



Kinetic and mechanistic investigation of Pd(II)-catalysed and Hg(II)-co-catalysed oxidation of D(+)-melibiose by N-bromoacetamide in acidic medium

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ABSTRACT

The kinetic and mechanistic study of homogeneously Pd(II)-catalysed and Hg(II)-co-catalysed oxidation of D(+)-melibiose (mel) by N-bromoacetamide (NBA) in perchloric acid medium have been made at temperature $40\text{ }^{\circ}\text{C} \pm 0.1\text{ }^{\circ}\text{C}$. Kinetic results show first-order kinetics with respect to NBA at its low concentrations, tending to zero-order at its high concentrations. The oxidation rate is directly proportional to [Pd(II)] and [sugar], indicating first-order kinetics with respect to Pd(II) and sugar. Zero effect of Cl^- and H^+ ions throughout their variation have been noted. First-order kinetics with respect to Hg(II) at its low concentration tends to zero-order at its higher concentration. Addition of acetamide (NHA) decreases the first-order rate constant (k_1) while the rate of reaction is not influenced by the change in ionic strength (μ) of the medium. The first-order rate constant decreases with an increase in dielectric constant of the medium. Arabinonic acid, lyxonic acid and formic acid were identified as oxidation products of the reaction. Various activation parameters including the entropy of activation were also calculated. A plausible mechanism conforming to kinetic data, spectrophotometric observations, reaction stoichiometry and product analysis has been proposed.

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1. Introduction

N-Haloimides such as N-bromosuccinimide (NBS), N-bromoacetamide (NBA), N-bromophthalimide and N-chlorosuccinimide (NCS) have been used as analytical reagents and also as very effective oxidants due to their specific oxidizing character. The use of N-bromoacetamide (NBA) has been made as an oxidizing and brominating reagent [1] in preparative organic chemistry and also to estimate various organic and inorganic compounds. Reports are available where NBA was used as an oxidant in presence of certain transition metal ions viz Ir(III) [2,3], Ru(III) [4–8], Rh(III) [9,10] and Os(VIII) [11,12]. Palladium-based catalysts [13] are found to have high catalytic activity in clean deionized water. Tobias Schalow et al. [14] have described the formation and catalytic activity of partially oxidized palladium-nanoparticles. Their report clearly shows that oxide supported metal nanoparticles are commonly used as catalysts for oxidation reactions in chemical industry, emission control and energy technology. Few reports [15–18] are also available where chloro-complex of Pd(II) has been used as homogeneous catalyst in the oxidation of monosaccharides using either NBA or NBS as an oxidant.

These studies have prompted us to probe the catalytic activity of Pd(II) chloride in the oxidation of D(+)-melibiose and to ascertain the oxidative mode of NBA along with the role of biologically important reducing sugar (D(+)-melibiose) in the redox system under investigation. In this study our main aim was to ascertain whether-

- (1) NBA as an oxidant in acidic medium behaves in the same way as it behaved in the reported Ru(III) [5]- and Ir(III) [2]- catalyzed oxidation of reducing sugars.
- (2) HOBr is the reactive species of NBA in acidic medium in the present investigation as is reported in Ru(III) [5]- and Ir(III) [2]- catalyzed oxidation of reducing sugars by NBA in acidic medium or not?
- (3) The role of reducing sugar molecule in the presence of Pd(II) chloride as catalyst and NBA as an oxidant in acidic medium is similar to the reported role of reducing sugar in the presence of Ir(III)/Ru(III) chloride and NBA in acidic medium.
- (4) Pd(II) chloride in acidic medium participates in the reaction under investigation in the same way as it is reported in Ru(III) [5]- and Ir(III) [2]- catalyzed oxidation of reducing sugars by NBA in acidic medium.
- (5) The role of Hg(II) is similar to its reported role as Br^- ion scavenger and co-catalyst in Ru(III) [5]- and Ir(III) [2]- catalyzed oxidation of reducing sugars by NBA in acidic medium or not?

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- (6) Effect of $[H^+]$ on the rate of oxidation in the present investigation is same as is reported in Ru(III) [5]- and Ir(III) [2]-catalyzed oxidation of reducing sugars or not?
- (7) The formation of most reactive activated complex results by the interaction of two oppositely charged species in the same way as it is reported for Ru(III) [5]- and Ir(III) [2]-catalyzed oxidation of reducing sugars by NBA in acidic medium.
- (8) The role of Cl^- ions and the effect of [NHA] on the rate of oxidation in the present investigation are similar to the role reported in Ru(III) [5]- and Ir(III) [2]-catalyzed oxidation of reducing sugars by NBA in acidic medium or not?
- (9) There is an enhancement in the catalytic activity of Pd(II) chloride in comparison to the catalytic activities of Ru(III) and Ir(III) in the oxidation of reducing sugars by NBA in acidic medium or not?

2. Experimental

2.1. Materials

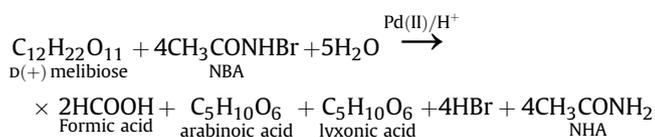
Stock solution of Palladium(II) chloride (Qualigens 'Glaxo' Chem.) was prepared by dissolving its sample in known volume of hydrochloric acid. The overall strength of hydrochloric acid was maintained at 11.71×10^{-2} M and the strength of Pd(II) chloride was 5.64×10^{-3} M. N-bromoacetamide (NBA) solution was prepared by weighing and dissolving it in doubly distilled water every day. Standardization of NBA solution was done iodometrically by titrating it against standard sodium thiosulphate (hypo) solution. Reducing substrate i.e., D(+)-melibiose solution was prepared daily by weighing and dissolving it in doubly distilled water. The aqueous solution of mercuric acetate (Loba chemicals) was acidified with 20% acetic acid solution. All other reagents namely $NaClO_4$, $HClO_4$, acetamide and KCl were prepared from their samples (E. Merck) in doubly distilled water.

2.2. Kinetic measurements

A black coated reaction vessel containing requisite volumes of solution of NBA, $HClO_4$, Pd(II) chloride, KCl, $NaClO_4$ and $Hg(OAc)_2$ was placed in an electrically operated thermostatic water bath maintained at $40 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$ for thermal equilibrium. Another conical flask containing D(+)-melibiose solution was also placed in the same thermostat at the same temperature for thermal equilibrium. Requisite amount of D(+)-melibiose solution was added to the reaction vessel containing all other thermally equilibrated reactants to initiate the reaction. The progress of the reaction was determined by estimating the unconsumed N-bromoacetamide iodometrically.

2.3. Stoichiometry and product analysis

Several sets of experiments with different [NBA]: [sugar] ratio under the condition $[NBA] \gg [sugar]$, were performed at room temperature for 72 h. Estimation of unconsumed [NBA] was made iodometrically. On the basis of stoichiometric experiments it was found that 4 mol of NBA were required to oxidize 1 mol of D(+)-melibiose. Accordingly, the following stoichiometric equation can be formulated:



Kinetic and equivalence studies together with spot test [19a] and thin layer chromatography [19b] experiments helped us to identify formic acid and other reaction products of the reaction under investigation.

3. Kinetic results

Kinetic study of Pd(II)-catalysed oxidation of D(+)-melibiose by NBA in perchloric acid medium was made at $40 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$. Initial rate ($-dc/dt$) of reaction in each kinetic run was determined by the slope of the tangent of the plot drawn between remaining [NBA] and time. The method of initial rates was adopted to avoid possible complications due to interference by products during the course of reaction. The first-order rate constant (k_1) was calculated by the following equation:

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

Kinetic study of oxidation of D(+)-melibiose was made at several initial concentrations of all reactants. The reaction under investigation follows first-order kinetics with respect to N-bromoacetamide at its low concentration, which tends to zero-order at its higher concentration as shown by the plot of $-dc/dt$ vs [NBA] (Fig. 1). This result is further verified by the constant values of k_1 in lower [NBA] which decreases at higher NBA concentrations (Table 1). The order with respect to the [NBA] was taken as unity, as throughout the study, the concentration of NBA was fixed in its lower concentration. Straight line passing through the origin in the plot of k_1 vs [Pd(II)], indicates first-order dependence of reaction rate on [Pd(II)] throughout its variation (Fig. 2). The first-order rate constant (k_1) increases with the increase in [mel], suggesting first-order dependence of the reaction on [mel]. This observation is further confirmed by the straight line passing through the origin in the plot of k_1 vs [mel] (Fig. 3, Table 1). Effect of $[H^+]$ on the rate of reaction was found to be zero. Stoichiometric study indicates Br^- ion as reaction product in the present investigation. During progress of reaction Br^- ion interacts with NBA to form molecular bromine which sets parallel oxidation of D(+)-melibiose and this complicates the kinetic study of D(+)-melibiose by NBA in the presence of Pd(II). In order to ensure pure NBA oxidation, mercuric acetate has been used which scavenges Br^- ions and thus obviates parallel Br_2 oxidation. Hg(II) has also been reported earlier to act as an oxidant as well as co-catalyst. Therefore, here an attempt has also been made to study the role of Hg(II) in addition to its role as Br^- ions scavenger. Kinetic results of few experiments without NBA but with Hg(II) under similar kinetic conditions indicated that

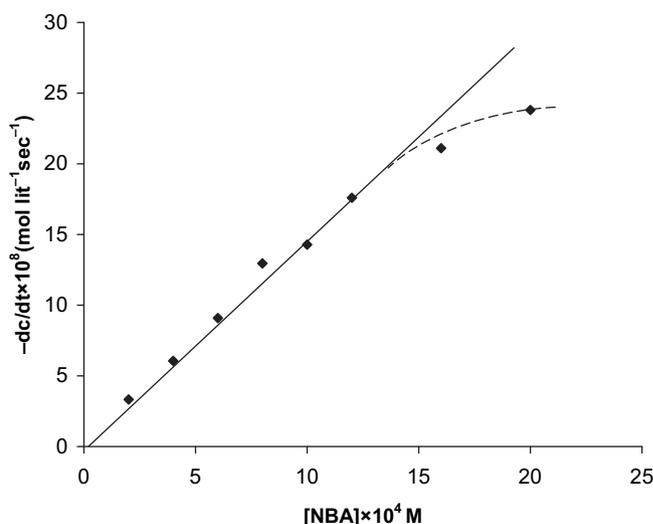


Fig. 1. Plot between $-dc/dt$ and [NBA] at $40 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$. $[mel] = 0.200 \times 10^{-2} \text{ mol dm}^{-3}$, $[PdCl_2] = 0.282 \times 10^{-5} \text{ mol dm}^{-3}$, $[HClO_4] = 0.133 \times 10^{-2} \text{ mol dm}^{-3}$, $[Hg(OAc)_2] = 2.22 \times 10^{-4} \text{ mol dm}^{-3}$.

Table 2
Effect of variation of $[\text{PdCl}_2]$ and $[\text{Hg}(\text{OAc})_2]$ on the first-order rate constant at $40 \pm 0.1 \text{ } ^\circ\text{C}$.^a

$[\text{PdCl}_2] \times 10^5 \text{ (mol dm}^{-3}\text{)}$	$[\text{Hg}(\text{OAc})_2] \times 10^3 \text{ (mol dm}^{-3}\text{)}$	$k_1 \times 10^4 \text{ (sec}^{-1}\text{)}$
1.41	1.25	2.90
2.82	1.25	5.82
5.62	1.25	11.70
8.46	1.25	16.67
11.28	1.25	23.33
14.10	1.25	31.00
16.92	1.25	37.00
22.56	1.25	50.00
2.82	1.25	2.50
2.82	1.50	3.00
2.82	2.00	4.20
2.82	2.50	5.83
2.82	3.00	6.67
2.82	3.50	7.50
2.82	4.00	7.80
2.82	4.50	8.30

^a Conditions: $[\text{NBA}] = 10.00 \times 10^{-4} \text{ mol dm}^{-3}$, $\text{D}(+)\text{melibiose} = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 02.00 \times 10^{-2} \text{ mol dm}^{-3}$ for $[\text{PdCl}_2]$ variation and $01.33 \times 10^{-2} \text{ mol dm}^{-3}$ for $[\text{Hg}(\text{OAc})_2]$ variation, $[\text{KCl}] = 06.00 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 50.00 \times 10^{-3} \text{ mol dm}^{-3}$.

From the above two sets of equilibria (a,b and c,d), it is clear that NBA in acidic medium exists in four different forms i.e., NBA itself, HOBr , $(\text{CH}_3\text{CONH}_2\text{Br})^+$ and $(\text{H}_2\text{OBr})^+$. In view of observed fractional negative order in $[\text{NHA}]$ and zero-order with respect to $[\text{H}^+]$, HOBr can be assumed as the reactive species of NBA in Pd(II)-catalysed oxidation of $\text{D}(+)\text{melibiose}$ out of aforesaid four possible oxidizing species of NBA. This result is further supported by the observed spectrum of NBA in perchloric acid where a single peak is observed at 205 nm (Fig. 6 (2)).

It is reported [20] that Pd(II) is the most common oxidation state of palladium and certainly the most important in the chemistry of its homogeneous catalysis. It is also reported that much of its catalytic chemistry is related to the fact that Pd(II) is an oxidant. Pd(II) is a d^8 ion and it prefers to form four co-ordinate square planar complexes. Reports [21] are available where the equilibrium constants for the following equilibria have been determined and found in agreement with a value of $\log \beta_4$ between 11 and 12 at $25 \text{ } ^\circ\text{C}$.

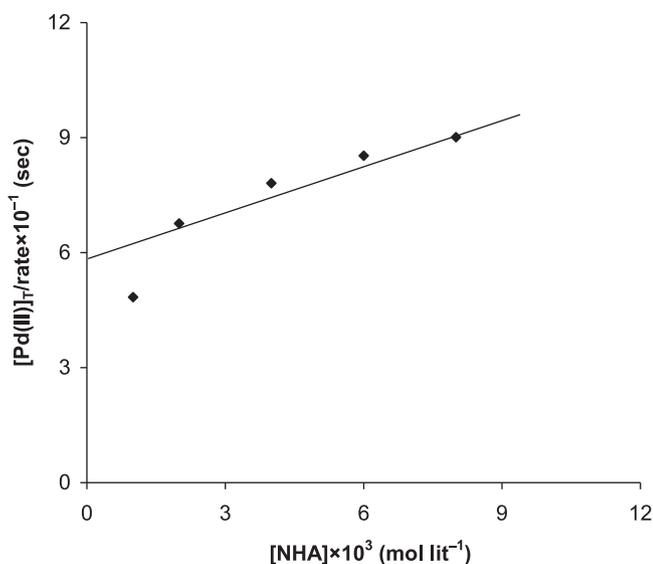


Fig. 5. Plot between $[\text{Pd}(\text{II})]_{\text{r}}/\text{rate}$ and $[\text{NHA}]$. $[\text{NBA}] = 10.00 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{meI}] = 02.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{PdCl}_2] = 02.82 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 01.33 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Hg}(\text{OAc})_2] = 12.50 \times 10^{-4} \text{ mol dm}^{-3}$.

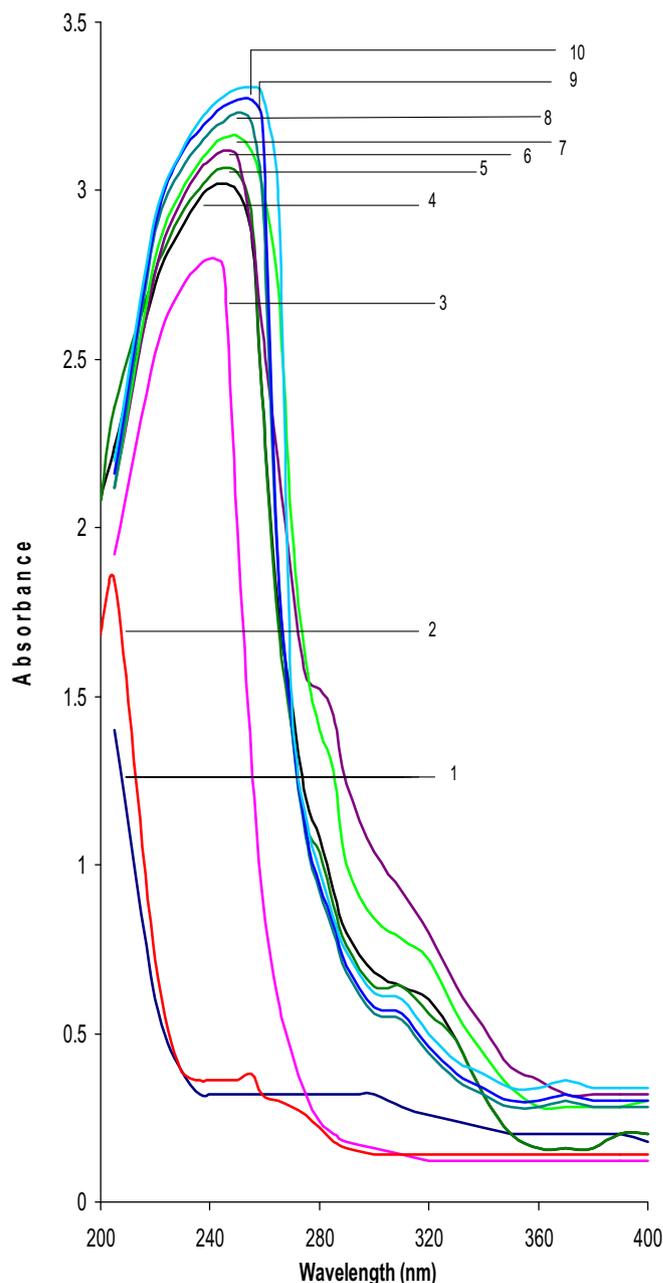
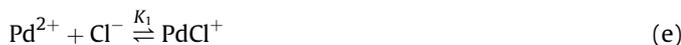


Fig. 6. spectra of solutions [1,2,3,4,5,6,7,8,9 and 10] recorded at room temperature. 1. $[\text{Sugar}] = 0.20 \text{ mol dm}^{-3}$, 2. $[\text{NBA}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.50 \text{ mol dm}^{-3}$, 3. $[\text{NBA}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Hg}(\text{II})] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$, 4. $[\text{Pd}(\text{II})] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, 5. $[\text{Pd}(\text{II})] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Sugar}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$, 6. $[\text{Pd}(\text{II})] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Sugar}] = 0.20 \text{ mol dm}^{-3}$, 7. $[\text{Pd}(\text{II})] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Sugar}] = 0.20 \text{ mol dm}^{-3}$, $[\text{NBA}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, 8. $[\text{Pd}(\text{II})] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Sugar}] = 0.20 \text{ mol dm}^{-3}$, $[\text{NBA}] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$, 9. $[\text{Pd}(\text{II})] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Sugar}] = 0.20 \text{ mol dm}^{-3}$, $[\text{NBA}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Hg}(\text{II})] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$, 10. $[\text{Pd}(\text{II})] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.20 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{Sugar}] = 0.20 \text{ mol dm}^{-3}$, $[\text{NBA}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{Hg}(\text{II})] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$.

Table 3

Activation parameters for Pd(II)-catalysed oxidation of D(+) melibiose by NBA in acidic medium Temp. = 40 °C ± 0.1 °C.

Reducing sugar	E_a (k cal mol ⁻¹)	k (mol ⁻² dm ⁻⁶ s ⁻¹)	ΔS^\ddagger (e.u.)	ΔH^\ddagger (k cal mol ⁻¹)	ΔG^\ddagger (k cal mol ⁻¹)	A (mol ⁻² dm ⁻⁶ sec ⁻¹)
D(+) melibiose	20.15 ± 0.39	1.74 × 10 ³	18.58 ± 0.26	19.53 ± 0.01	13.71 ± 0.11	1.65 × 10 ¹⁷



Elding [22] studied both the stability constants and rates of reaction and determined values of log K_1 to log K_4 as 4.47, 3.29, 2.41 and 1.37, respectively, with log β_4 equal to 11.54. Grinberg et al. [23] were also determined values of aforesaid stability constants and found as 4.3, 3.54, 2.68 and 1.68, respectively. On the basis of above equilibria, we can write



where β_4 is equal to $K_1K_2K_3K_4$

Ayres reported [24] that when a concentration ratio 2:1 for sodium chloride to palladium (II) chloride is maintained, it will result in the formation of tetrachloropalladate(II), $[\text{PdCl}_4]^{2-}$. Since throughout the study of oxidation of D(+) melibiose, the aforesaid concentration ratio was maintained, hence it is reasonable to assume that the catalyst palladium(II) chloride in the reaction under investigation remains in the form of $[\text{PdCl}_4]^{2-}$. Taking into consideration the observed catalytic role of Pd(II) chloride, it can be concluded that $[\text{PdCl}_4]^{2-}$ is the reactive species of Pd(II) chloride in the oxidation of D(+) melibiose by NBA in presence of perchloric acid. This result is further verified by the single peak observed at 245 nm for the solution containing Pd(II) chloride, H^+ and Cl^- ions (Fig. 6(4)).

It is reported that Pd(II) forms a complex with allyl alcohol [25] and also with sugar molecule [17]. In order to verify the probable formation of a complex between Pd(II) and D(+) melibiose, spectra for solutions containing Pd(II), H^+ and Cl^- , and Pd(II), H^+ and Cl^- with a sugar solution of two different concentrations have been collected. In the spectrum for Pd(II), H^+ and Cl^- , it is found that there is a single peak at 245 nm (Fig. 6(4)). When sugar solution of two different concentrations were added to the solution of Pd(II), H^+ and Cl^- , it has been observed that there is an increase in absorbance from 3.02 to 3.07 and 3.12 (Fig. 6(4,5 and 6)). On the basis of this observation, it can be concluded that an Organometallic complex between reactive species of Pd(II) i.e., $[\text{PdCl}_4]^{2-}$ and a sugar molecule is formed according to the following equilibrium:

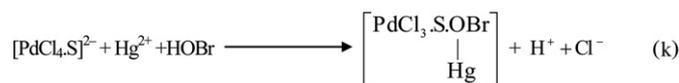


Above equilibrium indicates that with the addition of sugar molecule to the solution of Pd(II) chloride, the equilibrium will shift towards right hand side with more and more formation of $[\text{PdCl}_4 \cdot \text{S}]^{2-}$.

Attempts were also made to find out whether there is any possibility of the formation of a complex between $[\text{PdCl}_4 \cdot \text{S}]^{2-}$ and reactive species of NBA i.e., HOBr or not? For this, first of all the spectra after the addition of NBA solution of two different concentrations to the solution of Pd(II), H^+ , Cl^- and sugar at room temperature were collected. From the spectra, it is apparent that with the addition of NBA solution there is an increase in absorbance from 3.12 to 3.16 and 3.23 nm with a shift in λ_{max} value towards longer wavelength i.e., from 245 to 250 nm (Fig. 6(6), (7) and (8)). In

addition to this when Hg(II) solution of two different concentrations were added to the solution of Pd(II), H^+ , Cl^- , sugar and NBA, it was observed that with the addition of Hg(II) solution there is an increase in absorbance from 3.16 to 3.23 and 3.31 along with a shift in λ_{max} value towards longer wavelength i.e., from 250 to 255 nm (Fig. 6 (7) (9) and (10)). This overall increase in absorbance with a shift in λ_{max} towards longer wavelength can be considered as due

to formation of a new complex $\left[\begin{array}{c} \text{PdCl}_3 \cdot \text{S} \cdot \text{OBr} \\ | \\ \text{Hg} \end{array} \right]$ according to the following way-



On the basis of observed kinetic orders with respect to [NBA], [reducing sugar], [Pd(II)], [H^+], [Hg(II)], [NHA] and [Cl^-], spectrophotometric evidence collected for the formation of complex species

$[\text{PdCl}_4]^{2-}$, $[\text{PdCl}_4 \cdot \text{S}]^{2-}$ and $\left[\begin{array}{c} \text{PdCl}_3 \cdot \text{S} \cdot \text{OBr} \\ | \\ \text{Hg} \end{array} \right]$, a most probable reaction mechanism in the form of reaction Scheme 1, can be suggested.

According to the above reaction Scheme 1 the rate in terms of decrease in the concentration of NBA for the oxidation of D(+) melibiose can be expressed as

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = 4k_3[\text{C}_2][\text{Hg(II)}][\text{HOBr}] \quad (1)$$

where 4 indicates that 1 mol of D(+) melibiose is oxidized by 4 mol of NBA.

On applying steady-state approximation to the concentration of C_2 , we have eq. (2)

$$[\text{C}_2] = \frac{k_2[\text{C}_1][\text{S}]}{k_{-2} + k_3[\text{Hg(II)}][\text{HOBr}]} \quad (2)$$

On applying the law of chemical equilibrium to step (i) we have

$$[\text{HOBr}] = \frac{K_1[\text{NBA}]}{[\text{NHA}]} \quad (3)$$

According to reaction Scheme 1, the total concentration of Pd(II) i.e., $[\text{Pd(II)}]_{\text{T}}$ can be expressed as

$$[\text{Pd(II)}]_{\text{T}} = [\text{C}_1] + [\text{C}_2] \quad (4)$$

On substituting, the value of C_2 from eq. (2) in eq. (4), we get

$$[\text{Pd(II)}]_{\text{T}} = [\text{C}_1] + \frac{k_2[\text{C}_1][\text{S}]}{k_{-2} + k_3[\text{Hg(II)}][\text{HOBr}]}$$

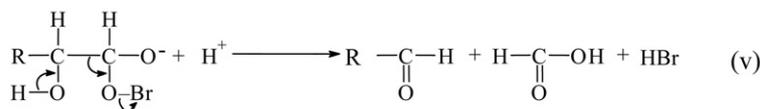
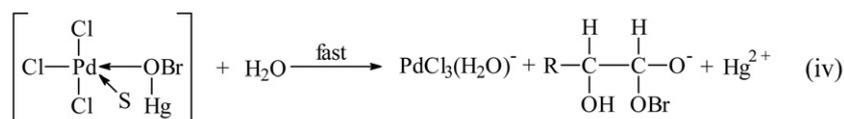
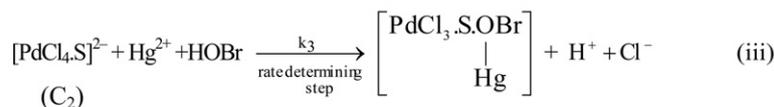
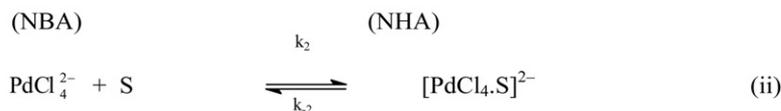
or

$$[\text{C}_1] = \frac{\{k_{-2} + k_3[\text{Hg(II)}][\text{HOBr}]\}[\text{Pd(II)}]_{\text{T}}}{k_{-2} + k_2[\text{S}] + k_3[\text{Hg(II)}][\text{HOBr}]} \quad (5)$$

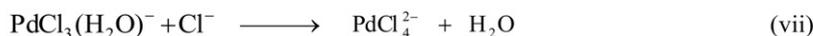
With the help of eqs. (2) and (5), we can write

$$[\text{C}_2] = \frac{k_2[\text{S}][\text{Pd(II)}]_{\text{T}}}{k_{-2} + k_2[\text{S}] + k_3[\text{Hg(II)}][\text{HOBr}]} \quad (6)$$

From eqs. (1), (3) and (6), we obtain eq. (7)



Where R is C₄H₉O₄



Scheme 1.

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{4k_2k_3K_1[\text{NBA}][\text{Pd(II)}]_T[\text{S}][\text{Hg(II)}]}{[\text{NHA}]\{k_{-2} + k_2[\text{S}]\} + k_3K_1[\text{NBA}][\text{Hg(II)}]} \quad (7)$$

If $k_2[\text{S}] \gg k_{-2}$, then according to eq. (7)

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{4k_2k_3K_1[\text{NBA}][\text{Pd(II)}]_T[\text{S}][\text{Hg(II)}]}{k_2[\text{S}][\text{NHA}] + k_3K_1[\text{NBA}][\text{Hg(II)}]} \quad (8)$$

Eq. (8) in the present case cannot be treated as the final rate law because it shows fractional positive order with respect to [mel] which is contrary to our observed experimental findings. On the other hand, if the inequality $k_{-2} \gg k_2[\text{S}]$ is assumed as valid one then eq. (7) will be reduced to eq. (9).

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{4k_2k_3K_1[\text{NBA}][\text{Pd(II)}]_T[\text{S}][\text{Hg(II)}]}{k_{-2}[\text{NHA}] + k_3K_1[\text{NBA}][\text{Hg(II)}]} \quad (9)$$

Eq. (9) is the final rate law and is in complete agreement with our experimental findings

Eq. (9) can also be written as

$$\frac{[\text{Pd(II)}]_T}{\text{rate}} = \frac{k_{-2}[\text{NHA}]}{4k_2k_3K_1[\text{NBA}][\text{S}][\text{Hg(II)}]} + \frac{1}{4k_2[\text{S}]} \quad (10)$$

where, $\text{rate} = -d[\text{NBA}]/dt$

Eq. (10) clearly shows that if a plot is made between $[\text{Pd(II)}]_T/\text{rate}$ and $[\text{NHA}]$, it will give a straight line having an intercept on $[\text{Pd(II)}]_T/\text{rate}$ axis. When a plot was made between $[\text{Pd(II)}]_T/\text{rate}$ and $[\text{NHA}]$, a straight line with intercept on $[\text{Pd(II)}]_T/\text{rate}$ axis was obtained (Fig. 5). This proves the validity of the rate law eq. (9) and hence the proposed reaction Scheme 1. From the intercept and the slope, the values of constants k_2 and k_{-2}/k_3K_1 were calculated and found as $1.95 \times 10^{-1} \text{ mol}^{-1}\text{dm}^3 \text{ sec}^{-1}$ and $6.17 \times 10^{-5} \text{ mol dm}^{-3}$ respectively in the oxidation of D(+) melibiose. Utilizing the values of constants k_2 and k_{-2}/k_3K_1 and taking the help of rate law eq. (9), the rates of variation of $[\text{NHA}]$ in the oxidation of D(+) melibiose were calculated and found to be in close agreement with the observed rates (Table 4). This further proves the validity of rate law eq. (9) and hence the proposed reaction Scheme 1.

Positive entropy of activation observed in Pd(II)-catalysed oxidation of D(+) melibiose by NBA in acidic medium clearly

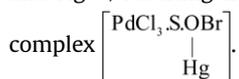
Table 4

Comparison between observed and calculated rates in variation of [NHA] on the basis of rate law eq. (10) at 40 °C±0.1 °C.^a

[NHA] × 10 ³ (mol dm ⁻³)	-dc/dt × 10 ⁷ (mol dm ⁻³ sec ⁻¹)	
	D(+) melibiose	
	Experimental	Calculated
1.00	5.83	4.19
2.00	4.17	4.01
4.00	3.61	3.61
6.00	3.30	3.39
8.00	3.13	3.16
10.00	3.05	2.95

^a Conditions: [NBA] = 10.00 × 10⁻⁴ mol dm⁻³, D(+) melibiose = 02.00 × 10⁻² mol dm⁻³, [PdCl₂] = 02.82 × 10⁻⁵ mol dm⁻³, [HClO₄] = 01.33 × 10⁻² mol dm⁻³, [Hg(OAc)₂] = 12.50 × 10⁻⁴ mol dm⁻³.

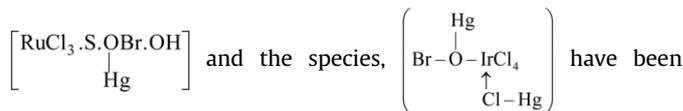
supports step (iii) of Scheme 1, where reaction is taking place between two oppositely charged species i.e., between [PdCl₄·S]²⁻ and Hg²⁺, resulting in the formation of most reactive activated complex



5. Comparison between the present study and the studies reported for Ru(III)- and Ir(III)-catalysed oxidation of reducing sugars

When an effort was made to compare the findings of Pd(II)-catalysed oxidation of D(+)melibiose with the results reported for Ru(III) [5] and Ir(III) [2]- catalyzed oxidation of reducing sugars, it was found that HOBr is the reactive species of NBA in each case. First-order kinetics in [sugar] was observed for both Pd(II) and Ru(III)[5] systems, but the reported reaction path for Ir(III) [2]- catalysed oxidation of reducing sugars clearly shows that there is no effect of [sugar] on the rate of reaction. The present study shows similarity with Ru(III) [5]- catalysed oxidation of reducing sugars as for as formation of a complex between transition metal-catalyst (Pd (II) or Ru(III)) with a sugar molecule is concerned, but it distinguishes itself from Ir(III) [2] system, where zero-order kinetics with respect to [sugar] was observed. Pd(II) and Ru(III) [5] systems show same behaviour in respect of the order in [Hg(II)], but observed second-order tending towards first-order kinetics in [Hg(II)] provides a reaction path, where two molecules of mercury before the rate determining step were involved in Ir(III) [2]- catalysed oxidation of reducing sugars. The present study entirely differs from other two studies as for as effect of [H⁺] on the rate of reaction is concerned. Negative effect of [H⁺] was observed in Ru(III) [5]- and Ir(III) [2]- catalysed oxidation of reducing sugars, whereas zero effect of [H⁺] on the rate of reaction was observed in the present

study. On the basis of observed kinetic data and observed positive entropy of activation, the species, $\left[\begin{array}{c} \text{PdCl}_3 \cdot \text{S} \cdot \text{OBr} \\ | \\ \text{Hg} \end{array} \right]$ is proposed as the most reactive species in the present study whereas the species,



and the species, $\left[\begin{array}{c} \text{Hg} \\ | \\ \text{Br}-\text{O}-\text{IrCl}_4 \\ \uparrow \\ \text{Cl}-\text{Hg} \end{array} \right]$ have been reported as the most reactive species for Ru(III) [5]- and Ir(III) [2]-catalysed oxidation of reducing sugars, respectively. Negative effect of [NHA] was observed in all the three catalyzed reactions.

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