Mechanistic studies of oxidation of D-arabinose and D-mannose by acidic solution of *N*-bromoacetamide in presence of chloro-complex of Ru(III) as homogeneous catalyst

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Abstract

The present paper deals with the kinetics and mechanism of Ru(III)-catalyzed and Hg(II)-*co*-catalyzed oxidation of D-arabinose(ara) and D-mannose(man) by acidic solution of *N*-bromoacetamide(NBA). First-order dependence of the reaction on both NBA and sugar at low concentrations shifts to zero-order at their higher concentrations. First-order kinetics with respect to [Ru(III)] throughout its variation was observed in the oxidation of both arabinose and mannose. A positive effect on the oxidation rate is observed for [Hg(II)] and [Cl$^-$] whereas a negative effect is observed for [H$^+$] and [acetamide]. Ionic strength does not influence the oxidation rate. The decrease in the rate of reaction with the increase in dielectric constant (D) of the medium was observed in the oxidation of both reducing sugars and the kinetic data thus obtained were utilized to calculate d_{AB}, the size of activated complex. Various activation parameters have also been calculated. Formic acid and erythronic acid for arabinose and formic acid and arabinonic acid for mannose were identified as main oxidation products of the reactions. Kinetic and equivalence studies together with spectral information, observed effect of dielectric constant on the rate of reaction, activation parameters and multiple regression analysis were made a basis for the formation of a common reaction mechanism for the catalyzed oxidation of both, arabinose and mannose.
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Keywords: Kinetics; *N*-Bromoacetamide oxidation; Arabinose; Mannose; Ruthenium(III) chloride catalysis; Perchloric acid medium

1. Introduction

N-Halo compounds, a group of mild oxidizing agents, have been extensively used for the catalyzed [1–5] and unanalyzed [6–9] oxidation of a variety of organic compounds. Under different conditions, these *N*-halo compounds [10] also react with olefins to add bromine to the double bond or act as source of hypohalous acid in aqueous solution. NBA has been widely used as an oxidizing and halogenating agent in preparative organic chemistry. The facile oxidative degradation of α-amino acids, peptide cleavages and reaction of human and bovine serum by *N*-halo compounds have also been reported [10] earlier. NBS or NBA [10] offers a specific and rapid methods for fragmenting high molecular weight peptides and proteins to smaller ones. A large number of examples are available in literature [10] which illustrate the use of *N*-bromo compounds for the introduction

of supplementary double bonds into the steroid nucleus. The action of NBA on α- and β-carotene has been studied in detail by Zechmeister and co-workers [10]. Besides fulfilling specific nutritional or pharmacological roles, sugars may also have therapeutic or pharmacological actions [11]. Mechanistic studies of the oxidation of the reducing sugars by NBA or NBS using transition metal ions such as Ru(VIII) [12], Pd(II) [1,3–5], Ir(III) [13] and Pt(IV) [14] as homogeneous catalyst are reported in acidic or alkaline medium. Reports regarding Ru(III)-catalysis in the oxidation of organic compounds by acidic solution of *N*-bromosuccinimide [15] and *N*-bromoacetamide [16,17] are also available in the literature. But to the best of our knowledge, there is only one report [2], where the oxidation of galactose and ribose by acidic solution of NBA in the presence of Ru(III) as homogeneous catalyst have been studied. In this study [2] the species, (RuCl$_6$)$^{3-}$, has been reported as the reactive species of Ru(III) chloride in acidic medium. In view of scant information available on the catalytic role of Ru(III) in the oxidation of reducing sugars by NBA in acidic medium and in order to probe the oxidative capacity of NBA with biologically important substrates

like reducing sugars, the present study has been undertaken. In this paper, an attempt has also been made to ascertain that which of the four species, i.e. $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$ of Ru(III) chloride existing in the pH range 0.4–2.0 can be chosen as the reactive species for the redox reactions under investigation?
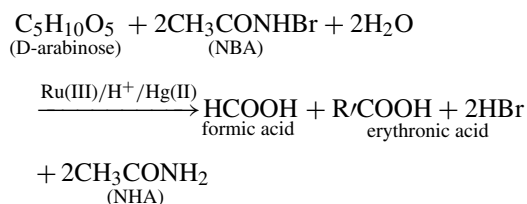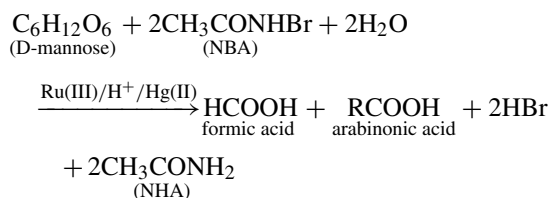
2. Experimental

An aqueous solution of NBA (E Merck) was prepared afresh by dissolving a weighed amount in doubly distilled water. The solution was standardized iodometrically against standard solution of sodium thiosulphate using starch as an indicator. The prepared solution was preserved in black-coated flask in order to avoid photochemical deterioration. The solution of Ru(III) chloride (Ubichem Limited) was prepared by dissolving the sample in hydrochloric acid of known strength. Aqueous solutions of sugars were prepared fresh each day. A standard solution of mercuric acetate (E Merck) was acidified with 20% acetic acid. Perchloric acid (E Merck) which is used in the reaction as a source of H^+ ions, was diluted with double distilled water and was standardized via acid base titration. All other standardized solutions of KCl, NaClO$_4$ and acetamide (E Merck) were prepared with double distilled water.

The reactants, i.e. NBA, Hg(OAc)$_2$, HClO$_4$, KCl, NaClO$_4$, NHA (acetamide) and Ru(III), was mixed in a black coated conical flask and thermostated at 40 °C for thermal equilibrium. A measured amount of sugar solution, also equilibrated at the same temperature, was rapidly added to the reaction mixture. The progress of the reaction was followed by measuring the unconsumed NBA iodometrically.

3. Stoichiometry and product analysis

Different sets of experiments with varying [NBA]:[sugar] ratios were performed for 72 h at room temperature and at constant concentrations of all other reactants under the conditions [NBA] ≫ [sugar]. Estimation of unconsumed [NBA] in different sets shows that 2 moles of NBA were consumed by 1 mole of each reducing sugar. Considering the fact that 1 mole of arabinose or mannose is oxidized by 2 moles of NBA, the following stoichiometric equations can be formulated

$$C_6H_{12}O_6 + 2CH_3CONHBr + 2H_2O$$
(D-mannose)   (NBA)

$$\xrightarrow{Ru(III)/H^+/Hg(II)} HCOOH + RCOOH + 2HBr$$
formic acid   arabinonic acid

$$+ 2CH_3CONH_2$$
(NHA)

$$C_5H_{10}O_5 + 2CH_3CONHBr + 2H_2O$$
(D-arabinose)   (NBA)

$$\xrightarrow{Ru(III)/H^+/Hg(II)} HCOOH + R'COOH + 2HBr$$
formic acid   erythronic acid

$$+ 2CH_3CONH_2$$
(NHA)

where

$$R = (CHOH)_3CH_2OH \quad and \quad R' = (CHOH)_2CH_2OH$$

Formic acid and erythronic acid in the case of D-arabinose and formic acid and arabinonic acid in the case of D-mannose were identified as the main oxidation products by the help of kinetic studies, equivalence, TLC and conventional spot test methods.

4. Results

Oxidation kinetics of D-arabinose and D-mannose by NBA have been investigated in the presence of acidic solution of ruthenium(III) chloride at different concentrations of reactants. The rate, i.e. $(-dc/dt)$ 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

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

Uniform pseudo first-order rate constant (k_1) values in the lower range of [NBA] clearly shows that the order with respect to [NBA] is unity, whereas decrease in k_1 values with the increase in [NBA] shows deviation from first-order kinetics at its higher concentrations (Table 1). Since throughout the study the concentration of NBA was fixed at its low concentration, hence for the purpose of calculation of pseudo-first-order rate constant, k_1, order with respect to NBA has been taken as unity in the oxidation of both, arabinose and mannose. In order to study the effect of [sugar] on the rate of reaction, the reactions have been studied with ten-fold variation in [sugar] at constant concentrations of all other reactants and at constant temperature, 40 °C. First- to

Table 1
Effect of variation of [NBA], [S] and [Ru(III)] on the rate of oxidation of D-arabinose and D-mannose at 40 °C

[NBA] × 10^4 (M)	[S] × 10^2 (M)	[Ru(III)] × 10^6 (M)	k_1 × 10^4 (s^{-1})	
			D-Arabinose	D-Mannose
2.50[a]	2.00	4.58	3.42	3.88
5.00[a]	2.00	4.58	3.36	3.60
10.00[a]	2.00	4.58	3.45	3.75
15.00[a]	2.00	4.58	2.90	3.65
17.50[a]	2.00	4.58	2.83	3.17
22.50[a]	2.00	4.58	2.39	2.60
10.00[b]	1.00	4.58	1.94	1.85
10.00[b]	2.00	4.58	3.25	3.34
10.00[b]	4.00	4.58	6.85	5.25
10.00[b]	6.00	4.58	7.99	7.65
10.00[b]	8.00	4.58	9.06	10.45
10.00[b]	10.00	4.58	9.85	12.05
10.00[b]	2.00	1.22	0.75	1.11
10.00[b]	2.00	3.05	1.82	2.45
10.00[b]	2.00	4.58	3.45	3.37
10.00[b]	2.00	6.10	4.85	5.95
10.00[b]	2.00	9.16	6.16	8.85
10.00[b]	2.00	12.21	8.75	12.65

Solution conditions: [Hg(OAc)$_2$] = [a]3.00 × 10^{-3} M (in [NBA] variation) and [b]1.25 × 10^{-3} M (in [S] and [Ru(III)] variations). [HClO$_4$] = 13.33 × 10^{-3} M, [KCl] = 3.00 × 10^{-4} M. [NHA] = [a]3.50 × 10^{-3} M (in [NBA] variation) and [b]1.11 × 10^{-3} M (in [S] and [Ru(III)] variations). μ = 5.00 × 10^{-2} M.

Table 2
Effect of variation of [HClO$_4$], [Hg(OAc)$_2$], [KCl] and [NHA] on the rate of oxidation of D-arabinose and D-mannose at 40 °C

[HClO$_4$] × 10^3 (M)	[Hg(OAc)$_2$] × 10^3 (M)	[KCl] × 10^4 (M)	[NHA] × 10^3 (M)	k_1 × 10^4 (s^{-1})	
				D-Arabinose	D-Mannose
1.00	1.25	3.00	1.11	14.85	15.65
2.00	1.25	3.00	1.11	12.62	8.75
4.00	1.25	3.00	1.11	7.24	6.25
6.00	1.25	3.00	1.11	5.50	4.25
8.00	1.25	3.00	1.11	4.37	3.90
10.00	1.25	3.00	1.11	3.68	3.05
13.33	1.11	3.00	1.11	1.99	2.35
13.33	2.00	3.00	1.11	3.95	4.50
13.33	4.00	3.00	1.11	6.03	6.45
13.33	6.00	3.00	1.11	8.32	8.15
13.33	8.00	3.00	1.11	10.47	8.75
13.33	10.00	3.00	1.11	11.08	9.65
13.33	1.25	1.60	1.11	2.18	2.55
13.33	1.25	2.60	1.11	3.05	3.33
13.33	1.25	3.60	1.11	3.65	3.75
13.33	1.25	4.60	1.11	3.95	3.95
13.33	1.25	5.60	1.11	4.25	4.15
13.33	1.25	6.60	1.11	4.65	4.35
13.33	1.25	3.00	1.00	3.85	5.38
13.33	1.25	3.00	2.00	3.66	2.85
13.33	1.25	3.00	4.00	1.99	2.15
13.33	1.25	3.00	6.00	1.42	1.53
13.33	1.25	3.00	8.00	1.08	1.30
13.33	1.25	3.00	10.00	0.85	0.96

Solution conditions: [NBA] = 10.00 × 10^{-4} M, [S] = 2.00 × 10^{-2} M. [Ru(III)] = 4.58 × 10^{-6} M, μ = 5.00 × 10^{-2} M.

Table 3
Energy of activation and other activation parameters observed for the oxidation of D-arabinose and D-mannose at 40 °C

Reducing sugars	E_a (kJ mol^{-1})	k (mol^{-2} dm^6 s^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	A (mol^{-2} dm^6 s^{-1})
D-Arabinose	52.46	2.86 × 10^5	7.50	49.83	51.92	1.45 × 10^{15}
D-Mannose	63.20	1.02 × 10^5	32.35	60.57	51.30	0.31 × 10^{15}
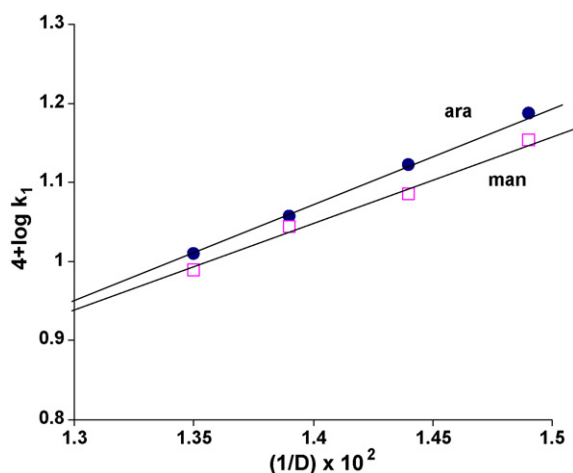
Fig. 1. Plots between $(4 + \log k_1)$ and $1/D$ at 40 °C [NBA] = 1.00 × 10^{-3} M; [sugar] = 2.00 × 10^{-2} M; [Ru(III)] = 4.58 × 10^{-6} M; [H$^+$] = 13.33 × 10^{-3} M; [Hg(II)] = 1.25 × 10^{-3} M; [NHA] = 1.11 × 10^{-3} M; [Cl$^-$] = 3.00 × 10^{-4} M; μ = 500 × 10^{-2} M.

zero-order kinetics with respect to each arabinose and mannose was observed up to their 10-fold variations (Table 1). Both the systems follow unity order in [Ru(III)] and show positive effects of [Hg(II)] and [Cl$^-$] on the rate of oxidation (Tables 1 and 2). Table 2 shows decrease in pseudo-first-order rate constant, k_1, with the increase in [H$^+$] and [NHA] indicating negative effects of [H$^+$] and [NHA] on the rate of reaction. Variation in ionic strength of the medium did not bring about any significant change in k_1 values under the constant experimental conditions. In the oxidation of both reducing sugars, it is found that the rate of reaction decreases with the increase in dielectric constant (D) of the medium (Fig. 1). The reactions were also studied at 30, 35, 40 and 45 °C and with the help of the values of the rate constant, k_1, the energy of activation and other activation parameters were calculated for the oxidation of both arabinose and mannose (Table 3).
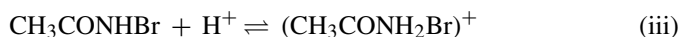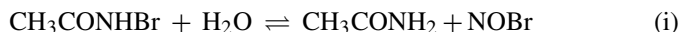
5. Test for free radicals

To test the presence of free radicals in the reaction, the reaction mixture with acrylamide was placed in an inert atmosphere

for 24 h. When the reaction mixture was diluted with methanol, it is found that there is no precipitate in the reaction mixture. This clearly shows that there is no formation of free radicals in the redox reactions under investigation.

6. Discussion

6.1. Reactive species of NBA

Two sets of equilibria showing the existence of NBA in acidic medium are reported [8,9,2–5] as under

$$CH_3CONHBr + H_2O \rightleftharpoons CH_3CONH_2 + NOBr \qquad (i)$$

$$HOBr + H^+ \rightleftharpoons H_2OBr^+ \qquad (ii)$$

$$CH_3CONHBr + H^+ \rightleftharpoons (CH_3CONH_2Br)^+ \qquad (iii)$$

$$(CH_3CONH_2Br)^+ + H_2O \rightleftharpoons CH_3CONH_2 + H_2OBr^+ \qquad (iv)$$

From the above two sets of equilibria, it is clear that there are four possible reactive species, i.e NBA itself, HOBr, $(CH_3CONH_2Br)^+$ and $(H_2OBr)^+$ of NBA in acidic medium. If NBA or $(CH_3CONH_2Br)^+$ is taken as the reactive species of NBA, then it will lead to a rate law which is incapable of explaining observed negative effect of [acetamide] on the rate of reaction. The species $(H_2OBr)^+$ can also not be considered as the reactive species because if with this reactive species, a reaction scheme is formulated and a rate law is derived then this rate law will show first-order kinetics with respect to $[H^+]$, which is contrary to the observed negative effect of $[H^+]$ on the rate of reaction, although it fully explains the negative effect of acetamide. At this stage we are left with no option but to assume HOBr as the reactive species of NBA in the oxidation of arabinose and mannose. When this species is taken as the reactive species of NBA in the oxidation of both arabinose and mannose, the derived rate law fully explains not only the observed negative effect of [acetamide] but also the fractional negative order in $[H^+]$.

6.2. Reactive species of ruthenium(III) chloride

It is reported that with the use of electrochemical and spectrophotometric techniques, a study for the chloro complexes of Ru(III) in 0.1 M KCl at pH 0.4, 1.0 and 2.0 and at temperature 25 °C has been made by M.M. Taqui Khan and co-workers [18]. Their report shows that at the instant of preparation, Ru(III) exists in solution in the pH range 0.4–2.0 as four major species, i.e. $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$. Out of these four species, the species $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$ and $[RuCl(H_2O)_5]^{2+}$ are reported to be fairly stable at pH 0.4, moderately stable at pH 1.0 and highly unstable at pH 2.0. It is also reported that the species $[RuCl_2(H_2O)_4]^+$ is fairly stable at pH 2.0 and is stabilized in its hydrolyzed form, $[RuCl_2(H_2O)_3OH]$, according to the following equilibrium (v).

$$[RuCl_2(H_2O)_4]^+ + H_2O \rightleftharpoons [RuCl_2(H_2O)_3OH] + H_3O^+ \quad (v)$$

In the present investigation pH of the solution was maintained at about 2.0 throughout the study and Ru(III) chloride, which is used as homogeneous catalyst, has been prepared by dissolving Ru(III) chloride in 0.01 M HCl, hence in the absence of any significant effect of $[Cl^-]$ on the rate of oxidation, the hydrolysed species, $[RuCl_2(H_2O)_3OH]$, can be taken as the reactive species of Ru(III) chloride in acidic medium. But it is apparent from observed kinetic data that there is positive effect of $[Cl^-]$ on the rate of oxidation of both the reducing sugars. When positive effect of $[Cl^-]$ on the rate of reaction is taken into consideration, then we are forced to assume that the following equilibrium is in existence in the reactions under investigation.
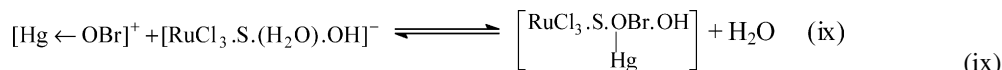
$$[RuCl_2(H_2O)_3OH] + Cl^- \rightleftharpoons [RuCl_3(H_2O)_2OH]^- + H_2O$$

$$(vi)$$
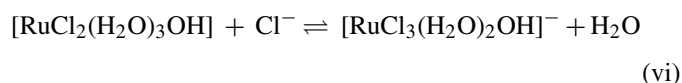
Out of the two species, $[RuCl_2(H_2O)_3OH]$ and $[RuCl_3(H_2O)_2OH]^-$, the species $[RuCl_3(H_2O)_2OH]^-$ can be assumed as the reactive species of Ru(III) chloride because only with this species, the observed fractional positive effect of $[Cl^-]$ on the rate of oxidation of arabinose and mannose can be justified. Our assumption for the reactive species of Ru(III) chloride and for the existence of equilibrium (vi) in the reactions under study is supported by the observed spectra of Ru(III) chloride solution alone and Ru(III) chloride solution with two different concentrations of chloride ions, where with the increase of chloride ions, an increase in absorbance from 2.96 to 3.00 and 3.06 was noted (Fig. 2: (1), (2), (3)). The increase in absorbance with the increase in chloride ion concentration is due to more and more formation of the reactive species, $[RuCl_3(H_2O)_2OH]^-$, according to the equilibrium (vi) indicated above.

6.3. Spectral evidence for the reactions shown in the proposed reaction scheme

With the reported [2,19] fact that Ru(III) forms a complex with sugar molecule, when we have proceeded to verify the existence of [Ru(III)–sugar] complex and to probe the possibility of formation of other complexes spectrophotometrically, it is found that the complex of the types $[RuCl_3 \cdot S \cdot (H_2O)OH]^-$, $[Hg \leftarrow OBr]^+$ and $\begin{bmatrix} RuCl_3 .S.OBr.OH \\ | \\ Hg \end{bmatrix}$ are formed in the reaction. When spectra of Ru(III) chloride and KCl solution and Ru(III) chloride and KCl solution with two different concentrations of sugar solution were recorded, it is found that there is an increase in absorbance from 3.00 to 3.14 and 3.22 (Fig. 2: (2), (9) and (10)) at 230 nm. The increase in absorbance with the addition of sugar solution can be considered as due to more and more formation of the complex, $[RuCl_3 \cdot S \cdot (H_2O)OH]^-$, according to the following equilibrium:

$$[RuCl_3(H_2O)_2OH]^- + S \rightleftharpoons [RuCl_3(H_2O)_2OH]^- + H_2O$$

$$(vii)$$
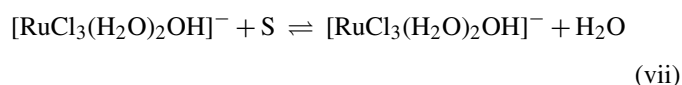
Further, when spectra of NBA solution alone and NBA solution with two different concentrations of Hg(II) were collected, an increase in absorbance from 1.44 to 2.12 and 2.24 was noted (Fig. 2: (5), (7) and (8)) showing the formation of a complex, $[Hg \leftarrow OBr]^+$, according to the following equilibrium:

$$[Hg \leftarrow OBr]^+ + [RuCl_3 \cdot S \cdot (H_2O) \cdot OH]^- \rightleftharpoons \begin{bmatrix} RuCl_3 \cdot S \cdot OBr \cdot OH \\ | \\ Hg \end{bmatrix} + H_2O \quad (ix)$$

$$Hg^{2+} + HOBr \rightleftharpoons [Hg \leftarrow OBr]^+ + H^+ \qquad (viii)$$

In the last, a possibility for the formation of a complex between the species $[Hg \leftarrow OBr]^+$ and $[RuCl_3 \cdot S \cdot (H_2O)OH]^-$ was also ascertained by recording the spectra of the solution of Ru(III) chloride, KCl and sugar and the solution of Ru(III) chloride, KCl, sugar and NBA with two different concentrations of Hg(II), where an increase in absorbance from 3.14 to 3.36 and 3.44 with a shift in λ_{max} value towards longer wavelength was observed (Fig. 2: (9), (11) and (12)). This result shows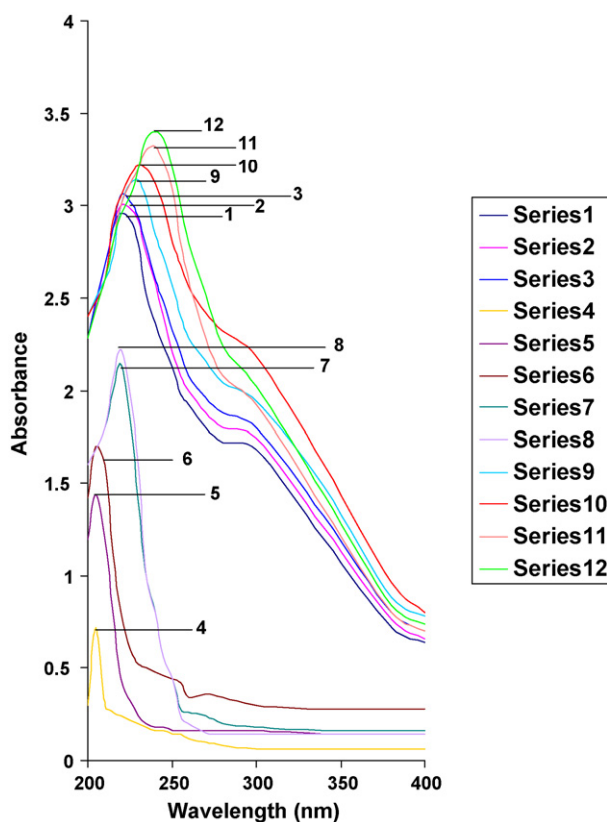 that with the addition of NBA and Hg(II) solution to the solution of Ru(III) chloride, KCl and sugar, more and more formation of a new complex, $\begin{bmatrix} RuCl_3 \cdot S \cdot OBr \cdot OH \\ | \\ Hg \end{bmatrix}$, takes place indicating the existence of the reaction in the form of equilibrium (ix).

The observed increase in absorbance with a shift in λ_{max} value towards longer wavelength not only supports the formation of a new complex, $\begin{bmatrix} RuCl_3 \cdot S \cdot OBr \cdot OH \\ | \\ Hg \end{bmatrix}$, but it also supports the fact that a chromophore (Hg(II)) after combining with an auxochrome (Cl$^-$ ion) gives rise to another chromophore, $\begin{bmatrix} RuCl_3 \cdot S \cdot OBr \cdot OH \\ | \\ Hg \end{bmatrix}$. The stoichiometry of the complex, $\begin{bmatrix} RuCl_3 \cdot S \cdot OBr \cdot OH \\ | \\ Hg \end{bmatrix}$, was further verified by recording spectra of the solution of Ru(III) chloride, KCl, sugar and NBA with more concentrations of Hg(II) and the observed data were utilized to make Job's plot [20] between $1/\Delta A$ and $1/[Hg(II)]$ (Fig. 3). ΔA on y-axis represents the difference in the absorbance of the solution with Hg(II) and that of the solution without Hg(II). The straight line with positive intercept on $1/\Delta A$ axis clearly supports the formation of 1:1 complex [21], $\begin{bmatrix} RuCl_3 \cdot S \cdot OBr \cdot OH \\ | \\ Hg \end{bmatrix}$, between $[RuCl_3 \cdot S \cdot (H_2O)OH]^-$ and $[Hg \leftarrow OBr]^+$.

6.4. Reaction scheme

Taking into account the reactive species of NBA and Ru(III) chloride and also the observed kinetic effects of [NBA], [reducing sugar], [Ru(III)], [H$^+$], [Hg(II)], [Cl$^-$], [NHA], ionic strength and dielectric constant of the medium on the rate of

Fig. 2. Spectra: (1) [Ru(III)] = 6.65 × 10^{-4} M; (2) [Ru(III)] = 6.65 × 10^{-4} M; [Cl$^-$] = 5.00 × 10^{-3} M; (3) [Ru(III)] = 6.65 × 10^{-4} M; [Cl$^-$] = 25.00 × 10^{-3} M; (4) [sugar] = 20 × 10^{-2} M; (5) [NBA] = 5.00 × 10^{-4} M; (6) [Hg(II)] = 5.00 × 10^{-4} M; (7) [NBA] = 5.00 × 10^{-4} M; [Hg(II)] = 5.00 × 10^{-4} M; (8) [NBA] = 5.00 × 10^{-4} M; [Hg(II)] = 20.00 × 10^{-4} M; (9) [Ru(III)] = 7.63 × 10^{-4} M; [Cl$^-$] = 5.00 × 10^{-3} M; [sugar] = 20.00 × 10^{-2} M; (10) [Ru(III)] = 7.63 × 10^{-4} M; [Cl$^-$] = 5.00 × 10^{-3} M; [sugar] = 80.00 × 10^{-2} M; (11) [Ru(III)] = 7.63 × 10^{-4} M; [Cl$^-$] = 5.00 × 10^{-3} M; [sugar] = 20.00 × 10^{-2} M; [NBA] = 5.00 × 10^{-4} M; [Hg(II)] = 5.00 × 10^{-4} M; (12) [Ru(III)] = 7.63 × 10^{-4} M; [Cl$^-$] = 5.00 × 10^{-3} M; [sugar] = 20.00 × 10^{-2} M; [NBA] = 5.00 × 10^{-4} M; [Hg(II)] = 20.00 × 10^{-4} M.

Fig. 3. Plot between $1/\Delta A$ and $1/[Hg(II)]$ [Ru(III)] = 7.63 × 10^{-4} M; [Cl$^-$] = 5.00 × 10^{-3} M; [sugar] = 20.00 × 10^{-2} M; [NBA] = 5.00 × 10^{-4} M.

oxidation along with the existence of several equilibrium steps supported by the spectral information, a most probable reaction scheme as given below has been proposed for the oxidation of both D-arabinose and D-mannose and is supported by entropy of activation and multiple regression analysis.

6.4.1. Reaction scheme

$$\text{NBA} + \text{H}_2\text{O} \overset{K_1}{\rightleftharpoons} \text{NHA} + \text{HOBr} \tag{I}$$

$$\underset{(C_1)}{[\text{RuCl}_2(\text{H}_2\text{O})_3\text{OH}]} + \text{Cl}^- \overset{K_2}{\rightleftharpoons} \underset{(C_2)}{[\text{RuCl}_3(\text{H}_2\text{O})_2\text{OH}]^-} + \text{H}_2\text{O} \tag{II}$$

$$\underset{(C_2)}{[\text{RuCl}_3(\text{H}_2\text{O})_2\text{OH}]^-} + \text{S} \overset{K_3}{\rightleftharpoons} \underset{(C_3)}{[\text{RuCl}_3 \cdot \text{S} \cdot (\text{H}_2\text{O})\text{OH}]^-} + \text{H}_2\text{O} \tag{III}$$

$$\text{Hg}^{2+} + \text{HOBr} \overset{K_4}{\rightleftharpoons} \underset{(C_4)}{[\text{Hg} \leftarrow \text{OBr}]^+} + \text{H}^+ \tag{IV}$$
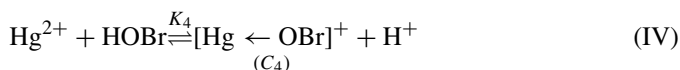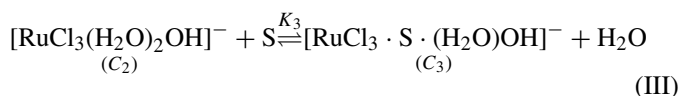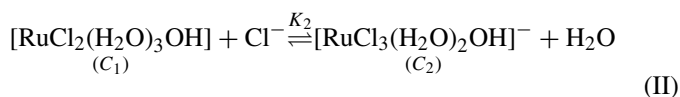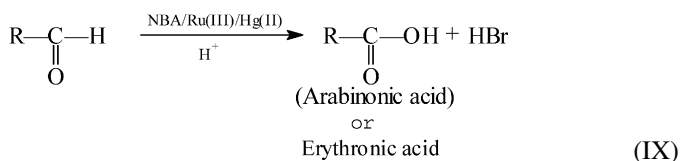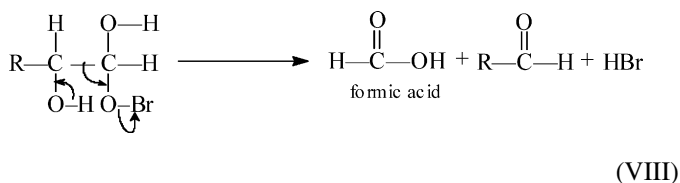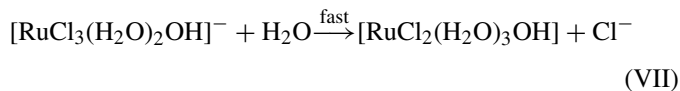
where 'S' stands for D-arabinose and D-mannose

$$\underset{(C_4)}{[\text{Hg} \leftarrow \text{OBr}]^+} + \underset{(C_3)}{[\text{RuCl}_3 \cdot \text{S} \cdot (\text{H}_2\text{O}) \cdot \text{OH}]^-} \overset{K_5}{\rightleftharpoons} \underset{(C_5)}{\left[\begin{array}{c} \text{RuCl}_3 \cdot \text{S} \cdot \text{OBr} \cdot \text{OH} \\ | \\ \text{Hg} \end{array} \right]} + \text{H}_2\text{O} \tag{V}$$

$$\left[\begin{array}{c} \text{RuCl}_3 \cdot \text{S} \cdot \text{OBr} \cdot \text{OH} \\ | \\ \text{Hg} \end{array} \right] + 2\text{H}_2\text{O} \xrightarrow[\text{determining step}]{\underset{\text{slow and rate}}{k_6}} [\text{RuCl}_3 \cdot (\text{H}_2\text{O})_2\text{OH}]^- + \text{OH}^- + \text{Hg}^{2+} + \overset{\text{OH}}{\underset{\text{H}}{\text{R}-\text{CH}}} - \overset{\text{OH}}{\underset{\text{OBr}}{\text{CH}}} \tag{VI}$$

(C_5)
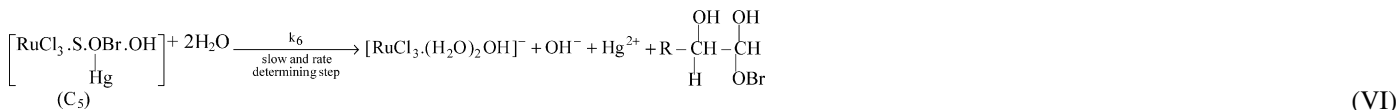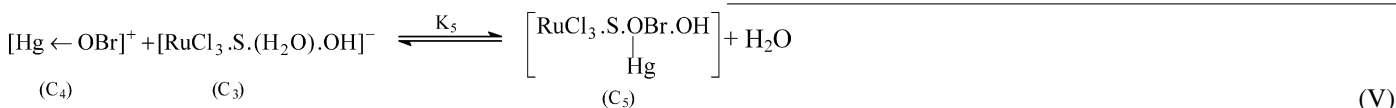
where 'R' stands for $\text{C}_4\text{H}_9\text{O}_4$ in the case of D-mannose and $\text{C}_3\text{H}_7\text{O}_3$ in the case of D-arabinose.

$$[\text{RuCl}_3(\text{H}_2\text{O})_2\text{OH}]^- + \text{H}_2\text{O} \xrightarrow{\text{fast}} [\text{RuCl}_2(\text{H}_2\text{O})_3\text{OH}] + \text{Cl}^- \tag{VII}$$

$$\tag{VIII}$$

$$\tag{IX}$$

According to the above reaction scheme and considering the fact that 1 mole of ara and man is oxidized by 2 moles of NBA, the rate in terms of decrease in the concentration of NBA can be expressed as:

$$\text{rate} = \frac{d[\text{NBA}]}{dt} = 2k_6[C_5] \tag{1}$$

On the basis of equilibrium steps (I)–(V), Eqs. (2)–(6) can be obtained in the following forms, respectively:

$$[\text{HOBr}] = \frac{K_1[\text{NBA}]}{[\text{NHA}]} \tag{2}$$

$$[C_2] = K_2[C_1][\text{Cl}^-] \tag{3}$$

$$[C_3] = K_2K_3[C_1][\text{S}][\text{Cl}^-] \tag{4}$$

$$[C_4] = \frac{K_1K_4[\text{NBA}][\text{Hg(II)}]}{[\text{NHA}][\text{H}^+]} \tag{5}$$

and

$$[C_5] = \frac{K_1K_2K_3K_4K_5[C_1][\text{S}][\text{NBA}][\text{Hg(II)}][\text{Cl}^-]}{[\text{NHA}][\text{H}^+]} \tag{6}$$

With the help of Eqs. (6) and (1), we can write Eq. (7) as:

$$\begin{aligned} \text{rate} &= -\frac{d[\text{NBA}]}{dt} \\ &= \frac{2k_6K_1K_2K_3K_4K_5[C_1][\text{S}][\text{NBA}][\text{Hg(II)}][\text{Cl}^-]}{[\text{NHA}][\text{H}^+]} \end{aligned} \tag{7}$$

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

$$[\text{Ru(III)}]_\text{T} = [C_1] + [C_2] + [C_3] + [C_5] \tag{8}$$

On substituting the values of $[C_2]$, $[C_3]$ and $[C_5]$ from Eqs. (3), (4) and (6), respectively, to Eq. (8), we get Eq. (9)

$$[C_1] = \frac{[\text{Ru(III)}]_\text{T}[\text{NHA}][\text{H}^+]}{\begin{aligned} &[\text{NHA}][\text{H}^+] + K_2[\text{Cl}^-][\text{NHA}][\text{H}^+] \\ &+ K_2K_4[\text{S}][\text{Cl}^-][\text{NHA}][\text{H}^+] \\ &+ K_1K_2K_3K_4K_5[\text{S}][\text{NBA}][\text{Hg(II)}][\text{Cl}^-] \end{aligned}} \tag{9}$$

From Eqs. (7) and (9), we get Eq. (10)

$$\begin{aligned} \text{rate} &= -\frac{d[\text{NBA}]}{dt} \\ &= \frac{2k_6K_1K_2K_3K_4K_5[\text{S}][\text{NBA}][\text{Hg(II)}][\text{Cl}^-][\text{Ru(III)}]_\text{T}}{\begin{aligned} &[\text{NHA}][\text{H}^+] + K_2[\text{Cl}^-][\text{NHA}][\text{H}^+] \\ &+ K_2K_4[\text{S}][\text{Cl}^-][\text{NHA}][\text{H}^+] \\ &+ K_1K_2K_3K_4K_5[\text{S}][\text{NBA}][\text{Hg(II)}][\text{Cl}^-] \end{aligned}} \end{aligned} \tag{10}$$

Table 4
Comparison of observed rates with the rates calculated[a] on the basis of rate law (10) and the rates calculated[b] by the help of multiple regression analysis under the conditions of Table 1

[Ru(III)] $\times 10^6$ (M)	$(-dc/dt) \times 10^7$ (mol l^{-1} s^{-1})					
	D-Arabinose			D-Mannose		
	Experimental	Calculated[a]	Calculated[b]	Experimental	Calculated[a]	Calculated[b]
1.22	0.75	0.82	0.73	0.85	0.78	0.69
3.05	1.82	1.69	1.98	2.75	2.90	2.56
4.58	3.45	3.66	3.58	3.55	3.88	3.96
6.10	4.85	5.05	5.12	5.65	5.72	5.86
9.16	7.35	7.56	7.08	7.15	7.02	7.34
12.21	9.65	9.88	9.39	9.05	9.32	9.16

Table 5
Comparison of observed rates with the rates calculated[a] on the basis of rate law (10) and the rates calculated[b] by the help of multiple regression analysis under the conditions of Table 2

[H$^+$] $\times 10^3$ (M)	$(-dc/dt) \times 10^7$ (mol l^{-1} s^{-1})					
	D-Arabinose			D-Mannose		
	Experimental	Calculated[a]	Calculated[b]	Experimental	Calculated[a]	Calculated[b]
1.00	15.06	15.06	14.68	15.65	15.88	15.42
2.00	12.62	12.82	12.43	8.75	8.92	8.96
4.00	7.24	7.05	7.36	6.25	6.43	6.38
6.00	5.50	5.46	5.28	4.25	4.08	7.42
8.00	4.37	4.66	4.52	3.90	3.66	3.83
10.00	3.68	3.72	3.56	3.05	3.18	3.27

Eq. (10) is the rate law on the basis of which observed kinetic orders with respect to each reactant of the reaction can very easily be explained.

On reversing Eq. (10), we have Eq. (11)

$$\frac{[Ru(III)]_T}{rate} = \frac{[NHA][H^+]}{2k_6 K_1 K_2 K_3 K_4 K_5 [S][NBA][Hg(II)][Cl^-]}$$
$$+ \frac{[NHA][H^+]}{2k_6 K_1 K_3 K_4 K_5 [S][NBA][Hg(II)]}$$
$$+ \frac{[NHA][H^+]}{2k_6 K_1 K_3 K_5 [NBA][Hg(II)]} + \frac{1}{2k_6} \quad (11)$$

Eq. (11), indicates that if a plot is made between [Ru(III)]$_T$/rate] and [NHA] or [H$^+$] or 1/[NBA] or 1/[Hg(II)] or 1/[S] or 1/[Cl$^-$], a straight line with positive intercept on *y*-axis will be obtained.

Straight lines with positive intercepts on *y*-axis obtained by the plots of [Ru(III)]$_T$/rate] versus [NHA], [H$^+$], 1/[NBA], 1/[Hg(II)], 1/[S] and 1/[Cl$^-$] on one hand proves the validity of the rate law (10) and on the other hand the proposed reaction scheme, on the basis of which the rate law (10) has been derived. From the values of the intercepts and slopes of the plots, the values of k_6, K_1, $K_3 K_5$, K_4 and K_2 have been calculated and found as 0.25 s^{-1}, 18.94, 20.8 and 12.02 $\times 10^3$ mol^{-1} l, respectively, for the oxidation of D-arabinose and 0.17 s^{-1}, 17.41, 49.99 and 8.84 $\times 10^3$ mol^{-1} l, respectively, for the oxidation of D-mannose. Utilizing these values of the constants, the reaction rates were calculated for the variations of [Ru(III)], [H$^+$], [Hg(II)], [Cl$^-$] and [NHA] and are presented in Tables 4–8 along with the experimental rates. Almost the same values of two rates, i.e. the calculated and observed, further proves the validity of the rate law (10) and hence the proposed reaction scheme.

Table 6
Comparison of observed rates with the rates calculated[a] on the basis of rate law (10) and the rates calculated[b] by the help of multiple regression analysis under the conditions of Table 2

[Hg(II)] $\times 10^3$ (M)	$(-dc/dt) \times 10^7$ (mol l^{-1} s^{-1})					
	D-Arabinose			D-Mannose		
	Experimental	Calculated[a]	Calculated[b]	Experimental	Calculated[a]	Calculated[b]
1.11	1.99	2.03	1.86	2.35	2.28	2.42
2.00	3.95	3.88	4.05	4.50	4.37	4.61
4.00	6.03	6.16	6.09	6.45	6.66	6.38
6.00	8.32	8.46	8.30	8.15	8.32	8.09
8.00	1047	1052	10.37	8.75	8.92	8.68
10.00	11.08	11.16	10.97	9.65	9.83	9.59

Table 7

Comparison of observed rates with the rates calculated[a] on the basis of rate law (10) and the rates calculated[b] by the help of multiple regression analysis under the conditions of Table 2

$[Cl^-] \times 10^4$ (M)	$(-dc/dt) \times 10^7$ (mol l^{-1} s^{-1})					
	D-Arabinose			D-Mannose		
	Experimental	Calculated[a]	Calculated[b]	Experimental	Calculated[a]	Calculated[b]
1.6	2.18	1.99	2.05	2.55	2.68	2.47
2.6	3.05	3.12	2.98	3.33	3.42	3.09
3.6	3.65	3.72	3.57	3.75	3.98	4.03
4.6	3.95	4.05	3.88	3.95	4.02	3.88
5.6	4.25	4.32	4.16	4.15	4.33	4.12
6.6	4.65	4.66	4.39	4.35	4.56	4.62

6.5. Multiple regression analysis

Efforts have been made to calculate the rates on the basis of equations of fitted model obtained by the multiple regression analysis for arabinose and mannose for the variation of each [Ru(III)], [H$^+$], [Hg(II)], [Cl$^-$] and [NHA]. The calculated rates in each case being very close to the observed rates clearly supports the rate equation (10) and hence the reactions shown in the proposed reaction scheme (Tables 4–8). Eqs. (12) and (13) shown below as fitted model equations were used to calculate the rates for the effects of [Ru(III)], [H$^+$], [Hg(II)], [Cl$^-$] and [NHA] on the rate of oxidation of arabinose and mannose

$$k_1 = [\text{ara}]^{0.80}[\text{Ru(III)}]^{1.14}[\text{H}^+]^{-0.64}[\text{Hg(II)}]^{0.60}$$
$$\times [\text{NHA}]^{-0.51}[\text{Cl}^-]^{0.44} \quad (12)$$

$$k_1 = [\text{man}]^{0.79}[\text{Ru(III)}]^{1.04}[\text{H}^+]^{-0.59}[\text{Hg(II)}]^{0.59}$$
$$\times [\text{NHA}]^{-0.46}[\text{Cl}^-]^{0.45} \quad (13)$$

where

$$k_1 = -\frac{d[\text{NBA}]/dt}{[\text{NBA}]}$$

6.6. Calculation of the size of activated complex (d_{AB}) in oxidation of D-arabinose and D-mannose

In order to calculate the size of the activated complex (d_{AB}) and also to study the effect of dielectric constant of the medium

(*D*) on the rate of oxidation, the percentage concentration of ethanol has been varied from 5 to 20% at constant concentrations of all other reactants and at a constant temperature of 40 °C. For each set, pseudo-first-order rate constant (k_1) has been calculated and it is found that there is an increase in the rate of reaction with the decrease in dielectric constant of the medium. The effect of dielectric constant of the medium on the rate constant of a reaction between two ions has been described by the well known Eq. (14) given below

$$\log k = \log k_0 - \frac{Z_A Z_B e^2 \tilde{N}}{2.303(4\pi \in_0)d_{AB}RT} \times \frac{1}{D} \quad (14)$$

where k_0 is the rate constant in a medium of infinite dielectric constant, Z_A and Z_B are the changes of reacting ions, d_{AB} refers to the size of activated complex, T is absolute temperature and D is dielectric constant of the medium.

Eq. (14) shows that if a plot is made between $\log k_1$ and 1/*D*, straight line having slope equal to $-Z_A Z_B e^2 \tilde{N}/ 2.303(4\pi \in_0)d_{AB}RT$ will be obtained. When $\log k_1$ values observed for the oxidation of ara and man were plotted against 1/*D*, straight lines shown in Fig. 1 were obtained. From the slopes of the straight lines, the values of d_{AB} have been calculated and found as 3.16 and 3.29 Å for arabinose and mannose, respectively. Positive slopes obtained in both the cases clearly supports step (VI) of the proposed reaction scheme, where the formation of most reactive activated complex, $\left[\begin{array}{c} \text{RuCl}_3.\text{S.OBr.OH} \\ | \\ \text{Hg} \end{array}\right]$, takes place by the interaction of two oppositely charged species, i.e. $[\text{Hg} \leftarrow \text{OBr}]^+$ and $[\text{RuCl}_3 \cdot \text{S} \cdot (\text{H}_2\text{O})\text{OH}]^-$. It is

Table 8

Comparison of observed rates with the rates calculated[a] on the basis of rate law (10) and the rates calculated[b] by the help of multiple regression analysis under the conditions of Table 2

$[\text{NHA}] \times 10^3$ (M)	$(-dc/dt) \times 10^7$ (mol l^{-1} s^{-1})					
	D-Arabinose			D-Mannose		
	Experimental	Calculated[a]	Calculated[b]	Experimental	Calculated[a]	Calculated[b]
1.00	3.85	3.92	4.03	5.38	4.98	5.05
2.00	3.66	3.88	3.57	2.85	2.95	3.03
4.00	1.99	2.02	1.79	2.15	2.20	2.16
6.00	1.42	1.43	1.37	1.53	1.62	1.48
8.00	1.08	1.15	1.18	1.30	1.28	1.19
10.00	0.85	0.83	0.74	0.96	0.87	0.88

reported [10] that although primary alcohols are oxidized by *N*-chlorosuccinimide, which is treated as strong oxidant but NBA or NBS fails to oxidize aliphatic primary alcohols. Later on, a report [8] came into existence which indicates that in the catalyzed range of [H$^+$] between 0.2 and 0.75 M, primary alcohols are oxidized by NBA. Since in the present study, ethanol was used only to vary the solvent composition and as a result the dielectric constant of the medium, it was necessary to verify whether ethanol is oxidized by NBA under our experimental conditions or not? In order to ascertain the role of ethanol, few experiments were performed by taking ethanol as an organic substrate in place of reducing sugar under our experimental conditions and it has been found that ethanol is not oxidized by NBA in the range of [H$^+$] between 1.00×10^{-3} and 13.33×10^{-3} M. Thus the observed increase in the rate of reaction with the addition of ethanol in the reaction mixture is only due to the change in the dielectric constant of the medium.

6.7. Role of entropy of activation and other activation parameters

On the basis of solvation theory, it has been concluded that in the case of a reaction between two ions of opposite charge, their union will result in a lowering of the net charge and due to this some frozen solvent molecules will be released with an increase of entropy. In the present study of Ru(III)-catalyzed oxidation of arabinose and mannose, observed positive entropy of activation($\Delta S^{\#}$) very well supports the reaction step VI shown in the proposed scheme, where the most reactive activated complex, $\begin{bmatrix} RuCl_3.S.OBr.OH \\ | \\ Hg \end{bmatrix}$, with zero net charge is formed by the interaction of two oppositely charged species, i.e. [Hg ← OBr]$^+$ and [RuCl$_3$·S·(H$_2$O)OH]$^-$ (Table 3). A common reaction scheme proposed for the oxidation of arabinose and mannose finds support from the same order of frequency factor (*A*) and also by almost same values of free energy of activation ($\Delta G^{\#}$) observed for both the redox systems (Table 3).

7. Comparative studies

Efforts were also made to compare the findings of this paper with the results reported for Ru(III)-catalyzed [22] oxidation of reducing sugars by sodium metaperiodate in aqueous alkaline medium and Pd(II)-catalyzed [1] oxidation of reducing sugars by NBS in acidic medium. First of all, focus was made on the points that how oxidants, i.e. NBA and sodium metaperiodate in acidic and alkaline medium, respectively, affect the oxidation of reducing sugars, catalytic activity of Ru(III) and the mode of participation of other reactants of the reaction in the formation of most unstable activated complex? It is found that the reducing sugar molecule in the present study forms a complex with the reactive species of Ru(III) chloride as order with respect to sugar varies from first to zero, whereas in the reported Ru(III)-catalyzed [22] oxidation of reducing sugars by sodium metaperiodate there is no formation of a complex between reactive species of Ru(III) and enediol form of

sugar as the reaction rate is unaffected by the change in [sugar]. As far as the formation of most reactive activated complex is concerned, it is formed by the interaction of two oppositely charged species, i.e. [Hg ← OBr]$^+$ and [RuCl$_3$·S·(H$_2$O)OH]$^-$ in the present case and by the interaction of two similarly charged species [RuCl$_3$·(OH)$_2$·H$_2$O]$^{2-}$ and IO$_4^-$ in the reported [22] Ru(III)-catalyzed oxidation of reducing sugars by sodium metaperiodate in alkaline medium. In the present case, the formation of most unstable activated complex is supported by the observed positive entropy of activation and in the reported [22] periodate oxidation of arabinose and galactose, it is supported by the negative entropy of activation. In the reported Pd(II)-catalyzed [1] oxidation of reducing sugars by NBS, observed first-order kinetics with respect to [Pd(II)] and [NBS] and first- to zero-order kinetics with respect to [sugar] led the author to propose the formation of a complex of the type [PdCl$_2$(OBr)OHC-R]$^-$ in the rate determining step by the interaction of the charged species [PdCl$_3$·OBr]$^{2-}$ and the reducing sugar molecule. The present study with respect to the positive effect of [Cl$^-$] on the rate of oxidation being very similar with the reported [22] Ru(III)-catalyzed oxidation by sodium metaperiodate entirely differs from the reported [1] Pd(II)-catalyzed oxidation by NBS where negative fractional order in [Cl$^-$] was observed. The present study distinguishes itself from the reported [1] Pd(II)-catalyzed oxidation of reducing sugars by NBS in acidic medium as far as order with respect to [Hg(II)] is concerned. In Ru(III)-catalyzed oxidation by NBA, the role of Hg(II) was determined both as Br$^-$ ion scavenger and as co-catalyst but in Pd(II)-catalyzed oxidation by NBS, observed nil effect of [Hg(II)] on the rate of reaction forced the author to conclude that in this case the role of Hg(II) is limited only up to Br$^-$ ion scavenger. HOBr as the reactive species of NBA in the case of Ru(III) catalyzed oxidation and as the reactive species of NBS in the case of Pd(II)-catalyzed [1] oxidation was proposed on the basis of negative effect of [acetamide] and negligible effect of [succinimide] on the rate of reaction, respectively. Spectral information was made a basis to propose IO$_4^-$ as the reactive species of sodium metaperiodate in Ru(III)-catalyzed [22] oxidation of reducing sugars in alkaline medium.

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