA}]$ and $[\text{Hg}(\text{II})]$.

Eq. (10) can also be written as

$$\text{Rate} = -\frac{d[\text{NBA}]}{dt} = \frac{4k_6 K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+]^2 [\text{Rh}(\text{III})]_{\text{T}} [\text{Cl}^-]}{[\text{NHA}] + K_3 [\text{Cl}^-] [\text{NHA}] + K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+][\text{Cl}^-] (1 + K_5 [\text{Hg}(\text{II})])} \quad (11)$$

According to equilibrium (V),

$$K_5 = \frac{[\text{C}_4]}{[\text{C}_3][\text{Hg}(\text{II})]}$$

or

$$K_5 [\text{Hg}(\text{II})] = \frac{[\text{C}_4]}{[\text{C}_3]} \quad (12)$$

At very low concentration of Hg (II) ions, since the concentration of C_4 is very-very small in comparison to the concentration of C_3 hence the inequality $K_5 [\text{Hg}(\text{II})] \ll 1$, can be assumed as valid one. Under the condition $K_5 [\text{Hg}(\text{II})] \ll 1$, Eq. (11) will be reduced to Eq. (13).

$$\begin{aligned} \text{rate} &= -\frac{d[\text{NBA}]}{dt} \\ &= \frac{4k_6 K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+]^2 [\text{Rh}(\text{III})]_{\text{T}} [\text{Cl}^-]}{[\text{NHA}] (1 + K_3 [\text{Cl}^-]) + K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+][\text{Cl}^-]} \end{aligned} \quad (13)$$

Eq. (13) is the rate law valid for low concentrations of Hg(II).

Since throughout the study, the concentration of Cl^- ions was maintained at 3.00×10^{-3} M for maltose and at 1.20×10^{-3} M for lactose, hence $K_3 [\text{Cl}^-]$ being very small in comparison to 1, can be neglected in the denominator of Eq. (13). Now under this condition Eq. (13) will take the shape of Eq. (14)

$$\begin{aligned} \text{rate} &= -\frac{d[\text{NBA}]}{dt} \\ &= \frac{4k_6 K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+]^2 [\text{Rh}(\text{III})]_{\text{T}} [\text{Cl}^-]}{[\text{NHA}] + K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+][\text{Cl}^-]} \end{aligned} \quad (14)$$

Eq. (14) is the rate law valid for low concentrations of Hg(II) and Cl^- ions.

On reversing Eq. (14)

$$\frac{[\text{Rh}(\text{III})]_{\text{T}}}{\text{rate}} = \frac{[\text{NHA}]}{4k_6 K_1 K_2 K_3 K_4 [\text{NBA}][\text{H}^+]^2 [\text{Cl}^-]} + \frac{1}{4k_6 [\text{H}^+]} \quad (15)$$

where $\text{rate} = -\frac{d[\text{NBA}]}{dt}$.

According to Eq. (15), if a plot is made between $\frac{[\text{Rh}(\text{III})]_{\text{T}}}{\text{rate}}$ and $[\text{NHA}]$, a straight line having positive intercept on

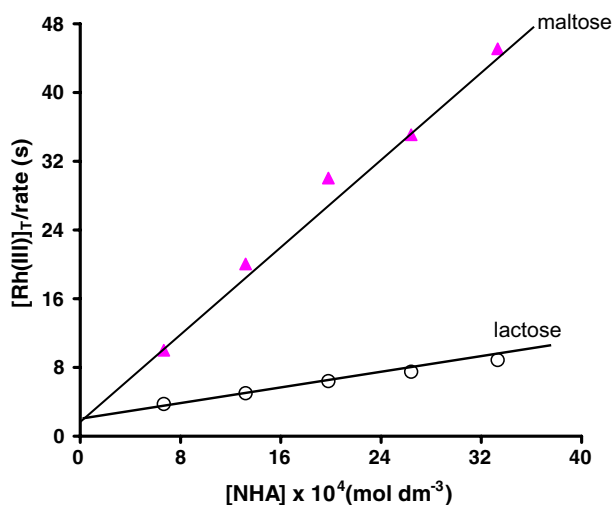


Fig. 5. Plots between $[\text{Rh(III)}]_{\text{T}}/\text{rate}$ and $[\text{NHA}]$ at $40\text{ }^{\circ}\text{C}$. $[\text{NBA}] = 6.66 \times 10^{-4}\text{ mol dm}^{-3}$, $[\text{Sugar}] = 2.00 \times 10^{-2}\text{ mol dm}^{-3}$, $[\text{Rh(III)}] = 3.79 \times 10^{-6}\text{ mol dm}^{-3}$, $[\text{HClO}_4] = 10.00 \times 10^{-1}\text{ mol dm}^{-3}$, $[\text{Hg(OAc)}_2] = 7.14 \times 10^{-4}\text{ mol dm}^{-3}$, $[\text{Cl}^-] = 3.00 \times 10^{-3}\text{ mol dm}^{-3}$.

Y-axis will be obtained. When plots were made between $\frac{[\text{Rh(III)}]_{\text{T}}}{\text{rate}}$ and $[\text{NHA}]$ for the oxidation of both maltose and lactose, straight lines having positive intercepts on Y-axis were obtained (Fig. 5). This proves the validity of rate law (14) and hence the proposed reaction Scheme 1. From the slopes and intercepts of the straight lines, the values of $K_1K_2K_3K_4$ and k_6 were calculated and found as $0.78 \times 10^2\text{ mol}^{-2}\text{ dm}^6$ and $12.5 \times 10^{-2}\text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}$ respectively for the oxidation of maltose and $4.85 \times 10^2\text{ mol}^{-2}\text{ dm}^6$ and $11.9 \times 10^{-2}\text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1}$, respectively for the oxidation of lactose. Utilizing the values of $K_1K_2K_3K_4$ and k_6 , the rates were calculated for the variation of $[\text{NHA}]$ by the help of rate law (14) in the oxidation of both maltose and lactose and found very close to the experimental rates (Table 5). This further proves the validity of rate law (14) and hence the proposed mechanism.

In the present investigation, observed positive entropy of activation in the oxidation of each reducing sugar clearly supports the interaction between an ion and a neutral molecule in the rate determining step leading to the formation of a less polar activated complex, $[\text{RhCl}_4(\text{H}_3\text{O})(\text{H}_2\text{OBr})]^+$, which ultimately converts into products via several fast steps. The same order of Arrhenius frequency factor observed in the oxidation of each reducing sugar supports the proposed common reaction Scheme 1.

5. Comparative studies

Efforts were made to compare the findings of this paper with the results reported for Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation of reducing sugars by NBA in acidic medium. The present study is similar to the reported two studies [11,25] as far as order with respect to oxidant and catalyst is concerned. In all the three cases the observed order with respect to oxidant is unity at its low concentrations and tends towards zero-order at its higher concentra-

tions. First-order kinetics with respect to Rh(III)/Pd(II)/Ru(III) was observed throughout the variation. The involvement of reducing sugar molecule before the rate determining step of the reaction schemes proposed for Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation distinguishes the reported two studies from the present study where sugar molecule participates in the reactions after the rate determining step. In Rh(III)-catalyzed oxidation of maltose and lactose, order with respect to $[\text{H}^+]$ was found to be 1.5 whereas in the reported Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation, it was found to be fractional negative. On the basis of positive effect of $[\text{H}^+]$ and negative effect of $[\text{NHA}]$ on the rate of oxidation, $(\text{H}_2\text{OBr})^+$ was taken as the reactive species of NBA in acidic medium in the present investigation. Negative effect observed for $[\text{NHA}]$ and $[\text{H}^+]$ led the authors to propose that HOBr is the reactive species of NBA in Pd(II) [11]- and Ru(III) [25]-catalyzed oxidation of reducing sugars. The present study shows similarity with the reported Ru(III) [25] catalyzed oxidation as far as positive effect of $[\text{Cl}^-]$ on the rate of reaction is concerned whereas it distinguishes itself with the reported Pd(II) [11]-catalyzed oxidation, where negative effect of $[\text{Cl}^-]$ on the rate of oxidation was observed. In the Rh(III)-catalyzed oxidation of reducing sugars, the negative effect of $[\text{Hg(II)}]$ on the rates makes the present study entirely different from other two reported studies [11,25] where the role of Hg(II) was found as co-catalyst in addition to its role as Br^- ion scavenger. The formation of most reactive activated complex in the present study results by the interaction of $[\text{RhCl}_4(\text{H}_2\text{O})(\text{H}_2\text{OBr})]$ and H^+ whereas in the reported Pd(II)-catalyzed [11] oxidation, it takes place by triple collisions between $[\text{PdCl}_3 \cdot \text{S}]^-$, Hg^{2+} and HOBr. In Ru(III)-catalyzed [25] oxidation, the formation of most reactive activated complex takes place by the interaction of $[\text{RuCl}_3 \cdot \text{S}(\text{H}_2\text{O})\text{OH}]^-$ and $[\text{Hg} \leftarrow \text{OBr}]$. The facts presented above force us to conclude that the present study in many respects differ from the other two reported studies [11,25].

6. Conclusions

On the basis of observed kinetic data for Rh(III)-catalyzed oxidation of maltose and lactose by NBA in acidic medium, it has been concluded that:

1. $(\text{H}_2\text{OBr})^+$ is the reactive species of NBA in acidic medium.
2. $[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ is the reactive species of Rh(III) chloride in acidic medium.
3. There is formation of a most reactive activated complex, $[\text{RhCl}_4(\text{H}_3\text{O})(\text{H}_2\text{OBr})]^+$, between reactive species of Rh(III) chloride and reactive species of NBA in acidic medium.
4. Hg(II) as one of the reactants plays the role of inhibitor in addition to its role as Br^- ion scavenger.
5. Positive entropy of activation observed for the oxidation of maltose and lactose supports the interaction between

an ion and a neutral molecule in the rate determining step leading to the formation of a less polar most reactive activated complex.

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