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Pd(II) catalysed and Hg(II) co-catalysed oxidation of D-arabinose and D-ribose by N-bromoacetamide in perchloric acid medium: A kinetic and mechanistic study

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The kinetics and mechanism of the homogeneously Pd(II) catalysed oxidation of D-arabinose (Arb) and D-ribose (Rib) by N-bromoacetamide (NBA) in perchloric acid medium, using mercuric acetate as scavenger for Br^- ions as well as co-catalyst have been investigated in the temperature range 308-323 K. The kinetic results exhibit first order kinetics at low [NBA] and [sugars] (Arb and Rib), tend towards zero-order at high [NBA] and [sugars]. The oxidation rate is directly proportional to [Pd(II)], while inverse fractional order in each of $[H^+]$, $[Cl^-]$ and [acetamide] is observed. A positive effect on the rate of the reaction has been found on the successive addition of $[Hg(OAc)_2]$, whereas change in the ionic strength (μ) of the medium does not influence the reaction rate. Formic acid and D-erythronic acid for the oxidation of both Arb and Rib have been identified as main oxidation products of the reactions. The various activation parameters have also been evaluated. A plausible mechanism involving reaction stoichiometry, product analysis has also been proposed.

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The organic N-halogeno compounds[1,2] are well-known for their diverse nature like as source of halonium cations, hypohalate species, nitrogen anions and strong electrolytes in aqueous solution[3], due to strongly polarised N-linked halogens which are in the +1 state. They are capable of affecting an array of molecular transformations, including limited oxidation of specific groups. However, potential applications of such compounds remain unrealized as an oxidant in uncatalysed and catalysed redox processes. Although kinetic studies involving NBA as an oxidant have been made for uncatalysed reactions, there seems to be few reports[1,4] in presence of certain transition metal ions, viz. Ir(III), Ru(III), Os(VIII) and Hg(II)[4] on its oxidative mode in catalysed processes. Surprisingly, there are few reports on analogous Pd(II) ion as homogeneous catalyst from mechanistic point of view. The N-halogeno compounds such as NBA/NBS oxidation of organic substrate is complicated by parallel bromine oxidation which is obviated by using Hg(II)[1]. In some NBS[1] reactions, Hg(II) also plays a catalytic role. But, its role as co-catalyst is not well known, especially with Pd(II) and sugar (a biologically and industrially important substrate). These reports and recent publications[5,6] concerning the oxidation of sugars by haloamines have prompted us to undertake Pd(II)-Hg(II) co-catalysis during the oxidation of pentose sugars {i.e. D-arabinose (Arb) and D-ribose (Rib)} by NBA in perchloric acid medium. This study will enable understanding the complicated biochemical reaction in living bodies and will also help to understand the mechanistic aspects of catalytic activities of Pd(II) and Hg(II) ions along with oxidative capacity of NBA in solution.

Materials and Methods

A Pd(II) stock solution (2.82×10^{-3} mol dm^{-3}) was prepared by dissolving known weight of palladium(II) chloride (Qualigen 'Glaxo' Chem.) in HCl (1.00×10^{-3} mol dm^{-3}). Aqueous solution of NBA was prepared fresh daily and was standardized iodometrically against standard sodium thiosulphate solution using starch as an indicator. Aqueous solutions of Arb and Rib were also prepared fresh each day. Both, NBA and Pd(II) chloride solutions were stored in black coated flask to prevent photochemical deterioration. A standard aqueous solution of mercuric acetate (E. Merck) was acidified with 20% acetic acid. Perchloric acid (E. Merck) was used as source of H^+ ions while

the ionic strength of the reaction was maintained using $NaClO_4$ (E. Merck). All other reagents namely KCl and acetamide (NHA) were from E. Merck. Double distilled water was used during the reaction and black-coated reaction bottles were used to avoid any photochemical effect of the reactions.

All the kinetic measurements were carried out at constant temperature 40°C (±0.1°C). The requisite volumes of all the reactants, i.e. NBA, Pd(II), $HClO_4$, $Hg(OAc)_2$, KCl, $NaClO_4$ and water (for make up constant volume) were taken in a reaction bottle (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 reaction mixture to initiate the reaction. Progress of the reaction was monitored by estimating the amount of unconsumed NBA iodometrically in aliquots withdrawn from reaction mixture at regular intervals.

Stoichiometry and product analysis

Several sets of reaction mixtures containing different amounts of [NBA] : [reducing sugar] ratios at constant acidity and ionic strength were allowed to react for 72 h at 40°C in closed vessels. Under the conditions of [NBA]>>[sugar], the estimation of residual [NBA] was determined iodometrically and after accounting for the remaining oxidant concentration. It was found that each mol of pentose sugar (i.e., both Arb and Rib) consumed 2 mol of NBA. Thus, the ratio of consumption of reductant to oxidant is 1:2. Accordingly, the following stoichiometric equations can be formulated:

(i) $C_5H_{10}O_5 + 2MeCONHBr + 2H_2O \xrightarrow{Pd(II)/H^+/Hg(II)}$

D-Arabinose (NBA)

$HCOOH + R_1COOH + 2MeCONH_2 + 2HBr$

formic acid D-erythronic acid (NHA)

(ii) $C_5H_{10}O_5 + 2MeCONHBr + 2H_2O \xrightarrow{Pd(II)/H^+/Hg(II)}$

D-Ribose

$HCOOH + R_1COOH + 2MeCONH_2 + 2HBr$

D-erythronic acid

where $R_1 = (CHOH)_2 CH_2OH$.

The residues of the reaction mixture (detected after about 70% completion of the reaction) by TLC and also by conventional spot test[7,8] showed formic and D-erythronic acids as the main oxidation products in the redox reactions.

Results and Discussion

In order to propose a reaction mechanism for the reaction between reducing sugar (Arb or Rib) and NBA in presence of Pd(II) as homogeneous catalyst, a series of experiments were performed at 40°C. In each kinetic run, the initial rate of reaction was determined from the slope of the tangent drawn at fixed [NBA]. In case [NBA] was varied, slope of the tangent was drawn at fixed time. If NBA, reducing sugar (Arb or Rib), H^+ ions, Pd(II) chloride and Hg(II) are considered as the main reactants, the rate equation for the reaction can be written as:

$$\text{Rate} = k[\text{NBA}]^{\alpha}\,[\text{Sugar}]^{\beta}\,[H^+]^{\gamma}\,[\text{Pd(II)}]^{\delta}\,[\text{Hg(II)}]^{\eta}$$

For the experimental rate law, a series of experiments with varying initial [NBA] were performed at constant concentration of all other reactants and at constant temperature. Throughout, [NBA] was kept much lower than the [sugar]. Maintaining the concentrations of other reactants except NBA, the above rate law becomes:

$$\text{Rate} = -\frac{d[\text{NBA}]}{dt} = J[\text{NBA}]^{\alpha}$$

where J, the apparent rate constant

$= k[\text{sugar}]^{\beta}\,[H^+]^{\gamma}\,[\text{Pd(II)}]^{\delta}\,[\text{Hg(II)}]^{\eta}$.

In the case of α being equal to one, the reaction rate will be directly proportional to the [NBA] and J, can be calculated by dividing initial rate of the reaction with the initial [NBA]. Table 1 shows the variation of [NBA] at 40°C for the oxidation of both Arb and Rib. 'J' calculated as above for the oxidation of both the reducing sugars, shows a decreasing trend with the increasing [NBA]. Thus, it is not possible to assume that the order of reaction with respect to [NBA] is unity. The decrease in 'J' with the increase in [NBA] may be due to two reasons. The first reason is that since observed order with respect to [NHA] is fractionally negative, decrease in J with increase in [NBA] can be due to increasing [NHA] according to the following equilibrium[2]:

$$\text{NBA} + H_2O \rightleftharpoons \text{NHA} + \text{HOBr}$$

The second reason is that a part of NBA may be involved in the formation of an intermediate complex. As a result, order with respect to [NBA] becomes fractionally positive instead of being first order throughout the variation of [NBA]. The first possibility means that upon the formation of 10, 20 and 40% NHA at the initial stage, the rate constant k' becomes uniform throughout the variation of [NBA], except at very high [NBA] where decrease in k' with

Table 1 — Effect of variation of [NBA] on the rate constant at 40°C

$[NBA]\times10^{4}$	D-Arabinose[a]				D-Ribose[a]			
(mol dm^{-3})	$J\times10^{5}$ (s^{-1})	$k'\times10^{7}$ (s^{-1}) (10% conv.)	$k'\times10^{7}$ (s^{-1}) (20% conv.)	$k'\times10^{7}$ (s^{-1}) (40% conv.)	$J\times10^{5}$ (s^{-1})	$k'\times10^{7}$ (s^{-1}) (10% conv.)	$k'\times10^{7}$ (s^{-1}) (20% conv.)	$k'\times10^{7}$ (s^{-1}) (40% conv.)
2.50	12.50	3.68	5.38	8.30	18.00	3.74	5.66	8.58
4.00	10.80	4.11	6.03	8.80	13.06	3.30	5.00	7.58
6.00	8.52	4.01	5.94	8.70	9.72	2.84	4.32	6.54
8.00	7.83	4.36	6.39	9.37	8.17	2.84	4.32	6.54
12.00	5.17	3.61	5.28	7.73	6.15	2.73	4.14	6.30
16.00	4.10	3.35	4.90	7.18	4.56	2.41	3.65	5.53
20.00	3.57	3.30	4.83	7.07	3.73	2.25	3.41	5.17

[a]Solution conditions:[substrate] = 10.0×10^{-2} mol dm^{-3} (Arb), 6.0×10^{-2} mol dm^{-3} (Rib); [Pd(II)] = 22.56×10^{-6} mol dm^{-3} (Arb), 28.0×10^{-6} mol dm^{-3} (Rib); [H^+] = 0.83×10^{-3} mol dm^{-3} (Arb), 0.50×10^{-3} mol dm^{-3} (Rib) [$Hg(OAc)_2$] = 3.0×10^{-3} mol dm^{-3} (Arb and Rib);

$k' = \frac{J}{[NHA]^n}$ with n = –0.55 for Arb and n = –0.60 for Rib

Table 2 — Effect of variation of [substrate] and [H^+] on the apparent first order rate constant at 40°C

[Substrate] $\times10^{2}$ (mol dm^{-3})	[H^+] $\times10^{4}$ (mol dm^{-3})	[a]$J\times10^{5}$ (s^{-1})	
		D-Arb	D-Rib
1.00[b,c]	8.30[b]/5.00[r]	0.52	1.29
2.00[b,c]	8.30[b]/5.00[r]	1.03	2.47
4.00[b]/3.50[r]	8.30[b]/5.00[r]	2.09	4.38
6.00[b]/5.00[r]	8.30[b]/5.00[r]	3.37	6.58
8.00[b]/7.00[r]	8.30[b]/5.00[r]	4.17	8.77
10.00[b,c]	8.30[b]/5.00[r]	5.39	10.86
12.00[b,c]	8.30[b]/5.00[r]	5.58	11.56
10.00[b]/6.00[r]	3.00[b]/2.50[r]	10.41	14.61
10.00[b]/6.00[r]	5.00[b]/5.00[r]	8.01	11.96
10.00[b]/6.00[r]	6.00[b]/7.50[r]	6.51	10.53
10.00[b]/6.00[r]	10.00[b]/10.00[r]	5.21	8.19
10.00[b]/6.00[r]	20.00[b]/12.50[r]	4.07	4.62
10.00[b]/6.00[r]	30.00[b]/15.00[r]	3.12	3.72

[a]Solution conditions: [NBA]=10.00×10^{-4}mol dm^{-3}(Arb and Rib); [$Hg(OAc)_2$] = 1.42×10^{-3}mol dm^{-3}(Arb and Rib); [Pd(II)] =22.56×10^{-6} mol dm^{-3} (Arb), 28.20×10^{-6} mol dm^{-3} (Rib); where a = Arb, r = Rib

Table 3 — Effect of variation of [Pd(II)] and [$Hg(OAc)_2$] on the apparent first order rate constant at 40°C

[Pd(II)] $\times10^{6}$ (mol dm^{-3})	[$Hg(OAc)_2$] $\times10^{3}$ (mol dm^{-3})	[a]$J\times10^{5}$ (s^{-1})	
		D-Arb	D-Rib
2.82	1.42	0.77	1.90
5.64	1.42	1.24	–
8.64	1.42	–	4.24
11.28	1.42	2.74	–
14.10	1.42	–	6.33
16.92	1.42	3.83	–
22.56	1.42	4.56	–
25.38	1.42	–	11.37
28.20	1.42	5.67	–
33.84	1.42	6.82	–
36.66	1.42	–	16.57
39.48	1.42	7.94	–
50.76	1.42	10.23	22.42
22.56[a]/28.20[r]	1.10[a]/1.00[r]	1.96	2.51
22.56[a]/28.20[r]	2.00	3.20	3.60
22.56[a]/28.20[r]	3.00	3.79	4.63
22.56[a]/28.20[r]	4.00	4.63	5.55
22.56[a]/28.20[r]	5.00	5.14	6.17
22.56[a]/28.20[r]	6.00	5.70	6.53

[a]Solution conditions: [NBA] = 10.00×10^{-4}mol dm^{-3}(Arb and Rib); [substrate] = 10.00×10^{-2}mol dm^{-3}(Arb) 6.0×10^{-2} mol dm^{-3} (Rib); [H^+] = 0.83×10^{-3} mol dm^{-3} (Arb), 0.50×10^{-3} mol dm^{-3} (Rib); where a = Arb, r = Rib

the increase in [NBA] is noted. This shows that order of reaction with respect to [NBA] (except at very high [NBA]) is unity and decrease in 'J' with the increase in [NBA] is only due to increased formation of NHA resulting negative fraction order. The decrease in k' values at very high [NBA] may be assumed due to involvement of substantial amount of NBA in the formation of intermediate complex because with the formation of intermediate complex, there will be decrease in free [NBA] resulting in a decrease in 'J'. This indicates that at very high [NBA], the second possibility comes into existence and non-linear dependence of [NBA] on pseudo first order rate constant 'J' is observed.

Since [NBA] (1.0×10^{-3} mol dm^{-3}) is kept low, order of the reaction with respect to [NBA] has been taken as unity. Under pseudo first order condition, the [sugar] has been varied from 1.00×10^{-2} to 12.00×10^{-2} mol dm^{-3} (Table 2). 'J' of the reaction initially increases in the same proportion in which the concentration of substrate is increased. But, at very

Table 4 — Effect of variation of [NHA] and [Cl^-]on the rate constant at 40°C

$[NHA]\times10^3$ (mol dm^{-3})	$[Cl^-]\times10^3$ (mol dm^{-3})	$^x(-dc/dt)\times10^8$ (mol dm^{-3} s^{-1})			
		D-Arabinose		D-Ribose	
		Observed	Calculated	Observed	Calculated
1.00[a]/2.00[r]	1.00[a,r]	4.17	5.00	11.66	12.01
1.50[a]/3.00[r]	1.00[a,r]	3.85	4.32	10.42	10.02
3.00[a]/5.00[r]	1.00[a,r]	3.33	3.08	8.75	7.52
6.00[a]/7.00[r]	1.00[a,r]	2.22	1.95	6.86	6.01
10.00[a,r]	1.00[a,r]	1.15	1.31	4.80	4.63
1.00[a,r]	1.00[a]/3.21[r]	4.17	5.00	9.72	10.39
1.00[a,r]	1.88[a]/5.21[r]	3.70	4.05	9.17	9.42
1.00[a,r]	2.88[a]/7.21[r]	3.17	3.34	8.33	8.60
1.00[a,r]	3.88[a]/10.21[r]	2.77	2.84	7.69	7.62
1.00[a,r]	4.08[a]/15.21[r]	2.22	2.46	6.25	6.40

[x]Solution conditions: [NBA] = 10.00×10^{-4} mol dm^{-3} (Arb and Rib); [substrate] = 10.0×10^{-2} mol dm^{-3} (Arb), 6.00×10^{-2} mol dm^{-3} (Rib); [Pd(II)] = 22.56×10^{-6} mol dm^{-3} (Arb), 28.20×10^{-6} mol dm^{-3} (Rib); $[H^+] = 0.83\times10^{-3}$ mol dm^{-3} (Arb), 0.50×10^{-3} mol dm^{-3} (Rib); $[Hg(OAc)_2] = 1.42\times10^{-3}$ mol dm^{-3} (Arb and Rib); where a = Arb, r = Rib

high concentration of substrate, a slight deviation from the direct proportionality is observed. The order of reaction with respect to $[H^+]$ has been determined at constant temperature by varying its concentration from 3.0×10^{-4} mol dm^{-3} to 30.0×10^{-4} mol dm^{-3} in the case of Arb and from 2.5×10^{-4} mol dm^{-3} to 15.0×10^{-4}mol dm^{-3} in the case of Rib, maintaining the concentration of other reactants (Table 2). The ionic strength of the medium was maintained constant at 0.8×10^{-2} mol dm^{-3} for Arb and 1.5×10^{-2} mol dm^{-3} for Rib. The sharp decrease in 'J' with the addition of H^+ ions in low concentration range and very small change in 'J' in the higher concentration range of H^+ ions can be viewed in terms of negative fractional order with respect to H^+ at its low concentration and almost no effect at very high $[H^+]$ ions. Linear increase in 'J' with the increase in Pd(II) chloride concentration throughout its nearly 18-fold variation exhibits first order kinetics with respect to [Pd(II)] (Table 3). The effect of $Hg(OAc)_2$ addition on the rate of reaction has also been studied. Table 3 indicates that 'J' is enhanced by the addition of $Hg(OAc)_2$, suggesting the involvement of Hg(II) as co-catalyst, along with its role as Br^- ion scavenger[1,2]. The positive effect of Hg(II) on the apparent rate constant was also supported by the plot of log J versus log [Hg(II)], where order in case of arabinose and ribose was found to be 0.66 and 0.61, respectively.

Effect of added reactants

Since acetamide is one of reaction products and its role is significant in ascertaining the reactive species of NBA, the effect of variation of NHA on the apparent rate constant has also been studied. Table 4 shows that with the increase in [NHA], there is a retardation in 'J', suggesting that NHA was formed before the rate determining step of the reaction. The order with respect to NHA has been found to be –0.55 (Arb) and –0.60 (Rib) from the slope of the plot of log J versus log [NHA]. In Pd(II) chloride catalysed oxidation of Arb and Rib, the role of Cl^- ions is also important in ascertaining the reactive species of Pd(II) chloride and in the formation of complex between the reactive species of Pd(II) chloride and a reducing sugar molecule. Hence, the effect of [Cl^-] on 'J' has also been studied. The decrease in 'J' with the increase in [Cl^-] is an indication for the appearance of Cl^- ion in any of the steps before the rate determining step. Throughout the variation of [Cl^-], the decrease in 'J' with the increase in [Cl^-] was obtained in the oxidation of both Arb and Rib (Table 4). The order with respect to [Cl^-] in the oxidation of Arb was found to be –0.38 (Arb), and for Rib it was found to be –0.29 (Rib). To study the effect of ionic strength 'μ', $NaClO_4$ was varied from 1.00×10^{-3} to 4.88×10^{-3} mol dm^{-3} for Arb and 1.21×10^{-3} to 5.21×10^{-3} mol dm^{-3} for Rib, showing an insignificant effect on 'J', suggesting involvement of at least one neutral species in the rate determining step.

On the basis of observed order with respect to reducing sugar, H^+ ions Pd(II) chloride and Hg(II) and taking into consideration the effect of added reactants, i.e., NHA and Cl^- ions on 'J', the experimental rate laws for both Arb and Rib at low [NBA] can be written as:

Rate =

$$k[NBA][Arb][Pd(II)][H^+]^{-0.61}[Hg(II)]^{0.66}[NHA]^{-0.55}[Cl^-]^{-0.38}$$

Rate =

$$k[NBA][Rib][Pd(II)][H^+]^{-0.73}[Hg(II)]^{0.61}[NHA]^{-0.60}[Cl^-]^{-0.29}$$

Above rate laws are also supported by simple regression analysis.

Effect of temperature

The reactions were studied at four different temperatures (35, 40, 45 and 50°C) and observed rate constants were used to calculate the activation parameters. The Arrhenius plots of log J versus $1/T$ were found to be linear. The activation energies (E_a) were calculated from the slopes of the plots and from these values, the activation parameters $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were evaluated (Table 5).

Reactive species of NBA

It has been established that in acidic medium, NBA[1,2] is found in following two sets of equilibria:

$$\underset{(NBA)}{MeCONHBr}+H_2O \rightleftharpoons \underset{(NHA)}{MeCONH_2}+HOBr$$

$$HOBr+H_3O^+ \rightleftharpoons (H_2OBr)^+ + H_2O$$

or,

$$MeCONHBr+H_3O^+ \rightleftharpoons (MeCONH_2Br)^+ + H_2O$$

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

In the present investigation, either or both of the above two sets of equilibria may be operative. Hence, there may be four possible reactive NBA species i.e. NBA itself, HOBr, protonated NBA i.e. $(MeCONH_2Br)^+$ and cationic bromine i.e. $(H_2OBr)^+$. Addition of acetamide in reaction mixture decreases the rate of oxidation in acidic media suggesting that the pre equilibrium step involves a process in which acetamide is one of the products as shown in the steps of both the sets of equilibria. When NBA or $(MeCONH_2Br)^+$ is assumed as the reactive species, the derived rate laws fail to explain the negative effect of acetamide. Hence, neither of these species can be considered as 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 our observed negative fractional order in $[H^+]$, although it fully explains the negative effect of acetamide. Therefore, the possibility of cationic bromine as reactive species is also ruled out. Thus, the only choice left is HOBr, which when considered as the reactive species of NBA, leads to rate law capable of explaining all the kinetic observations and other effects. Hence, under the present experimental conditions and on the basis of above arguments, we can safely propose HOBr as the main reactive species of NBA.

Table 5 — Effect of temperature on the apparent rate constant and values of activation parameters[a]

Parameters	Temperature	Values	
		D-Arb	D-Rib
$J \times 10^5(s^{-1})$	308	4.38	11.69
$J \times 10^5(s^{-1})$	313	6.82	16.57
$J \times 10^5(s^{-1})$	318	8.77	19.49
$J \times 10^5(s^{-1})$	323	12.65	26.31
k_r ($dm^6\ mol^{-1}s^{-1}$)	313	10.37	18.26
$A \times 10^{-9}$ ($dm^6\ mol^{-1}s^{-1}$)	313	3.76	3.72
E_a (kJ/mol)	313	51.25	49.74
$\Delta H^{\#}$ (kJ/mol)	313	48.63	47.13
$\Delta S^{\#}$ (J/K/mol)	313	–70.25	–70.42
$\Delta G^{\#}$ (kJ/mol)	313	70.62	69.17

[a]Solution conditions: [NBA] = 10.00×10^{-4} mol dm^{-3} (Arb and Rib); [substrate] = 10.0×10^{-2} mol dm^{-3} (Arb), 6.00×10^{-2} mol dm^{-3} (Rib); [Pd(II)] = 33.84×10^{-6} mol dm^{-3} (Arb), 36.67×10^{-6} mol dm^{-3} (Rib); $[H^+] = 0.83 \times 10^{-3}$ mol dm^{-3} (Arb), 0.50×10^{-3} mol dm^{-3} (Rib); [$Hg(OAc)_2$] = 1.42×10^{-3} mol dm^{-3} (Arb and Rib)

Reactive species of $PdCl_2$

The complexes of palladium group metals are well known. Various possible mononuclear complexes of Pd(II), namely $[PdCl_3]^{-1}$, $[PdL_2Cl_2]$, $[PdL_3Cl]^+$ and $[PdL_4]^{2+}$ (where 'L' represents a ligand like amine, phosphine, sulphide, etc.) are reported[9]. In most of the studies using Pd(II) as a homogenous catalyst, it has been employed in the form of Pd(II) chloride. Pd(II) chloride[10] is rather insoluble in aqueous solution but does dissolve in presence of chloride ion as $[PdCl_3(H_2O)]^-$ and $[PdCl_4]^{2-}$. The equilibrium constants corresponding to the following equilibria have been determined by several workers, and all are in fair agreement with a value of log β_4 between 11 and 12 at 25°C.

$$Pd^{2+} + Cl^- \overset{K_1}{\rightleftharpoons} [PdCl]^+$$

$$[PdCl]^+ + Cl^- \overset{K_2}{\rightleftharpoons} [PdCl_2]$$

$$[PdCl_2] + Cl^- \overset{K_3}{\rightleftharpoons} [PdCl_3]^-$$

$$[PdCl_3]^- + Cl^- \overset{K_4}{\rightleftharpoons} [PdCl_4]^{2-}$$

Values of log K_1 to log K_4 have been reported as 4.47, 3.29, 2.41 and 1.37 respectively, with log β_4 = 11.54. It is also reported that K_4 is probably the most important stability constant for catalytic chemistry. The existence of $PdCl_2$, exclusively in the form of $[PdCl_4]^{2-}$ is reported by Ayres[11] who has observed that when a reaction ratio of 2 : 1 for sodium chloride (Cl^- ion) to Pd(II) chloride is maintained, it will result in the formation of well known tetrachloropalladate(II), $[PdCl_4]^{2-}$. This is also supported by UV spectra of Pd(II) chloride with different [Cl^-] ions, where the observed single peak at 236 nm clearly indicates the existence of lone $PdCl_4^{2-}$ species in the solution of Pd(II) chloride. Since throughout the experiments, ratio of Cl^- ion to the palladium(II) chloride concentration, i.e. $[Cl^-]/[PdCl_2]$ was maintained more than 2, it can safely be assumed that the species $[PdCl_4]^{2-}$ is the most reactive species of Pd(II) chloride in HCl. Such species of palladium (II) chloride has also been reported in the oxidation of amino alcohols by chloromine-T[12], N-bromosuccinimide[3], and in the oxidation of some sugars by N-bromosuccinimide[13] and N-bromoacetamide[14,15] (NBA).

It is reported[1,16] that Pd(II) forms a complex with organic substrates, i.e allyl alcohol and reducing sugar(mannose or maltose). In order to verify the formation of a complex between reactive species of Pd(II) chloride, i.e. $PdCl_4^{2-}$ and sugar in the present investigation, UV-spectra of $PdCl_2$ solution, sugar solution and Pd(II) chloride with different concentrations of sugar solutions were collected. From the spectra, it is quite clear that with the increase in [sugar], there is an increase in absorbance of pure Pd(II) chloride solution from 2.88 to 2.90 and 2.92. This increase in absorbance with the increase in [sugar] is due to shift in equilibrium to the right side by which more and more formation of [Pd(II)–sugar] complex is ensured:

$$[PdCl_4]^{2-} + S \rightleftharpoons [PdCl_3S] + Cl^- \quad \ldots (a)$$

This relation, where formation of [Pd(II)–sugar] complex is indicated, is also supported by the observed negative effect of chloride ion concentration on the rate of reaction.

When NBA solution (10.00×10^{-4} mol dm^{-3}) was added to the solution of Pd(II), Cl^- and reducing sugar, it was observed that with the addition of NBA, there is an increase in absorbance from 2.90 to 2.98 at 240 nm. This increase in absorbance can be considered as due to formation of a complex[1] between $[PdCl_3.S]^{1-}$ and [HOBr] according to:

$$[PdCl_3.S]^{1-} + HOBr \rightleftharpoons \left[Cl-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Pd}}\!\!\leftarrow\!\!-OBr \right]^{2-} + H^+ \quad \ldots (b)$$

(S coordinated to Pd)

The shift in λ_{max} towards longer wavelength with an increase in absorbance is due to combination of a chromophore like reactive species of NBA, i.e. HOBr and an auxochrome (Cl^-) already present in the complex $[PdCl_3.S]^-$ to give rise to another chromophore $[PdCl_3.S.OBr]^{2-}$.

Further, when Hg(II) solution (1.25×10^{-3} mol dm^{-3}) was added to the solution of Pd(II), Cl^-, reducing sugar and NBA, it was again observed that with the addition of Hg(II) solution, there is an increase in absorbance from 2.98 to 3.12 at 244 nm. This increase in absorbance with a shift in λ_{max} value towards longer wavelength might be considered as due to formation of another complex $[PdCl_3.S.OBr(Hg)]$, which has the property of a chromophore showing absorption in the ultra-violet region according to:

$$[PdCl_3.S.OBr]^{2-} + Hg^{2+} \rightleftharpoons [PdCl_3.S.OBr]\text{–Hg} \quad \ldots (c)$$

Kinetic data of the present investigation have led us to assume that the complex $[PdCl_3.S]^-$ formed through reversible step (a) will combine with reactive species of NBA, i.e. HOBr and Hg(II) to form another complex via reversible step (d) where reversible steps (b) and (c) are shown to be merged into one step.

$$[PdCl_3.S]^- + Hg^{2+} + HOBr \rightleftharpoons [PdCl_4.S.OBr]\text{–Hg} + H^+ \quad \ldots (d)$$

Reaction mechanism and rate law

On the basis of above discussion and kinetic studies, a probable reaction mechanism can be proposed for the Pd(II) catalysed and Hg(II) co-catalysed oxidation of Arb and Rib in acidic medium as Scheme 1. The fast equilibrium step I and reversible steps II and III are well in accordance with the experimental findings and spectral evidences.

$$MeCONHBr + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} MeCONH_2 + HOBr \quad \text{(I)}$$
(NBA) (NHA)

$$[PdCl_4]^{2-} + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [PdCl_3S]^- + Cl^- \quad \text{(II)}$$
C_1 C_2

where 'S' stands for Arb and Rib.

$$[PdCl_3.S]^- + Hg^{2+} + HOBr \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \left(Cl-\underset{Cl}{\overset{Cl}{Pd}}\leftarrow \underset{S}{} \overset{OBr}{\underset{Hg}{}} \right) + H^+ \quad \text{(III)}$$
(C_2) (C_3)

$$\left(Cl-\underset{Cl}{\overset{Cl}{Pd}}\leftarrow \underset{S}{} \overset{OBr}{\underset{Hg}{}} \right) + H_2O \xrightarrow[\text{Slow and rate determining Step}]{k_4} [PdCl_3(H_2O)]^- + R-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OBr}{C}}-O^- + Hg^{2+} \quad \text{(IV)}$$
(C_3)

where R stands for $C_5H_7O_3$

$$R-\overset{H}{\underset{H\cdots O}{C}}-\overset{H}{\underset{O-Br}{C}}-O^- + H^+ \xrightarrow{\text{fast}} R-\underset{O}{\overset{\|}{C}}-H + H-\underset{O}{\overset{\|}{C}}-OH + HBr \quad \text{(V)}$$

$$R-\underset{O}{\overset{\|}{C}}-H \xrightarrow[H^+]{\text{NBA / Pd(II) / Hg(II)}} R-\overset{OH}{\underset{O-Br}{C}}-H \quad \text{(VI)}$$

$$R-\overset{OH}{\underset{H}{C}}-O-Br \longrightarrow R-\underset{O}{\overset{\|}{C}}-OH + HBr \quad \text{(VII)}$$
(Erythronic acid)

$$[PdCl_3.(H_2O)]^- + Cl^- \longrightarrow [PdCl_4]^{2-} + H_2O \quad \text{(VIII)}$$

Scheme (1)

On the basis of above mechanism and stoichiometric equations for both D-arabinose and D-ribose, the rate in terms of decrease in concentration of [NBA] can be expressed as:

$$\text{rate} = -\frac{d[NBA]}{dt} = 2k_4[C_3] \quad \ldots (1)$$

On applying the law of chemical equilibrium to step I, we get:

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

On applying steady state approximation to steps (II) and (III), we get Eqs (3) and (4), respectively:

$$[C_2] = \frac{k_2[C_1][S][NHA]}{k_{-2}[Cl^-][NHA]+k_3K_1[Hg(II)][NBA]} \quad \ldots (3)$$

$$[C_3] = \frac{K_1k_2k_3[C_1][S][NBA][Hg(II)]}{(k_{-3}[H^+]+k_4)(k_{-2}[Cl^-][NHA] + k_3K_1[Hg(II)][NBA])} \quad \ldots (4)$$

According to the Scheme 1, the total concentration of Pd(II), i.e. $[Pd(II)]_T$ can be expressed as:

$$[Pd(II)]_T = [C_1]+[C_2]+[C_3] \quad \ldots (5)$$

With the help of Eqs (3), (4) and (5), we get:

$$[C_1]=\frac{(k_{-3}[H^+]+k_4)(k_{-2}[Cl^-][NHA]+k_3K_1[Hg(II)][NBA])[Pd(II)]_T}{(k_{-3}[H^+]+k_4)(k_{-2}[Cl^-][NHA]+k_3K_1[Hg(II)][NBA])+k_2[S][NHA](k_{-3}[H^+]+k_4)+K_1k_2k_3[S][NBA][Hg(II)]} \quad \ldots (6)$$

Eqs (1) and (4) give:

$$\text{rate}=\frac{-d[NBA]}{dt}=\frac{2K_1k_2k_3k_4[NBA][S][Hg(II)][C_1]}{(k_{-3}[H^+]+k_4)(k_{-2}[Cl^-][NHA]+K_1k_3[NBA][Hg(II)]} \quad \ldots (7)$$

On substituting the value of $[C_1]$ from Eq. (6) to Eq.(7), the rate law can be obtained as:

$$\text{rate}=-\frac{d[NBA]}{dt}=\frac{2K_1k_2k_3k_4[NBA][S][Pd(II)]_T[Hg(II)]}{(k_{-3}[H^+]+k_4)(k_{-2}[Cl^-][NHA]+K_1k_3[Hg(II)][NBA])+k_2[S][NHA](k_{-3}[H^+]+k_4)+K_1k_2k_3[S][NBA][Hg(II)]} \quad \ldots (8)$$

Since order with respect to $[H^+]$ is negative, probability of step (III) being reversible is more and more. Under this condition, it is reasonable to assume that $k_{-3}[C_3][H^+] >> k_4[C_3]$ or $k_3[H^+] > k_4$. When $k_3[H^+] > k_4$, Eq.(8) will be reduced to a relation, the numerator and denominator of which when divided by k_2k_3, will take the shape of Eq (9):

$$\text{rate}=-\frac{d[NBA]}{dt}=\frac{2K_1k_4[S][NBA][Hg(II)][Pd(II)]_T}{\frac{k_{-2}k_{-3}}{k_2k_3}[H^+][Cl^-][NHA]+\frac{K_1k_{-3}}{k_2}[H^+][Hg(II)][NBA]+\frac{k_{-3}}{k_3}[S][NHA][H^+]+K_1[S][NBA][Hg(II)]} \quad \ldots (9)$$

Eq.(9) can also be written as:

$$\text{rate}=-\frac{d[NBA]}{dt}=\frac{2K_1k_4[S][NBA][Hg(II)][Pd(II)]_T}{a[H^+][Cl^-][NHA]+b[H^+][Hg(II)][NBA]+c[S][NHA][H^+]+K_1[S][NBA][Hg(II)]} \quad \ldots (10)$$

where

$$a=\frac{k_{-2}k_{-3}}{k_2k_3},\quad b=\frac{K_1k_{-3}}{k_2}\quad \text{and}\quad c=\frac{k_{-3}}{k_3}$$

On reversing Eq. (10), we get:

$$\frac{1}{\text{rate}}=\big(a[H^+][Cl^-][NHA]\big)/(2K_1k_4[S][NBA][Hg(II)][Pd(II)]_T+\big(b[H^+]\big)/\big(2K_1k_4[S][Pd(II)]_T\big)+\big(c[NHA][H^+]\big)/(2K_1k_4[NBA][Hg(II)][Pd(II)]_T)+1/(2k_4[Pd(II)]_T) \quad \ldots (11)$$

According to Eq.(11), if a plot is made between (1/rate) and $[H^+]$ or [NHA] or $[Cl^-]$, straight lines having positive intercept on (1/rate) axis should be obtained. When (1/rate) values are plotted against $[H^+]$, [NHA] and $[Cl^-]$ straight lines with positive intercepts on (1/rate) axis were obtained (Figs 1 and 2) which prove the validity of the rate law (10) and hence the proposed mechanism. From the intercepts of the plots of 1/rate versus $[H^+]$ and 1/rate versus [NHA] and from the slopes and the intercepts of the plots of 1/rate versus $[Cl^-]$, the values of the constants k_4, b/K_1, c/K_1 and a/K_1 have been calculated in the oxidation of both Arb and Rib at 40°C. The values, thus obtained, are presented in Table 6. Utilizing the values of rate constant k_4 and other constants, i.e. a/K_1, b/K_1 and c/K_1, the values of the rate of reaction for the variation of [NHA] and $[Cl^-]$ have been calculated and found to be very close to the observed values of the rate of reaction (Table 4). The close similarity between the observed and the calculated rates clearly proves the validity of the rate law (10) and hence the proposed reaction mechanism shown as Scheme 1.

It is well known that if a reaction occurs with the approach of ions of the same sign, or a separation of ions of opposite sign, there is an intensification of electric field. Therefore, an increase in electrostriction and resulting decrease in volume, there is also decrease in entropy owing to the loss of freedom of the solvent molecules. In the present study of oxidation of reducing sugars by Pd(II) as homogeneous catalyst, the observed negative entropy of activation can be considered due to increase in electrostriction when reaction occurs with a separation of ions of opposite sign in the rate determining step (V) of the proposed reaction Scheme 1.

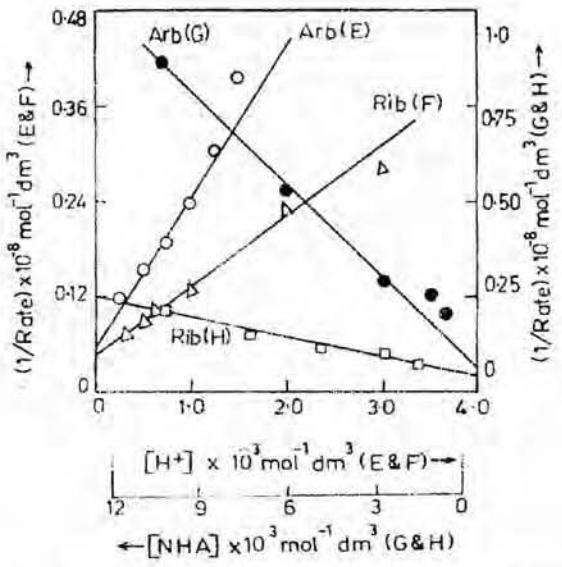

Fig. 1 — Verification of rate law (10) under the conditions of Table 4 for 1/rate *vs.* [NHA] and Table 2 for 1/rate *vs.* [H^+] {E and G = D-arabinose (Arb), F and H = D-ribose (rib)}.

Table 6 — Calculation of constants (k_4, a/K_1, b/K_1 and c/k_1) from the plots of (1/rate) vs. [H^+], (1/rate) *vs.* [NHA] and (1/rate) *vs.* [Cl^-] for Pd(II) catalysed oxidation of Arb and Rib by NBA at 40°C under the conditions of Table 2 and Table 4

Plots	Constants	D-Arb	D-Rib
$\frac{1}{\text{rate}}$ vs. [H^+]	k_4	3.69×10^{-3} sec^{-1}	4.22×10^{-3} sec^{-1}
$\frac{1}{\text{rate}}$ vs.[NHA]	b/K_1	1.56×10^{2}	0.23×10^{2}
$\frac{1}{\text{rate}}$ vs.[Cl^-]	c/K_1	2.70×10^{1}	20.30×10^{1}
	a/K_1	1.51×10^{2}	0.20×10^{2}

The order of frequency factor being the same for both reducing sugars clearly indicates the operation of single mechanism in the present study of oxidation of pentoses by NBA in presence of Pd(II) as homogeneous catalyst.

Comparison of the present study with the reported results[2,17] for Ru(III)- and Ir(III)-catalysed oxidation of reducing sugars by NBA in presence of perchloric acid and results reported for Pd(II)-catalysed oxidation of reducing sugars by NBS[13] has also been made. With the change in catalyst from Ru(III) or Ir(III) to Pd(II), it is found that there is no change in order with respect to catalyst concentration (except at very high [Ir(III)]). But, a significant change is observed with respect to [Hg(II)] and [reducing sugar]. Observed first to zero-order kinetics in [arabinose], [ribose] and in [Hg(II)] distinguishes the present investigation from Ir(III)-catalysed oxidation

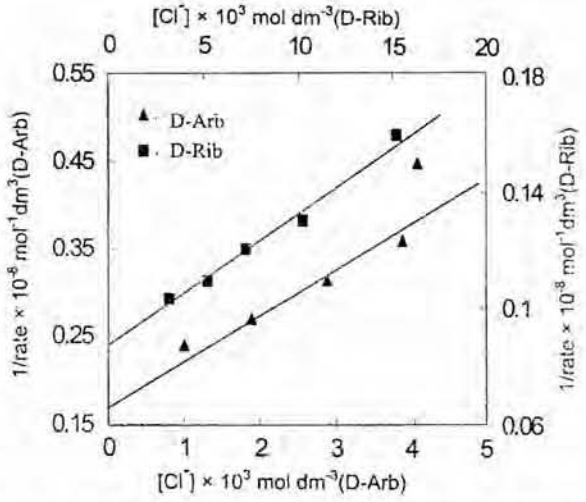

Fig. 2 — Verification of rate law (10) under the conditions of Table 4 for 1/rate *vs.* [Cl^-] {Arb: D-arabinose, and Rib: D-ribose}.

of reducing sugars by NBA where the rate law does not involve reducing sugar concentration and shows that order with respect to [Hg(II)] varies from two to one. The present study being very similar to Ir(III)-catalysed oxidation of reducing sugars by NBA as far as negative effect of [Cl^-] on the rate of reaction is concerned has a distinguishing feature with Ru(III)-catalysed oxidation of reducing sugars by NBA where order with respect to [Cl^-] has been found to be fractionally positive. Negative fractional order in [H^+], retarding effect of [NHA] and no effect of ionic strength of the medium on the rate of reaction are the common features of the present study and other two studies reported earlier. Negative entropy of activation observed in the oxidation of arabinose and ribose as against observed positive entropy of activation in the reported Ru(III)- or Ir(III)-catalysed oxidation of reducing sugars by NBA gives an additional support for the rate determining step where the activated complex as neutral species dissociates into oppositely charged species.

Conclusions

When comparison is made between the present study and the study reported for Pd(II)-catalysed oxidation of reducing sugars by NBS, it is found that this study is distinguishable with the previous study in two respects, one with respect to [Hg(II)] and the other with respect to one of the reaction products, i.e. NHA in the present case and NHS in the case reported earlier. Observed fractional positive order in [Hg(II)] in the oxidation of reducing sugars by NBA indicates

that Hg(II) in addition to its role as Br^- ion scavenger also functions as co-catalyst whereas insignificant effect of [Hg(II)] on the rate of reaction in the oxidation of reducing sugars by NBS shows that the role of $Hg(OAc)_2$ is limited up to the Br^- ion scavenger. In the present case, negative effect of [NHA] on 'J', is contrary to the reported nil effect of [NHS] on the rate of reaction.

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