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A Kinetic Approach for $(H_2OBr)^+$ Oxidation of Glucose in Presence of $[RhCl_4(H_2O)_2]^{1-}$ as Catalyst

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ABSTRACT

The kinetics and mechanism of Rh (III)-catalyzed oxidation of D-glucose by N-bromoacetamide (NBA) in acidic medium has been studied at 40^o *C using Hg* $(OAc)_2$ *as scavenger for* Br^- *ions. The reaction follows first-order kinetics in [NBA] at its lower concentration range tending towards zero order at its higher concentrations. The order of reaction was found to be unity with respect to Rh (III) throughout its variation. The reaction exhibits zero-order kinetics with respect to glucose and fractional positive order with respect to* H^+ *and* Cl^- *in the oxidation of glucose. Negative effects of Hg (II) and NHA on the rate of reaction have been observed. The reaction remains unaffected by the change in ionic strength of the medium. Formic acid and arabinonic acid were identified as the main oxidation products of the 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. On the basis of observed kinetic data, spectral information and activation parameters, a suitable mechanism for the oxidation of D-glucose has been proposed. The most reactive activated complex,* $[RhCl_3(H_2O)_2(H_2OBr)]$ *formed between reactive species of Rh(III) chloride and reactive species of NBA and an unreactive complex,* $[RhCl_4(H_2O)(H_2OBrHg)]^{2+}$*, formed between Hg(II) and* $[RhCl_4(H_2O)(H_2OBr)]$ *,were identified by spectral evidence which supports the most probable reaction path proposed for the oxidation of D-glucose.*

Keywords: D-Glucose, Oxidation, N-bromoacetamide, Rh (III) catalysis, Acidic medium, Kinetic study.

INTRODUCTION

Sugars [1] also called as carbohydrates are vital to human survival. The study of sugars containing antibiotics has provided some of most fascinating and challenging problems in the field of carbohydrate chemistry [2]. Besides fulfilling specific nutritional or physiological roles, sugars may also have therapeutic or pharmacological actions. Various oxidation products of the redox reactions involving reducing sugars as reductant are reported to have industrial and biological significance. Glucose, a monosaccharide is an important carbohydrate and one of the main product of photosynthesis and starts cellular respiration in both prokaryotes and eukaryotes. Several workers have investigated the kinetics and mechanism of uncatalyzed [3-9] and catalyzed [10-16] oxidation of glucose by using different oxidants in acidic or alkaline media in presence of transition metal ions such as Os (VIII), Pd (II), Pt (IV), Ru (III) and Ir (III) as homogeneous catalyst. Rhodium plays an important role in biological activities. Rhodium complexes are reported [17] to have chemical reactivity, antitumor activity and catalytic functions with potential industrial applications. Little literature are available dealing with the kinetics and mechanism of reactions including oxidation of some reducing sugars [18-21] using Rh (III) and its chloro complexes as homogeneous catalyst. In view of the biological importance of rhodium, NBA and glucose and also in view of the fact that no report is available on Rh (III)-catayzed oxidation of D-glucose by NBA in acidic medium, the present study has been undertaken.

MATERIALS AND METHODS

Preparation of solutions: An aqueous solution of N-bromoacetamide was prepared fresh and its concentration was ascertained iodometrically. In order to avoid photochemical deterioration the solution of NBA was preserved in black coated flask. The solution of rhodium (III) chloride was prepared by dissolving the sample in 3M HCl and its concentration was determined as 3.80 x 10^{-3} M. An aqueous solution of glucose was prepared fresh each day. All other reagents used in the reaction were prepared in double distilled water.

Method of study: The requisite amounts of all the reactants i.e. NBA, Rh(III), $HClO_4$, Hg $(OAc)_2$ and water except glucose solution were taken in reaction bottle and equilibrated at 40°C in the thermostatic water bath. The reaction was initiated by adding the calculated amount of already equilibrated glucose solution at the same temperature to the reaction mixture. 5mL aliquots of the reaction mixture were pipetted out at regular intervals of time and poured into a conical flask containing 5 mL of 4 % KI solution and 5 mL of dilute $HClO_4$ solution. The liberated iodine equivalent to unconsumed NBA was estimated iodometrically.

Stoichiometry of Rh (III)-catalyzed oxidation of glucose by NBA: The stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing an excess of NBA over glucose at room temperature for 48 h. Under the condition of NBA>> glucose, the estimation of unconsumed NBA showed that the 2 mol. of NBA was consumed to oxidize 1 mol. of glucose. Accordingly, the following stoichiometric equation can be suggested as

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{NBA}}{2CH_3CONHBr} + 2H_2O \xrightarrow{\mathrm{RhCl_3/H^+}} \underset{\text{Formic acid}}{2HCOOH} + \underset{\text{Arabinonic acid}}{C_5H_{10}O_6} + 2HBr + \underset{\text{NHA}}{2CH_3CONH_2}$$

Formic acid and arabinonic acid were identified as the main reaction products by the help of equivalence, kinetic data, spot test [22] and thin layer chromatography [23].

RESULTS AND DISCUSSION

In order to propose a reaction mechanism for Rh (III)-catalyzed oxidation of glucose by NBA in perchloric acid medium using Hg $(OAc)_2$ as scavenger for Br^- ions, a series of experiments were performed at constant temperature 40°C. The order of reaction with respect to each reactant was determined by varying the concentrations of NBA, glucose, Rh(III) , H^+ ions, Cl^- ions, mercuric acetate and acetamide one by one in different sets keeping concentrations of all other reactants constant at a constant temperature 40^0 C.

To investigate the dependence of rate on NBA in Rh (III)-catalyzed oxidation of glucose, the concentration of NBA was varied from 5.00 x 10^{-4}M to 25.00 x 10^{-4}M at constant concentration of all other reactants at 40^0 C. Initial rates have been calculated from the slopes of the plots of unconsumed NBA, time and first-order rate constant, k_1 was calculated as :

$$k_1 = (-dc/dt) / [NBA]$$

The observed values of –dc/dt clearly show that there is first-order kinetics with respect to NBA at low concentration range which tends to zero-order at higher concentrations of NBA. This result is further verified by the plot made between (-dc/dt) values and [NBA], where a straight line passing through the origin was observed and deviation from straight line was observed at higher concentrations of NBA (Fig. 1). The direct proportionality between k_1 and Rh (III) indicates that the order with respect to Rh (III) is unity as is evident from the plot of k_1 vs [Rh(III)] , where a straight line passing through the origin is obtained (Fig.-2). Zero-order kinetics with respect to glucose is evident from the very similar values of first-order rate constant, k_1. Positive effect of H^+ on the rate of oxidation was observed throughout its tenfold variation (Table-1). This result is further verified by the plot of log k_1 against log $[H^+]$, where a straight line with a positive slope (0.83) was observed. A negative effect on the rate of reaction was observed on the addition of mercuric acetate in the oxidation of glucose (Table-1). Positive effect was observed by varying the concentration of Cl^- ions in the Rh (III)-catalysed oxidation of glucose by NBA (Table-1). Successive addition of acetamide (NHA) shows a negative effect on the rate of oxidation of glucose (Table-2).

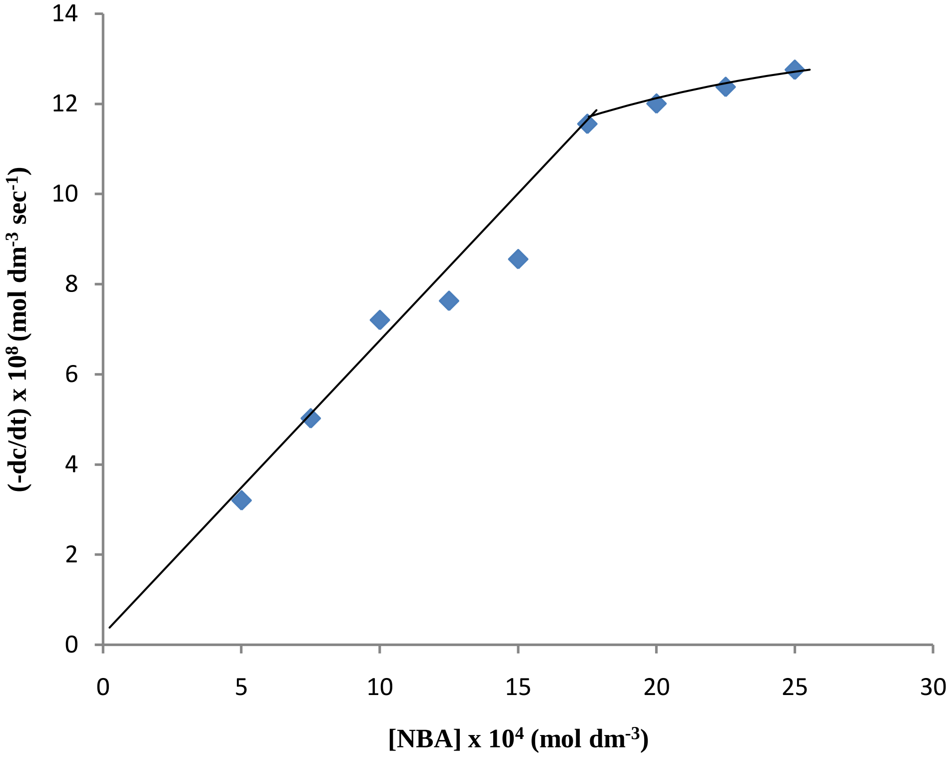


Fig 1 : Plot between –dc/dt and [NBA] at 40°C

[Glucose] = 1.00×10^{-2} mol dm^{-3} , [Rh(III)] = 3.79×10^{-8} mol dm^{-3} , $[H^+]$ = 5.00×10^{-1} mol dm^{-3} , [Hg(II)] = 3.00 $\times 10^{-3}$ mol dm^{-3}

On changing the ionic strength (μ) of the medium, the values of k_1 remain constant throughout the variation showing nil effect of ionic strength (μ) on the rate of oxidation of glucose. In order to find out the influence of temperature on the reaction rate, the reaction was studied at four different temperatures i.e. 30, 35, 40 & 45^{0}C. The values of first-order rate constant, k_1, obtained at four different temperatures were utilized to calculate activation parameters such as specific rate constant (k_r), Arrhenius frequency factor (A), energy of activation (E_a), enthalpy of activation ($\Delta H^\#$) ,entropy of activation ($\Delta S^\#$) and Gibb's free energy of activation($\Delta G^\#$) at 40 ^{0}C and found as 6.28 mol^{-2}dm^6 sec^{-1} , 38.60 $\times 10^{14}$ mol^{-2}dm^6 sec^{-1}, 21.32 k J mol^{-1} , 20.69 k J mol^{-1}, 11.14 k J mol^{-1} and 17.20 k J mol^{-1} , respectively.

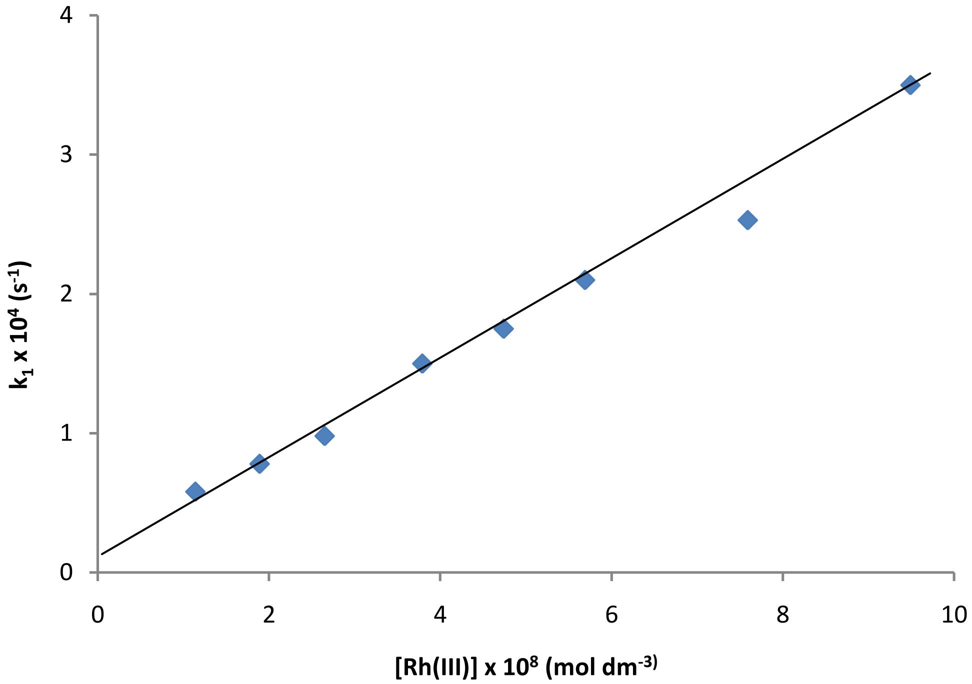


Fig 2 : Plot between k_1 and [Rh(III)] at 40°C

[NBA] = 10.00 × 10^{-4} mol dm^{-3}, [Glucose] = 1.00 × 10^{-2} mol dm^{-3} , [H^+] = 5.00× 10^{-1} mol dm^{-3}, [Hg(II)] = 1.25 × 10^{-3} mol dm^{-3}

Reactive species of NBA: It has been reported [24-27] earlier that NBA in acidic medium exists in the following equilibria:

$$\underset{\text{(NBA)}}{CH_3CONHBr} + H_2O \rightleftharpoons \underset{\text{(NHA)}}{CH_3CONH_2} + HOBr \qquad \text{(I)}$$

$$HOBr + H^+ \rightleftharpoons H_2OBr^+ \qquad \text{(II)}$$

Or

$$\underset{\text{(NBA)}}{CH_3CONHBr} + H^+ \rightleftharpoons \underset{\text{(NBAH}^+\text{)}}{(CH_3CO\,NH_2Br)^+} \qquad \text{(III)}$$

$$(CH_3CONH_2Br)^+ + H_2O \rightleftharpoons CH_3CONH_2 + H_2OBr^+ \qquad \text{(IV)}$$

Table1: Observed values of pseudo-first-order rate constant (k_1) for the variations of $[H^+]$, [Hg(II)] and $[Cl^-]$ in Rh(III)-catalyzed oxidation of D-glucose by NBA at 40^0C

$[H^+]$ (mol dm^{-3})	**[Hg(II)] $\times 10^4$ (mol dm^{-3})**	**$[Cl^-] \times 10^3$ (mol dm^{-3})**	**$k_1 \times 10^4$ (sec^{-1})**
0.20	12.50	0.03	0.65
0.40	12.50	0.03	0.72
0.60	12.50	0.0.	0.87
0.80	12.50	0.03	1.17
1.00	12.50	0.03	1.36
1.40	12.50	0.03	1.65
1.60	12.50	0.03	1.75
1.80	12.50	0.03	1.87
2.00	12.50	0.03	1.93
1.00	1.82	0.03	3.54
1.00	2.00	0.03	3.46
1.00	2.50	0.03	3.21
1.00	3.33	0.03	3.06
1.00	5.00	0.03	2.64
1.00	6.66	0.03	2.16
1.00	12.50	1.00	2.20
1.00	12.50	2.00	2.76
1.00	12.50	3.00	4.02
1.00	12.50	4.00	4.82
1.00	12.50	5.00	5.81

Solution conditions: [NBA] = 1.00×10^{-3} mol dm^{-3} (for $[H^+]$ and $[Cl^-]$ variation) and 1.66×10^{-3} mol dm^{-3} (for [Hg(II)] variation) [Glucose] = 1.00×10^{-2} mol dm^{-3} , [Rh(III)] = 3.79×10^{-8} mol dm^{-3}

Table 2: The rates calculated on the basis of rate law and the rates observed experimentally for the Variation of [NHA] in the oxidation of glucose at 40°C

$[NHA] \times 10^4$ ($mol\ dm^{-3}$)	$-dc/dt \times 10^8$ ($mol\ dm^{-3}\ sec^{-1}$)	
	Experimental	**Calculated**
10.00	12.50	11.98
20.00	8.33	9.29
30.00	7.41	7.59
40.00	6.66	6.42
50.00	5.55	5.56

Solution conditions: [NBA] = 10.00×10^{-4} mol dm^{-3} , [Glucose] = 1.00×10^{-2} mol dm^{-3} , [Rh(III)] = 3.79×10^{-8} mol dm^{-3}
$[H^+]$ = 5.00×10^{-1} mol dm^{-3} , [Hg(II)] = 12.50×10^{-4} mol dm^{-3}, $[Cl^-]$ = 3.00×10^{-5} mol dm^{-3}

From two sets of equilibria (I & II) and (III & IV) as indicated above, it is clear that there are four possible reactive species of NBA in acidic media i.e. NBA, HOBr, $NBAH^+$ and H_2OBr^+. Out of these four possible oxidizing species of NBA in acidic medium, the reactive species of NBA in the present investigation shall be decided by the observed kinetic data, specially by the effect of [NHA] and $[H^+]$ on the rate of oxidation of glucose. If NBA itself is taken as the reactive species of NBA, then it will lead to the positive effect of [NHA] on the rate of the reaction, contrary to the observed negative fractional order with respect to [NHA]. If HOBr is assumed to be the reactive species of NBA, then the observed positive effect with respect to $[H^+]$ can not be explained, although the negative effect of [NHA] on the rate of the reaction can be explained. If $NBAH^+$ is taken as reactive species of NBA, then the observed positive effect with respect to $[H^+]$ can be explained, but it will fail to explain the negative effect of [NHA]. If $(H_2OBr)^+$ is considered as the reactive species of NBA, then both the observed negative effect of [NHA] as well as the positive effect in $[H^+]$ can be explained. On the basis of discussion made above and the observed kinetic data concerning the variation of [NHA] and $[H^+]$ on the rate of oxidation, it can be concluded that the species $(H_2OBr)^+$ is the main reactive species of NBA in Rh(III)- catalysed oxidation of glucose.

Reactive species of Rh(III) in acidic medium: Wayne C. Wolsey et al [28] 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. The observations reported by them clearly show that with the change in concentration of hydrochloric acid from 0.010M to 2.00 M, there is change in complexes species from $RhCl^{2+}$ to $RhCl_6{}^{3-}$.A number of co-workers [29-33] have reported the absorption spectrum of rhodium(III) in perchloric acid where the species present is $Rh(H_2O)_6^{3+}$. B.R. James and G.L Remple [34] also reported a correlation between catalytic activity and the nature of the Rhodium(III) chloride species present in Rh(III) / H_2 / Fe(III) system. They observed that the anionic complexes $[RhCl_6]^{3-}$, $[Rh(H_2O)Cl_5]^{2-}$, and $[Rh(H_2O)_2Cl_4]^{1-}$ 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. It is also reported [35] that on aquation $[RhCl_6]^{3-}$ produces $[RhCl_5(H_2O)]^{2-}$, cis $[RhCl_4(H_2O)_2]^{1-}$ and fac $RhCl_3(H_2O)_3$. In the present study, the solution of Rhodium(III) chloride was prepared in 3M solution of hydrochloric acid . In view of reported literature on the preparation of various complexes formed between Rhodium(III) and chloride ion in dilute hydrochloric acid and also on the basis of spectrum collected for Rhodium(III) chloride solution, it can be concluded that at the time of preparation of Rhodium(III) chloride solution, the lone species present is $[RhCl_6]^{3-}$ (Fig. 3(1)). With the dilution of Rhodium(III) chloride solution there is every possibility of converting $[RhCl_6]^{3-}$ into $[RhCl_5(H_2O)]^{2-}$, $[RhCl_4(H_2O)_2]^{1-}$ and $RhCl_3(H_2O)_3$. Equilibrium reactions producing species $[RhCl_5(H_2O)]^{2-}$, $[RhCl_4(H_2O)_2]^{1-}$ and $RhCl_3(H_2O)_3$ from the original solution of Rhodium(III) chloride in which concentration of HCl was maintained at 3M can be shown as follows,

$$[RhCl_6]^{3-} + H_2O \rightleftharpoons [RhCl_5(H_2O)]^{2-} + Cl^- \quad (V)$$

$$[RhCl_5(H_2O)]^{2-} + H_2O \rightleftharpoons [RhCl_4(H_2O)_2]^{1-} + Cl^- \quad (VI)$$

$$[RhCl_4(H_2O)_2]^{1-} + H_2O \rightleftharpoons RhCl_3(H_2O)_3 + Cl^- \quad (VII)$$

It is clear from above equilibria (V, VI and VII) that the species $[RhCl_6]^{3-}$ present in 3M HCl solution changes into $[RhCl_5(H_2O)]^{2-}$, $[RhCl_4(H_2O)_2]^{1-}$ and $RhCl_3(H_2O)_3$ with the dilution of Rhodium(III) chloride solution. Earlier [28], it is described that in between 0.07M and 2.00M concentration of Cl^- ion, the various species present are $[RhCl_4]^{1-}$, $[RhCl_5]^{2-}$ and $[RhCl_6]^{3-}$. At 0.035M concentration of Cl^- ion, the reported species is $RhCl_3$ whereas at 0.020M and 0.010M concentration of Cl^-, the reported species are $RhCl_2^+$ and $RhCl^{2+}$, respectively. Since throughout the study, the concentration of Cl^- ion is maintained at $3x\ 10^{-5}$M , hence is reasonable to assume that the neutral species $RhCl_3(H_2O)_3$ being lone species in the reaction can be considered as the reactive species of Rhodium(III) chloride in the oxidation of D-glucose by NBA in presence of perchloric acid.

Observed positive effect of $[Cl^-]$ 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 $[RhCl_4(H_2O)_2]^-$ is the reactive species of rhodium(III) chloride in the oxidation of glucose.

$$RhCl_3(H_2O)_3 + Cl^- \rightleftharpoons [RhCl_4(H_2O)_2]^- + H_2O$$

Role of mercuric acetate: It is reported [12, 15, 18] in the literature that in the oxidation of reducing sugars by NBA in acidic medium, $Hg(OAc)_2$ has been used as scavenger to eliminate Br^- ions. In the absence of mercuric acetate, the oxidation of reducing sugars by NBA is complicated by parallel oxidation with bromine which is librated by NBA. Hence parallel oxidation is obviated by using mercuric acetate and thus ensures that the oxidation proceeds solely through NBA. For certain reactions, Hg (II) is reported to acts as an oxidant. Therefore, to ascertain the role of mercury in the oxidation of glucose by NBA, efforts have also been made to assume whether in the absence of NBA and in the presence of Hg(II), the oxidation of glucose in presence of Rh(III)chloride and perchloric acid is possible or not? It is observed that the reaction does not proceed, showing that mercuric acetate does not play any role as an oxidant. 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 glucose by NBA alone throughout the course of reaction. Additionally it is also found that the rate of reaction decreases with the increase in mercuric acetate concentration. The reason for this result might be assumed as due to the formation of unreactive complex between a part of reactive species, $[RhCl_4(H_2O)(H_2OBr)]$ and mercury (II) in the reactions. Therefore , on the basis of kinetic observations, it can be assumed that the role of mercury (II) in our experimental findings is not only as scavengers for Br^- ions but also it acts as inhibitor by making an unreactive complex in the oxidation of glucose by NBA in acidic medium.

Spectroscopic evidence for the formation of complex or complexes in the reaction under investigation

In order to verify the formation of probable complex or complexes in the reaction, spectra for various solutions containing Rh(III) chloride, H^+ ,Cl^- solution, Rh(III) chloride, H^+ and Cl^- ion solution with two different concentrations of NBA solution and Rh(III), H^+, Cl^- ions and NBA solution with two different concentrations of Hg(II) solution have been collected at room temperature (Fig. 3). When spectra for Rh(III) chloride, H^+ and Cl^- ion solution with two different concentrations of NBA solutions were collected, it is found that with the increase in the concentration of NBA, there is an increase in absorbance from 2.92 to 3.04 and 3.12 (Fig.3(1,2 and 3)). The increase in absorbance with a shift in λ_{max} value towards longer wave length clearly shows that there is formation of a complex between $[RhCl_4(H_2O_2)]^-$ and $(H_2OBr)^+$ according to the following equilibrium

$$[RhCl_4(H_2O)_2]^- + (H_2OBr)^+ \rightleftharpoons [RhCl_4(H_2O)(H_2OBr)] + H_2O \qquad \text{(VIII)}$$

The shift in λ_{max} towards longer wave length with a significant increase in absorbance is due to combination of the reactive species of NBA which acts as a chromophore and an auxochrome Cl^- present in the complex to give rise to a new chromophore $[RhCl_4(H_2O)(H_2OBr)]$. Further, when two different solutions of Hg(II) (1.25×10^{-3}M and 3.33×10^{-3}M) have been added to the solution of Rh(III), Cl^-, H^+ and NBA, it is found that there is an increase in absorbance from 3.04 to 3.08 and 3.22 (Fig.3(b), (d) and (e)). The shift in λ_{max} towards longer wavelength and an increase in absorbance with the increase in Hg(II) concentrations can be considered as due to combination of a part of activated complex i.e. $[RhCl_4(H_2O)(H_2OBr)]$ with Hg(II) to form an unreactive complex of the type $[RhCl_4(H_2O)(H_2OBrHg)]^{2+}$ according to the following equilibrium,

$$[RhCl_4(H_2O)(H_2OBr)] + Hg^{2+} \rightleftharpoons [RhCl_4(H_2O)\ (H_2OBrHg)]^{2+} \quad \text{(IX)}$$

Hg(II), when combines with a complex $[RhCl_4(H_2O)\ (H_2OBr)]$ containing an auxochrome Cl^- produces another chromophore $[RhCl_4(H_2O)(H_2OBrHg)]^{2+}$ because Hg(II) is in itself a chromophore and as a result there is a shift in λ_{max} value towards longer wavelength with a significant increase in absorbance.

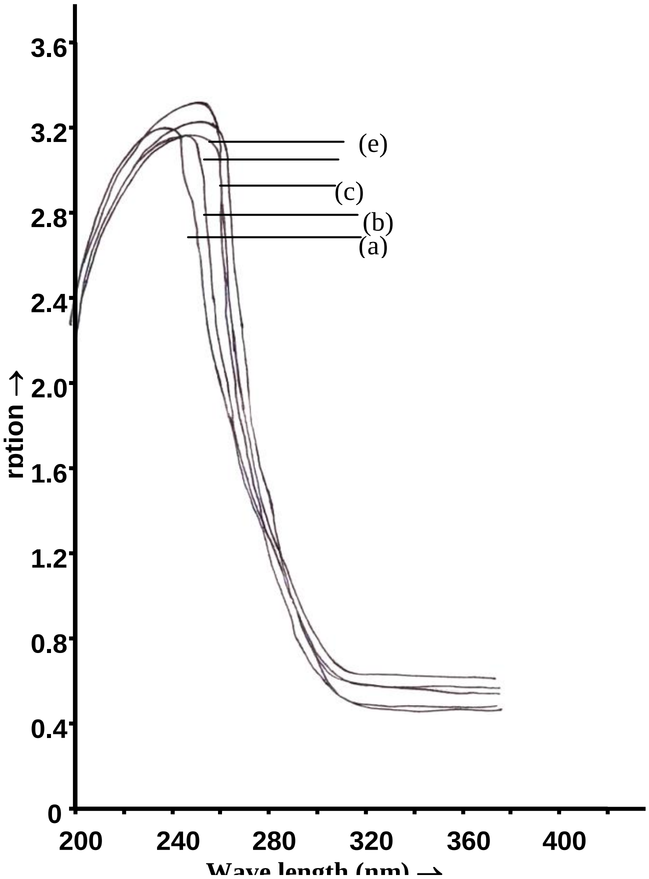


Fig.3. Spectra for various solutions containing Rh(III), H^+, Cl^- , NBA and Hg(II) at room temperature

(a) [Rh(III)] = 3.79×10^{-4}M
[H^+] = 1.00 M
[Cl^-] = 0.30 M
(b) [Rh(III)] = 3.79×10^{-4}M
[H^+] = 1.00 M
[NBA] = 1.00×10^{-3}M
(c) [Rh(III)] = 3.79×10^{-4}M
[H^+] = 1.00 M
[Cl^-] = 0.30 M
[NBA] = 2.00×10^{-3}M

(d) [Rh(III)] = 3.79×10^{-4}M
[H^+] = 1.00 M
[Cl^-] = 0.30 M
[NBA] = 1.00×10^{-3}M
[Hg(II)] = 1.25×10^{-3}M
(e) [Rh(III)] = 3.79×10^{-4}M
[H^+] = 1.00 M
[Cl^-] = 0.30 M
[NBA] = 1.00×10^{-3}M
[Hg(II)] = 3.33×10^{-3}M

The absorbance shown by NBA solution, Hg (II) solution and Rh(III), H^+ and Cl^-solution clearly supports the above experimental findings, where formation of the activated complex $[RhCl_4(H_2O)(H_2OBr)]$ and the formation of unreactive complex $[RhCl_4(H_2O)_2(H_2OBrHg)]^{2+}$ are indicated according to equilibrium (VIII) and (IX) respectively.

Mechanism and the Derivation of Rate Law: On the basis of kinetic orders with respect to each reactant, spectral information collected for the probable formation of complex or complexes in the reaction and taking cognizance of the effect of the dielectric constant of the medium and [NHA] on the rate of reaction as well as the activation parameters, a reaction scheme-1 for the reactions under investigation can be proposed in the following way:

$$MeCONHBr + H_2O \overset{K_1}{\rightleftharpoons} \mathrm{MeCONH_2} + \mathrm{HOBr} \qquad \text{(i)}$$

(NBA) (NHA)

$$\mathrm{HOBr} + \mathrm{H^+} \overset{K_2}{\rightleftharpoons} \mathrm{(H_2OBr)^+} \qquad \text{(ii)}$$

$$RhCl_3(H_2O)_3 + Cl^- \overset{K_3}{\rightleftharpoons} [RhCl_4(H_2O)_2]^- + H_2O \qquad \text{(iii)}$$

$[C_1]$ $[C_2]$

$$[RhCl_4(H_2O)_2]^- + (H_2OBr)^+ \overset{K_4}{\rightleftharpoons} [RhCl_4(H_2O)(H_2OBr)] + H_2O \qquad \text{(iv)}$$

$[C_2]$ $[C_3]$

$$[RhCl_4(H_2O)(H_2OBr)] + Hg^{2+} \overset{K_5}{\rightleftharpoons} [RhCl_4(H_2O)\ (H_2OBrHg)]^{2+} \qquad \text{(v)}$$

$[C_3]$ unreactive complex $[C_4]$

$$[RhCl_4(H_2O)(H_2OBr)] + H_2O \xrightarrow[\text{rate determining step}]{k_6} [RhCl_3(H_2O)_2(H_2OBr)]^+ + Cl^- \qquad \text{(vi)}$$

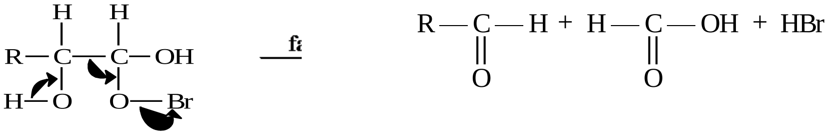
$[C_3]$ $[C_5]$

$$[RhCl_3(H_2O)_2(H_2OBr)]^+ + S \xrightarrow{\text{fast}} [RhCl_3(H_2O)SOBr]^{1-} + 2H^+ + H_2O \qquad \text{(vii)}$$

$[C_5]$ $[C_6]$

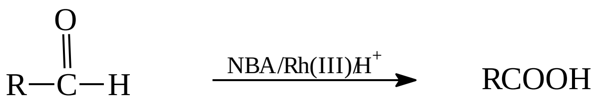
$$\mathrm{[RhCl_3(H_2O)SOBr]^{1-} + 3H_2O} \xrightarrow{\text{fast}} RhCl_3(H_2O)_3 + C_7 + OH^- \qquad \text{(viii)}$$

$[C_6]$



(ix)

$[C_7]$



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow{NBA/Rh(III)/H^+} RCOOH$$

(x)

Where R for glucose is $C_4H_9O_4$.

Scheme 1

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

$$rate = -\frac{d[NBA]}{dt} = nk_6\ [C_3] \qquad (1)$$

where n stands for 2 for glucose.

On applying the law of chemical equilibrium to steps (I)-(V), and taking total concentration of Rh(III) chloride at any moment in the reaction as $[Rh(III)]_T = [C_1]+[C_2]+[C_3]+[C_4]$,the rate in terms of disappearance of [NBA] can be shown as

$$rate = -\frac{d[NBA]}{dt} = \frac{2k_6K_1K_2K_3K_4[NBA][H^+][Rh(III)]_T\,[Cl^-]}{[NHA]+K_3[Cl^-][NHA]+K_1K_2K_3K_4[NBA][H^+][Cl^-]+K_1K_2K_3K_4K_5[NBA][H^+][Cl^-][Hg(II)]} \qquad (2)$$

Under our experimental conditions the inequality $K_1K_2K_3K_4K_5[NBA][H^+][Cl^-][Hg(II)]+[NHA] >> K_1K_2K_3K_4[NBA][H^+][Cl^-]+K_3[Cl^-][NHA]$ can be assumed as valid one and with this inequality Eq. (2) will be reduced to Eq. (3)

$$rate = -\frac{d[NBA]}{dt} = \frac{2k_6K_1K_2K_3K_4[NBA][H^+][Rh(III)]_T\,[Cl^-]}{[NHA]+K_1K_2K_3K_4K_5[NBA][H^+][Cl^-][Hg(II)]} \qquad (3)$$

Eq. (3) is the final rate law which clearly supports the first order kinetics with respect to [Rh(III)], less than unity order with respect to [NBA], fractional positive order with respect to $[H^+]$ and$[Cl^-]$ and fractional negative order with respect to [NHA] and [Hg(II)].

On reversing Eq.(3) we get Eq. (4)

$$\frac{[Rh(III)]_T}{rate} = \frac{[NHA]}{2k_6K_1K_2K_3K_4[NBA][H^+][Cl^-]} + \frac{K_5[Hg(II)]}{2k_6} \qquad (4)$$

According to equation (4), when a plot between $\frac{[Rh(III)]_T}{rate}$ vs. [NHA] for the oxidation of glucose was made, straight line having positive intercept on y-axis was obtained (Fig. 4). This proves the validity of rate law (3) and hence the proposed reaction scheme-1. From the slope and the intercept of the straight line, the values of $k_6K_1K_2K_3K_4$ and K_5/k_6 were calculated and found as 3.647 $mol^{-2}dm^6\ sec^{-1}$ and $3.60 \times 10^2\ mol^{-1}dm^3sec$, respectively for the oxidation of D-glucose. By substituting the values of $k_6K_1K_2K_3K_4$ and K_5/k_6 in equation (3) for the variation of [NHA], the rates of the reaction were calculated for each kinetic run and found to be very close to the experimental rates of the reaction (Table 2). This clearly confirms the validity of the rate law (3) and hence the proposed reaction scheme-1.

The observed positive entropy of activation in Rh(III)- catalysed oxidation of D(+) glucose supports the formation of most reactive activated complex, $[RhCl_4(H_2O)(H_2OBr)]$,where interaction is taking place between two oppositely charged species i.e. $[RhCl_4(H_2O_2)]^-$ and $(H_2OBr)^+$.

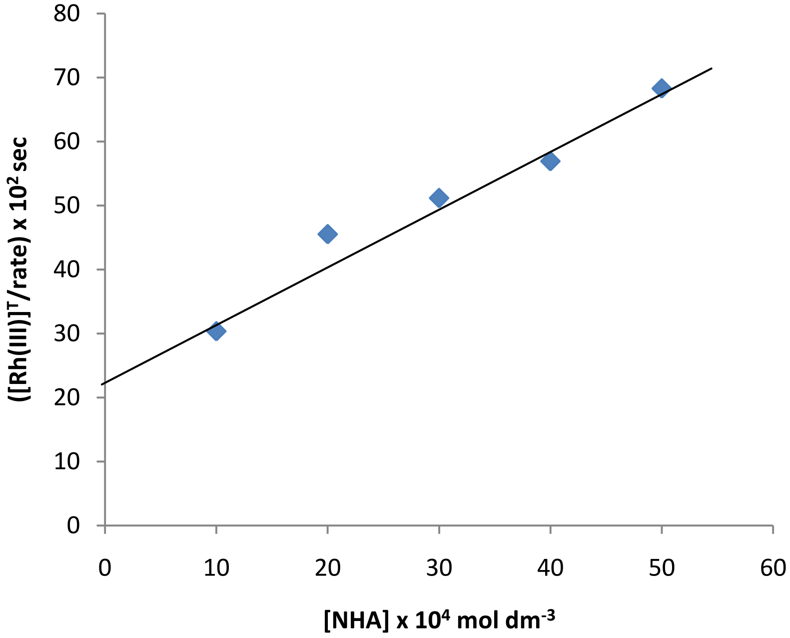


Fig 5: Plot between $\frac{[Rh(III)]_T}{rate}$ vs. [NHA] at 40°C

Comparative Studies: Efforts have been made to compare the findings of this paper with the results reported for Pd(II) [12] - and Ir(III) [15] - catalyzed oxidation of D- glucose by NBA in acidic medium. As far as order with respect to NBA is concerned, it is one to zero in all the three oxidation reactions. Based on kinetic parameters and spectrophotometric evidence, H_2OBr^+ has been concluded as the reactive species of NBA in Rh(III)- catalyzed oxidation as against HOBr in the reported Pd(II)- and Ir(III)- catalyzed oxidation. The zero order kinetics with respect to D(+) glucose in the present study is different from first to zero order reported for Pd(II)- catalyzed oxidation and shows similarity with Ir(III)- catalyzed oxidation where reducing sugar molecule takes part in the reaction after the rate determining step. When the role of catalyst Rh(III) in the present study was compared with the reported other two studies, it was found that the unity order in Rh(III) and Pd(II) is different from first to zero order in Ir(III) for the oxidation of glucose by NBA in acidic medium. The reactive species of Rh(III), Pd(II) and Ir(III) chloride in acidic medium are found as $[RhCl_4(H_2O)]^-$, $[PdCl_4]^{2-}$ and $[IrCl_5(H_2O)]^{2-}$, respectively. In the present study H^+ ions with fractional positive order play a very significant role in the formation of most reactive activated complex $[RhCl_4(H_2O)\ H_2OBr]$, but in other two reported studies their role is limited only in taking decision about the reactive species of NBA in acidic medium. The reported fractional positive order with respect to Hg(II) in Pd(II)- and second to first order in Ir(III)- catalyzed oxidation are entirely different from the fractional negative order observed in the present study of Rh(III)- catalyzed oxidation of glucose. The formation of an unreactive complex with Hg(II) distinguishes the present study from other two studies where Hg(II) plays a very important role in the formation of most reactive activated complex which in the rate determining step and subsequent steps disproportionate into product with regeneration of catalyst. The fractional positive order with respect to $[Cl^-]$ in the present study on one hand helps in deciding the reactive species of Rh(III) chloride in acidic medium and on the other hand it differs from the other two reported studies where a fractional negative order in $[Cl^-]$ has been observed. Negative effect of [NHA] on the rate of oxidation was observed in all the three cases. On the basis of the facts mentioned above, it can be said that the present study is different in many respect from other two studies reported earlier.

APPLICATIONS

A suitable reaction mechanism consistent with the observed kinetic data has been proposed for Rh(III)-catalyzed oxidation of D(+) glucose by NBA in acidic medium.

CONCLUSIONS

The following conclusions were drawn from the observed kinetic data and spectral information collected for Rh(III)-catalyzed oxidation of D(+) glucose by NBA in acidic medium.

1. $(H_2OBr)^+$ and $[RhCl_4(H_2O_2)]^-$ have been assumed as the reactive species of NBA and Rh(III) chloride in acidic medium, respectively.
2. The reaction exhibits first-order kinetics with respect to NBA at it low concentration tending towards zero order at its higher concentrations and zero-order kinetics with respect to [glucose].
3. Positive effects for $[H^+]$ and $[Cl^-]$ and negative effects for $[Hg(OAc)_2]$ and [NHA] have been observed in the oxidation of glucose.
4. The formation of an unreactive complex with Hg (II) indicating its role as an inhibitor is the peculiar feature of the present study.
5. The observed positive entropy of activation supports the interaction between two oppositely charged species $[RhCl_4(H_2O_2)]^-$ and $(H_2OBr)^+$ resulting in the formation of most reactive activated complex, $[RhCl_4(H_2O)(H_2OBr)]$.

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