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Kinetics and mechanism of Ru(III) and Hg(II) co-catalyzed oxidation of D-galactose and D-ribose by N-bromoacetamide in perchloric acid

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Abstract

Kinetics of oxidation of reducing sugars D-galactose (Gal) and D-ribose (Rib) by N-bromoacetamide (NBA) in the presence of ruthenium(III) chloride as a homogeneous catalyst and in perchloric acid medium, using mercuric acetate as a scavenger for Br⁻ ions, as well as a co-catalyst, have been investigated. The kinetic results indicate that the first-order kinetics in NBA at lower concentrations tend towards zero order at its higher concentrations. The reactions follow identical kinetics, being first order in the [sugar] and [Ru(III)]. Inverse fractional order in [H⁺] and [acetamide] were observed. A positive effect of [Hg(OAc)₂] and [Cl⁻] was found, whereas a change in ionic strength (μ) has no effect on oxidation velocity. Formic acid and D-lyxonic acid (for Gal) and formic acid and L-erythronic acid (for Rib) were identified as main oxidation products of reactions. The various activation parameters have been computed and recorded. A suitable mechanism consistent with experimental findings has been proposed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Mechanism; Ru(III), Hg(II) co-catalysis; HClO₄ medium; Reducing sugars; N-Bromoacetamide

1. Introduction

N-Bromoacetamide (NBA) has been used as an oxidizing and halogenating agent¹ in quantitative estimation of a large number of compounds and in preparative organic chemistry. Oxidations involving NBA and primary alcohols,² amino acids,³ aliphatic ketones,⁴ cyclic ketones,⁵ dimethyl sulfoxide,⁶ and hydroxy acids¹² in acidic or alkaline media have been reported. N-halo compounds such as *N*-bromoacetamide (NBA) or NBS oxidation of organic substrates is complicated by parallel bromine oxidation which is obviated by Hg(II).^{2–16} Although kinetic studies involving NBA as an oxidant have been made for a number of uncatalyzed reactions, there seems to be few reports^{7–12} about its oxidation mode in catalyzed processes. Surprisingly, attempts to probe its oxidation mode in catalyzed reactions, especially with biologically important substrates like sugars, is rather scanty. This prompted us to study the kinetics and mechanism of the Ru(III)-catalyzed oxidation of reducing sugars, Dgalactose and D-ribose, by NBA in acidic media, which may become helpful to understand the complicated biochemical and other problems in the living system.

2. Experimental

Materials.—An aqueous solution of NBA was prepared fresh from E. Merck grade recrystallized sample in double-distilled water and stored in a black-coated flask to prevent photochemical deterioration. The prepared solution was then standardized idometrically¹⁷ against standard sodium thiosulphate solution using starch as an indicator. An aqueous solution of Gal and Rib (A.R. grade) were also prepared fresh each day. A solution of Ru(III) chloride (Ubichem Ltd.) was prepared in HCl of known strength. The overall strength

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of HCl was maintained at 0.1N, and the strength of RuCl₃ was 9.64×10^{-3} mol dm⁻³. A standard aqueous solution of mercuric acetate (E. Merck) was acidified with 20% AcOH. Perchloric acid (E. Merck), diluted with double-distilled water, was standardized via acid-base titration. All other standard solutions of KCl, NaClO₄, and acetamide (E. Merck) were prepared with double-distilled water.

Methods.—The reactions were studied at constant temperature 40 °C (\pm 0.1 °C). The requisite volume of reactants, i.e., NBA, Ru(III), HClO₄ and Hg(OAc)₂, were taken in a black-coated (Jena glass) vessel and equilibrated at 40 °C. An appropriate volume of sugar solution, also equilibrated at 40 °C, was rapidly poured into the reaction mixture to initiate the reaction. The progress of the reaction was followed by estimating the amount of unconsumed NBA iodometrically in aliquots withdrawn from the reaction mixture at regular time intervals.

Stoichiometry and product analysis.—Various sets of experiments were performed with different [NBA]:[sugar] ratios, under the conditions of [NBA] \gg [sugar]. Determination of unreacted NBA indicated that the 2 mol of NBA were consumed to oxidize 1 mol of each of the sugars. Accordingly, the following stoichiometric equations could be formulated.

 $C_{6}H_{12}O_{6} + 2CH_{3}CONHBr + 2H_{2}O \xrightarrow{\text{RuCl}_{3}/\text{H}^{+}} \text{HCOOH}$ $+ 2CH_{3}CONH_{2} + 2HBr + C_{4}H_{9}O_{4}COOH$ D-lyxonic acid $C_{5}H_{10}O_{5} + 2CH_{3}CONHBr + 2H_{2}O \xrightarrow{\text{RuCl}_{3}/\text{H}^{+}} \text{HCOOH}$ $+ 2CH_{3}CONH_{2} + 2HBr + C_{3}H_{7}O_{3}COOH$ D-rythronic acid

The main products of the oxidation, formic, D-lyxonic and L-erythronic acids were detected¹⁷ chromatographically (TLC) and by conventional (spot test) methods.^{18,19}

3. Results and discussion

The oxidation of Gal and Rib were investigated at different initial concentrations of reactants. The rate (i.e., -dc/dt) of reaction in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of NBA, which is written as [NBA]*. The first-order velocity constant (k'_1) was calculated as

$$k'_1 = - dc/dt/[NBA]^*$$

The first-order dependence of reaction on NBA at its lower concentrations tends to zeroth order at its higher concentrations as demonstrated by the plot of -dc/dtversus [NBA] (Fig. 1), which is also verified by the decreasing values of k'_1 obtained at various initial concentrations of NBA (Table 1). A close examination of the data in Table 1 shows that the rate of reaction is directly proportional to the concentration of sugars,



Fig. 1. Plots of (-dc/dt) versus [NBA] at 40 °C for the oxidation of D-galactose (G) and D-ribose (R) under the experimental condition of Table 1.

indicating first order in each sugar. The order of reaction with respect to hydrogen ions (obtained from HClO₄) was determined as -0.37 (Gal) and -0.62 (Rib) from the slope of the plot between log k'_1 and log[H⁺] (Fig. 2). A log k'_1 versus log[Ru(III)] plot gives a straight line with a slope of nearly one (0.90 for Gal and 0.95 for Rib), which confirms the first order dependence of the reactions on [Ru(III)] (Fig. 2). First-order kinetics, with respect to [Ru(III)], is further verified by the plot of (-dc/dt) values against [Ru(III)], where a straight line passing through the origin is obtained (Fig. 3).

Table 2 shows the effect of the addition of $Hg(OAc)_{2}$, Cl⁻ and acetamide. A perusal of the results in Table 2 shows the positive effect of the addition of $Hg(OAc)_2$, indicating the involvement of Hg(II) as a co-catalyst in addition to its role as a Br- ion scavenger.²⁰⁻²² Successive addition of acetamide (NHA) shows a negative effect on the rates of reaction in oxidation of both Gal and Rib. A positive effect of the addition of chloride ions and the negligible effect of ionic strength ' μ ' of the medium varied by addition of a required amount of NaClO₄, i.e., from 0.62×10^{-3} to 5.62×10^{-3} mol dm⁻³ for (Gal) and 1.65×10^{-3} to 5.65×10^{-3} mol dm^{-3} for (Rib), on the rate constant were also observed. The reactions were studied at different temperatures, and the rate constants at 35, 40 and 45 °C used to compute activation parameters in the oxidation of Gal and Rib (Table 3). Identical kinetic results obtained for the oxidation of Gal and Rib suggest that both reactions follow a common mechanism.

It has been reported²⁻¹² that NBA exists in the following equilibria in acidic medium.

Table 1 Effect of [reactants] on the rate constants at 40 °C

$[NBA] \times 10^4 \text{ (mol } dm^{-3}\text{)}$	[Substrate] $\times 10^2$ (mol dm ⁻³)	$[Ru(III)] \times 10^7 \text{ (mol dm}^{-3})$	$k'_1 imes 10^5 \ ({ m s}^{-1})^{ m a}$	
			D-Gal	D-Rib
2.50ª	1.25	19.28	20.87	22.50
4.00 ^a	1.25	19.28	20.05	19.55
6.00 ^a	1.25	19.28	16.89	17.51
8.00^{a}	1.25	19.28	15.96	15.28
12.00 ^a	1.25	19.28	13.25	11.24
16.00 ^a	1.25	19.28	10.29	9.03
20.00 ^a	1.25	19.28	8.26	7.33
10.00 ^ь	0.31	19.28	6.44	
10.00 ^ь	0.40	19.28		5.09
10.00 ^ь	0.60	19.28		6.03
10.00 ^ь	0.62	19.28	7.37	
10.00 ^ь	1.25	19.28	11.27	10.42
10.00 ^b	1.87	19.28	16.91	14.40
10.00 ^ь	2.50	19.28	23.02	20.05
10.00 ^ь	3.12	19.28	28.82	24.69
10.00 ^ь	1.25	4.80	2.77	2.35
10.00 ^b	1.25	7.20		4.39
10.00 ^ь	1.25	9.60	5.76	
10.00 ^ь	1.25	19.30	9.37	8.83
10.00 ^ь	1.25	28.90	13.26	12.95
10.00 ^ь	1.25	38.60	16.66	16.83
10.00 ^b	1.25	48.30	18.75	
10.00 ^b	1.25	57.80	23.80	25.13
10.00 ^b	1.25	67.50	27.34	

^a Solution conditions: $[\text{HClO}_4] = 0.62 \times 10^{-3} \text{ mol } \text{dm}^{-3}$ (Gal), $0.60 \times 10^{-3} \text{ mol } \text{dm}^{-3}$ (Rib), $[\text{Hg}(\text{OAc})_2] = 3.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$ (a) and $1.25 \times 10^{-3} \text{ mol } \text{dm}^{-3}$ (b).

$$MeCONHBr + H_2O \rightleftharpoons MeCONH_2 + HOBr$$
(a)

$$HOBr + H^{+} \rightleftharpoons (H_{2}OBr)^{+} \tag{6}$$

 $MeCONHBr + H^+ \rightleftharpoons (MeCONH_2Br)^+$ (c)

$$(MeCONH_2Br)^+ + H_2O \rightleftharpoons MeCONH_2 + (H_2OBr)^+$$
(d)

It appears from the above two sets of equilibria that there could be four reactive NBA species, i.e., NBA itself, HOBr, protonated NBA, i.e., $(MeCONH_2Br)^+$ and cationic bromine, i.e., $(H_2OBr)^+$. Since on assuming NBA or $(MeCONH_2Br)^+$ as the reactive species, the rate law fails to explain the negative effect of acetamide; hence, neither of these species, i.e., NBA as such, or $(MeCONH_2Br)^+$, can be taken as the reactive species. When $(H_2OBr)^+$ is taken as the reactive species, the rate law obtained shows first-order kinetics with respect to $[H^+]$ contrary to the observed negative fractional order in $[H^+]$, although it fully explains the negative effect of acetamide. Thus the possibility of



Fig. 2. Plots of $\log k'_1$ versus $\log [\operatorname{Ru}(\operatorname{III})]$ and $\log k'_1$ versus $\log[\mathrm{H}^+]$ at 40 °C under the experimental condition of Table 1 for [Ru(III)] variation whereas in [H⁺] variation, [NBA] = 10.00×10^{-4} mol dm⁻³, [substrate] = 1.25×10^{-2} mol dm⁻³, [RuCl₃] = 19.28×10^{-7} mol dm⁻³ [Hg(OAc)₂] = 1.25×10^{-3} mol dm⁻³. [G = D-galactose and R = D-ribose].



Fig. 3. Plots of (-dc/dt) versus [RuCl₃] at 40 °C under the experimental condition of Table 1.

Table 3

Effect of temperature on the rate constant and values of activation parameters $^{\rm a}$

Parameter	Temperature (K)	D-Gal	D-Rib
$k'_1 \times 10^5 (s^{-1})$	308	14.62	9.92
$k'_1 \times 10^5 (\mathrm{s}^{-1})$	313	25.13	16.83
$k'_1 \times 10^5 (\mathrm{s}^{-1})$	318	35.71	23.81
$k_{\rm r} \times 10^{-2} ~({\rm dm}^6 ~{\rm mol}^{-2} ~{\rm s}^{-1})$	313	18.76	24.29
$A \times 10^{-13} (\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1})$	313	4.46	3.44
$E_{\rm a}$ (kJ mol ⁻¹)		64.08	60.78
$\Delta H^{\#}$ (kJ mol ⁻¹)	313	61.45	58.44
$\Delta S^{\#}$ (JK ⁻¹ mol ⁻¹)	313	13.91	5.52
$\Delta G^{\#}$ (kJ mol ⁻¹)	313	57.11	56.43

^a Solution conditions: [NBA] = 10.00×10^{-4} mol dm⁻³, [substrate] = 1.25×10^{-2} dm mol⁻³, [RuCl₃] = 19.25×10^{-7} mol dm⁻³, [HClO₄] = 0.62×10^{-3} mol dm⁻³ (Gal), 0.60×10^{-3} mol dm⁻³ (Rib), [Hg(OAc)₂] = 1.25×10^{-3} mol dm⁻³.

Table 2 Effect of variation of [Hg(OAc)₂], [KCl] and acetamide [NHA] on the rate constants at 40 °C

$[Hg(OAc)_2] \times 10^3 \text{ mol } dm^{-3}$	$[KCl] \times 10^3 \text{ mol } dm^{-3}$	$[NHA] \times 10^3 \text{ mol } dm^{-3}$	$k'_1 imes 10^5 (s^{-1})^{a}$	
			D-Gal	D-Rib
1.10				5.61
1.25			8.87	
2.00			10.99	7.81
3.00			13.88	8.81
4.00			16.67	11.11
6.00			19.94	
7.00				12.15
8.00			21.60	
10.00				13.05
1.25	$0.65^{\rm g}/0.62^{\rm r}$		5.79	3.01
1.25	$1.65^{\rm g}/1.62^{\rm r}$		10.41	5.14
1.25	$2.65^{\rm g}/2.62^{\rm r}$		13.01	6.79
1.25	$3.65^{\rm g}/3.62^{\rm r}$		16.02	7.71
1.25	4.65 ^g			8.68
1.25	$5.65^{\rm g}/5.62^{\rm r}$		19.34	9.25
1.25		1.25	8.54	
1.25		1.66	6.17	
1.25		2.00		6.26
1.25		2.50	4.90	
1.25		3.00		4.87
1.25		5.00	3.31	3.65
1.25		7.00		2.92
1.25		10.00	1.98	1.64

^a Solution conditions: [NBA] = 10.00×10^{-4} mol dm⁻³, [substrate] = 1.25×10^{-2} mol dm⁻³. [RuCl₃] = 19.28×10^{-7} mol dm⁻³ [HClO₄] = 0.62×10^{-3} mol dm⁻³ (Gal) and 0.60×10^{-3} mol dm⁻³ (Rib), where r = Rib, g = Gal.

cationic bromine $(H_2OBr)^+$ as the reactive species is remote. This leaves HOBr as the only choice to be the reactive species, which gives a rate law capable of explaining all the kinetic observations and other effects.

Ruthenium(III) chloride in hydrochloric acid forms $[RuCl_6]^{3-}$, which in aqueous solution follows the equilibrium.^{23,24}

$$[\operatorname{RuCl}_6]^{3-} + \operatorname{H}_2O \rightleftharpoons [\operatorname{RuCl}_5\operatorname{H}_2O]^{2-} + \operatorname{Cl}^{-}$$
(e)

The observed positive effect of the chloride ion suggests that the above equilibrium is favored to-wards the left;^{25–27} therefore, $[RuCl_6]^{3-}$ is the true reactive species of ruthenium(III) chloride in the present investigation.

It is reported that Ru(III) forms complexes with sugar molecules. In order to probe the possibility of Ru (III)–sugar complex formation, under our experimental conditions, UV spectra of Ru(III) chloride solution, reducing sugar solution, and Ru(III) chloride with different concentrations of sugar solution at 40 °C have been collected (Fig. 4). The absorption spectra of Ru(III) with different concentrations of sugar solution clearly indicate that the reactive species of Ru(III), i.e., $[RuCl_6]^{3-}$ forms a complex with the sugar molecule, showing an increase in absorbance of



Fig. 4. Spectra of Ru(III) and sugar solutions recorded at 40 °C. (1) [sugar] = 5.00×10^{-1} mol dm⁻³; (2) [Ru(III)] = 7.63×10^{-4} mol dm⁻³; (3) [Ru(III)] = 7.63×10^{-4} mol dm⁻³; (3) [Ru(III)] = 7.63×10^{-4} mol dm⁻³; (4) [Ru(III)] = 7.63×10^{-4} mol dm⁻³, [sugar] = 5.00×10^{-2} mol dm⁻³; (5) [Ru(III)] = 7.63×10^{-4} mol dm⁻³, [sugar] = 20.00×10^{-2} mol dm⁻³.

pure Ru(III) chloride solution from 3.14 to 3.52 (3), 3.58 (4) and 3.64 (5). This increase in absorbance is due to the fact that with the increase in sugar concentration, the equilibrium (f) between $[RuCl_6]^{3-}$ and a sugar molecule shifts towards the right, with more and more formation of Ru(III)-sugar complex, which becomes the sole factor for the increase in absorbance.

$$[RuCl_6]^{3-} + S \rightleftharpoons [RuCl_5S]^{2-} + Cl^-$$
(f)

On the basis of above discussion and experimental data, a probable reaction mechanism has been proposed for the Ru(III) and Hg(II) co-catalyzed oxidation of Gal and Rib by NBA in acidic medium in Scheme 1.

On the basis of the reactions in Scheme 1, the rate of disappearance of NBA can be expressed as

$$Rate = -d[NBA]/dt = k[C_3][C_5]$$
(1)

Upon applying the law of chemical equilibrium to steps (ii) and (iii), we have

$$[C_2] = \frac{[C_3][Cl^-]}{K_3[S]}$$
(2)

$$[C_1] = \frac{[C_3]}{K_2 K_3 [S]}$$
(3)

The total concentration of Ru(III), i.e., $[Ru(III)]_T$ can be expressed as

$$[Ru(III)]_{T} = [C_{1}] + [C_{2}] + [C_{3}]$$
(4)

From Eqs. (2)-(4), we obtain Eq. (5)

$$[C_3] = \frac{[Ru(III)]_T K_2 K_3[S]}{1 + K_2 [Cl^-] + K_2 K_3[S]}$$
(5)

Again on applying the law of chemical equilibrium to steps (iv) and (v), we have

$$[C_4] = \frac{K_4[Hg(II)][HOBr]}{[H^+]}$$
(6)

and

$$[C_5] = K_5[C_4][Cl^-]$$
(7)

On applying the steady-state approximation to [HOBr] and considering Eqs. (6) and (7), we have Eq. (8)

$$[C_{5}] = \frac{K_{5}K_{4}[Hg(II)][CI^{-}]k_{1}[NBA]}{[H^{+}]\{k_{-1}[NHA] + k_{4}[Hg(II)]\}}$$
(8)

On substituting the values of $[C_3]$ and $[C_5]$ from Eqs. (5) and (8), respectively, to Eq. (1), we obtain Eq. (9). Rate =

$$\frac{kk_1K_2K_3K_4K_5[\text{NBA}][S][\text{Ru}(\text{III})]_{\text{T}}[\text{Hg}(\text{II})][\text{Cl}^-]}{[\text{H}^+]\{1 + K_2[\text{Cl}^-] + K_2K_3[S]\}\{k_{-1}[\text{NHA}] + k_4[\text{Hg}(\text{II})]\}}$$
(9)

$$\operatorname{MeCONHBr}_{NBA} + \operatorname{H}_2O \stackrel{\times_1}{\cong} \operatorname{MeCONH}_2 + \operatorname{HOBr}_{NHA}$$
(i)

$$\begin{aligned} &[\operatorname{RuCl}_{i}H_{2}O]^{2^{-}} + \operatorname{Cl}^{-} \rightleftharpoons [\operatorname{RuCl}_{i}G]^{3^{-}} + H_{2}O \qquad (ii) \\ &[\operatorname{RuCl}_{i}G^{3^{-}} + S \rightleftharpoons [\operatorname{RuCl}_{i}S]^{2^{-}} + \operatorname{Cl}^{-} \qquad (iii) \end{aligned}$$

$$[\operatorname{RuCl}_{(C_2)}]^{3-} + S \rightleftharpoons [\operatorname{RuCl}_{(C_3)}S]^{2-} + Cl^{-}$$
(ii)

where S stands for Gal and Rib.

v.

$$Hg(II) + HOBr \xleftarrow{K_4} [Hg \leftarrow OBr]^+ + H^+$$
(iv)
(C₄)

$$[Hg \leftarrow OBr]^{+} + Cl^{-} \xleftarrow{K_{5}} \left[Hg \swarrow_{Cl}^{OBr}\right]$$
(v)
(C₅)

Where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$, $K_3 = k_3/k_{-3}$, $K_4 = k_4/k_{-4}$, $K_5 = k_5/k_{-5}$

$$[\operatorname{RuCl}_{5}S]^{2-} + \left[\operatorname{Hg} \swarrow_{Cl}^{OBr}\right] \xrightarrow{k} [\operatorname{RuCl}_{4} \swarrow_{S}^{OBr}\right]^{2-} + \operatorname{Hg}(II) + 2 \operatorname{Cl}^{-} (vi)$$

$$(C_{3}) \qquad (C_{5}) \qquad OH \qquad OH \qquad OH$$

$$\begin{bmatrix} \text{RuCl}_4 \swarrow \overset{\text{OBr}}{\text{S}} \end{bmatrix}^{2^-} + 3 \text{ H}_2\text{O} \xrightarrow{\text{fast}} \begin{bmatrix} \text{RuCl}_4(\text{H}_2\text{O})_2 \end{bmatrix}^- + \text{R} - \text{CH} - \text{CH} + \text{OH}^- \text{ (vii)} \\ | \\ \text{OBr} \end{bmatrix}$$

$$\begin{array}{c} H & O-H & O & O \\ R - C & - C - H & & & \parallel \\ O - H & O & Br \end{array} \xrightarrow{fast} H - C - OH + R - C - H + HBr \qquad (viii)$$

$$R \xrightarrow{C} P H + H \xrightarrow{C} OBr \xrightarrow{fast} R \xrightarrow{C} H (ix)$$

$$R \xrightarrow{O-H} OBr$$

$$R \xrightarrow{O-H} O$$

$$R \xrightarrow{O-H} R \xrightarrow{O} R \xrightarrow{O-H} R \xrightarrow{O} R \xrightarrow{O} OH (ix)$$

$$R \xrightarrow{O-H} O (ix)$$

$$R \xrightarrow{O-H} O$$

 $[\operatorname{RuCl}_4(\operatorname{H}_2O)_2]^- + 2 \operatorname{Cl}^- \xrightarrow{\text{fast}} [\operatorname{RuCl}_6]^{3-} + 2 \operatorname{H}_2O$ Scheme 1.

The total concentration of Hg(II), i.e., $[Hg(II)]_T$ can be expressed as

 $[Hg(II)]_{T} = [Hg(II)]_{free} + [C_4]$ (10)

Considering step (i), Eqs. (6) and (10), the final rate law with suitable approximations can be expressed as Eq. (11).

$$\frac{ka[\text{NBA}][\text{S}][\text{Ru}(\text{III})]_{\text{T}}[\text{Hg}(\text{II})]_{\text{T}}[\text{Cl}^{-}]}{b[\text{NBA}] + c[\text{H}^{+}][\text{NHA}][\text{Hg}(\text{II})]_{\text{T}}[\text{Cl}^{-}] + d[\text{Cl}^{-}][\text{NBA}]}$$
(11)

where $a = k_1 K_2 K_3 K_4 K_5$, $b = k_{-1} K_1 K_4$, $c = k_4 K_2$ and $d = k_{-1} K_1 K_2 K_4$.

The rate law (Eq. (11)) is in complete conformity with the observed data. Hence the proposed mechanism, which is also consistent with activation parameters (Table 3), is valid.

Eq. (11) can be rearranged as Eq. (12)

$$\frac{1}{\text{Rate}} = \frac{1}{x[S][\text{Ru(III)}]_{\text{T}}[\text{Hg(II)}]_{\text{T}}[\text{Cl}^{-}]} + \frac{k_{4}[\text{H}^{+}][\text{NHA}]}{y[\text{NBA}][S][\text{Ru(III)}]_{\text{T}}} + \frac{1}{z[S][\text{Ru(III)}]_{\text{T}}[\text{Hg(II)}]_{\text{T}}}$$
(12)

(xi)

where $x = kK_2K_3K_5$, $y = kk_1K_3K_4K_5$ and $z = kK_3K_5$.

According to Eq. (12), if a plot is made between 1/Rate and 1/[NBA] or 1/[Cl⁻] or [NHA], then a straight line having a positive intercept on the 1/Rate axis should be obtained. When 1/Rate values are plotted against 1/[NBA], 1/[Cl⁻] and [NHA], straight lines with positive intercepts on 1/Rate axis were obtained (Fig. 5), which clearly proves the validity of the rate law expression (Eq. (11)) and hence the proposed mechanism. Owing to the complicated rate law expression (Eq. (11)), it was not possible to calculate constants shown in the mechanistic steps. Positive entropy of activation ($\Delta S^{\#}$) observed in the oxidation of D-galac-



Fig. 5. Plots of 1/rate versus 1/[NBA], 1/[KCI] and [NHA] at 40 °C, under the experimental conditions as in Table 1 for [NBA] variation and Table 2 for [KCI] and [NHA] variations [G = D-galactose and R = D-ribose].

tose and D-ribose also supports the proposed mechanism where the activated state will be less polar than the reactants.

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