

Mechanism of Pd(II) and Hg(II) co-catalyzed oxidation of D-mannose and maltose by acidic solution of *N*-bromoacetamide

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Abstract

The kinetics of the homogeneously Pd(II) catalyzed oxidation of D-mannose (Man) and maltose (Mal) by *N*-bromoacetamide (NBA) in perchloric acid medium, using mercuric acetate as scavenger for Br⁻ ions as well as co-catalyst, have been studied in the temperature range 35–50 °C. The reactions exhibit first-order kinetics at low concentrations of sugars (Man and Mal) and NBA, tending to zero-order at high sugar and NBA concentrations. The oxidation rate is directly proportional to [Pd(II)], while inverse fractional order in each of [H⁺], [Cl⁻] and [acetamide] was found. A positive effect on the rate of the reaction was observed on successive addition of [Hg(OAc)₂], whereas change in ionic strength (μ) of the medium has no effect on the reaction velocity. Formic acid and arabinonic acid (for both reducing sugars, i.e. Man and Mal) were identified as main oxidation products of reactions. The various activation parameters have also been evaluated. A plausible mechanism from the results of kinetic studies, reaction stoichiometry and product analysis is proposed.

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Keywords: Mechanism; Pd(II); Hg(II) co-catalyzed; HClO₄; Reducing sugars; *N*-Bromoacetamide

1. Introduction

Recently, considerable attention has been focused on the diverse nature of the chemistry of *N*-halogeno compounds [1–6] due to their ability to act as a source of halonium cations, hypohalite species and nitrogen anions. The potential application of such compounds remain unrealized as an oxidant in uncatalysed redox systems in particular as is evident by scant information in the literature. Although kinetic studies involving NBA [7–9] as an oxidant have been made for uncatalysed reactions but there are apparently few

reports with transition metal ions viz. Ru(III) [10,12], Ir(III) [11], Hg(II) [13] and Os(VIII) [13a] on its oxidative capacity in catalyzed processes. There seems to be few reports on the analogous Pd(II) ion as homogeneous catalyst. However, studies of the kinetics of Pd(II) ion oxidation of olefins have been reported. The *N*-halogeno compounds such as NBA/NBS oxidations of organic substrates is complicated by parallel bromine oxidation which is obviated by using Hg(II) [4–8,13]. Interestingly, in some NBS [14,15] reactions, Hg(II) also plays a catalytic role, but its role as co-catalyst is unknown especially with Pd(II) and sugar (a biologically important substrate). These reports and recent publications [16] concerning the oxidation of sugars by organic halo amines in alkaline medium have prompted us to monitor Pd(II)-Hg(II)

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Table 1
Effect of variation in reactant concentration on the rate constant at 40 °C

[NBA] ($\times 10^4 \text{ mol dm}^{-3}$)	[Substrate] ($\times 10^2 \text{ mol dm}^{-3}$)	[Pd(II)] ($\times 10^6 \text{ mol dm}^{-3}$)	k'_1 ($\times 10^5 \text{ s}^{-1}$) ^a	
			Man	Mal
2.50 ^b	7.50 ^c /10.00 ^d	28.20	14.58	–
4.00 ^b	7.50 ^c /10.00 ^d	28.20	11.33	9.34
5.00 ^b	7.50 ^c /10.00 ^d	28.20	10.17	9.12
6.00 ^b	7.50 ^c /10.00 ^d	28.20	8.74	9.01
8.00 ^b	7.50 ^c /10.00 ^d	28.20	7.14	7.12
12.00 ^b	7.50 ^c /10.00 ^d	28.20	5.21	3.82
16.00 ^b	7.50 ^c /10.00 ^d	28.20	4.18	3.49
20.00 ^b	–/10.00 ^d	28.20	–	3.18
10.00 ^b /8.00 ^e	1.00	28.20	1.10	0.97
10.00 ^b /8.00 ^e	2.00	28.20	2.06	1.62
10.00 ^b /8.00 ^e	4.00	28.20	3.27	3.11
10.00 ^b /8.00 ^e	6.00	28.20	4.76	4.50
10.00 ^b /8.00 ^e	8.00	28.20	6.35	6.32
10.00 ^b /8.00 ^e	12.00	28.20	7.82	7.66
10.00 ^b /8.00 ^e	7.50 ^c /10.00 ^d	2.82	1.26	1.45
10.00 ^b /8.00 ^e	7.50 ^c /10.00 ^d	5.64	1.81	1.91
10.00 ^b /8.00 ^e	7.50 ^c /10.00 ^d	11.28	2.26	2.92
10.00 ^b /8.00 ^e	7.50 ^c /10.00 ^d	22.56	4.44	5.84
10.00 ^b /8.00 ^e	7.50 ^c /10.00 ^d	33.84	6.48	8.77
10.00 ^b /8.00 ^e	7.50 ^c /10.00 ^d	50.76	10.00	13.16

^a $[\text{HClO}_4] = 0.80 \times 10^{-3} \text{ mol dm}^{-3}$ (Man), $3.00 \times 10^{-3} \text{ mol dm}^{-3}$ (Mal).

^b $[\text{Hg}(\text{OAc})_2] = 3.00 \times 10^{-3} \text{ mol dm}^{-3}$ (Man), $4.00 \times 10^{-3} \text{ mol dm}^{-3}$ (Mal).

^c Man.

^d Mal.

^e $1.20 \times 10^{-3} \text{ mol dm}^{-3}$ (Man), $1.42 \times 10^{-3} \text{ mol dm}^{-3}$ (Mal).

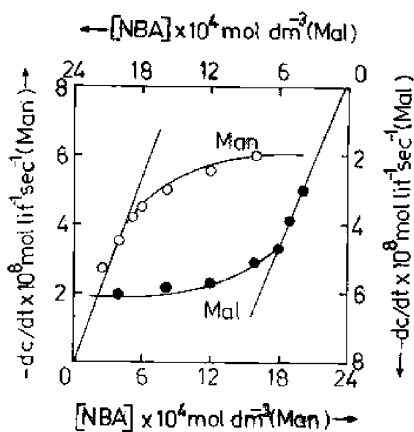


Fig. 1. Plots of $(-dc/dt)$ vs. [NBA] at 40 °C for the oxidation of D-mannose (Man) and maltose (Mal) under the experimental condition of Table 1.

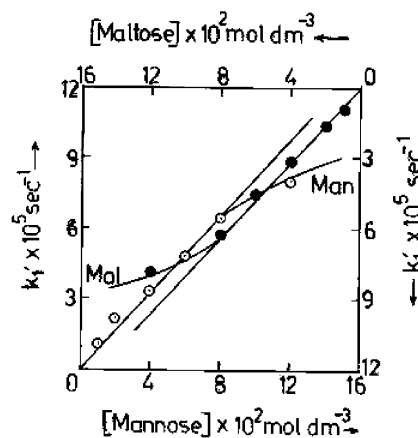


Fig. 2. Plots of k'_1 vs. [substrate] at 40 °C under the experimental condition of Table 1. Man: D-mannose and Mal: maltose.

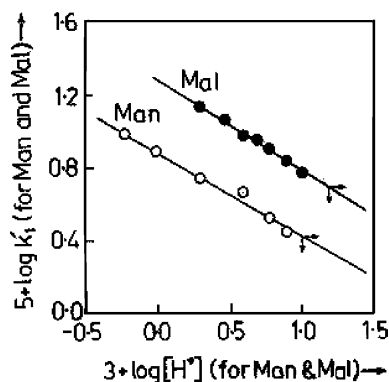


Fig. 3. Plots of $\log k'_1$ vs. $\log[H^+]$ at 40 °C under the experimental condition $[NBA] = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Man), $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Mal); [substrate] = $7.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Man), $10.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Mal); $[PdCl_2] = 28.20 \times 10^{-6} \text{ mol dm}^{-3}$; $[Hg(OAc)_2] = 1.20 \times 10^{-3} \text{ mol dm}^{-3}$ (Man), $1.42 \times 10^{-3} \text{ mol dm}^{-3}$ (Mal). Man: D-mannose and Mal: maltose.

of the substrate. It was also observed that on increasing $[H^+]$ in the reaction mixture, the values of k'_1 decreased, indicating thereby negative effect of $[H^+]$. The order of reaction with respect to hydrogen ions

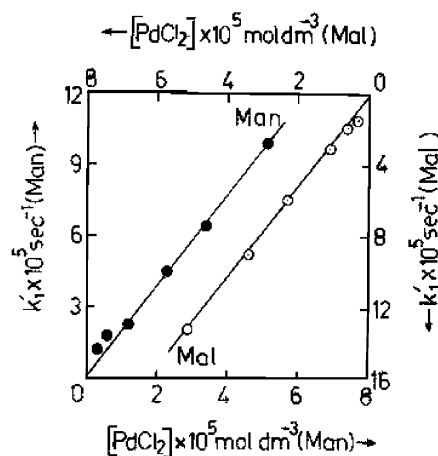


Fig. 4. Plots of (k'_1) vs. $[PdCl_2]$ at 40 °C under the experimental condition of Table 1. Man: D-mannose and Mal: maltose.

at fixed ionic strength was found as -0.48 (Man) and -0.50 (Mal) from the slope of plot between $\log k'_1$ and $\log[H^+]$ (Fig. 3). The rate of reaction was found to be highly influenced by $[Pd(II)]$. The plots of k'_1 against $[Pd(II)]$ were linear passing through origin suggesting

Table 2
Effect of variation of $[Hg(OAc)_2]$, $[KCl]$ and $[NHA]$ on the rate constant 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 ($\times 10^5 \text{ s}^{-1}$) ^a	
			Man	Mal
1.00			3.96	–
1.20 ^b /1.25 ^c			4.36	3.56
2.00			5.66	4.63
3.00			6.94	5.21
4.00			7.93	6.73
6.00			9.52	7.71
8.00			–	9.97
1.20 ^b /1.42 ^c	3.60 ^b /2.71 ^c		9.92	5.78
1.20 ^b /1.42 ^c	5.60 ^b /4.71 ^c		8.33	5.29
1.20 ^b /1.42 ^c	7.60 ^b /7.71 ^c		7.94	4.63
1.20 ^b /1.42 ^c	10.60 ^b /12.71 ^c		6.69	3.89
1.20 ^b /1.42 ^c	15.60 ^b /17.71 ^c		5.17	2.64
1.20 ^b /1.42 ^c		2.00	7.64	4.63
1.20 ^b /1.42 ^c		3.00	5.88	4.20
1.20 ^b /1.42 ^c		5.00	5.24	3.56
1.20 ^b /1.42 ^c		7.00	4.44	2.77
1.20 ^b /1.42 ^c		10.00	3.55	1.68

^a Solution condition: $[NBA] = 8.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Man), $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Mal); [substrate] = $7.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Man), $10.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Mal); $[PdCl_2] = 28.20 \times 10^{-6} \text{ mol dm}^{-3}$ $[HClO_4] = 0.80 \times 10^{-3} \text{ mol dm}^{-3}$ (Man), $3.00 \times 10^{-3} \text{ mol dm}^{-3}$ (Mal).

^b Man.

^c Mal.

Table 3
Effect of temperature on the rate constant and values of activation parameters^a

Parameters	Temperature (K)	Man	Mal
$k_1' (\times 10^5 \text{ s}^{-1})$	308	5.00	6.03
$k_1' (\times 10^5 \text{ s}^{-1})$	313	6.48	8.77
$k_1' (\times 10^5 \text{ s}^{-1})$	318	10.46	16.69
$k_1' (\times 10^5 \text{ s}^{-1})$	323	15.08	19.00
$k (\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1})$	313	17.97	34.37
$A (\times 10^{-12} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1})$	313	0.60	7.76
$E_a (\text{kJ mol}^{-1})$	–	76.28	82.80
$\Delta H (\text{kJ mol}^{-1})$	313	73.65	80.17
$\Delta S (\text{JK}^{-1} \text{ mol}^{-1})$	313	8.48	29.05
$\Delta G (\text{kJ mol}^{-1})$	313	70.97	71.10

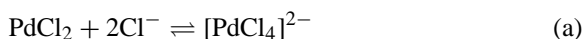
^a Solution condition: [NBA] = $8.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Man), $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Mal); [substrate] = $7.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Man), $10.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Mal); [PdCl₂] = $33.80 \times 10^{-6} \text{ mol dm}^{-3}$, [HClO₄] = $0.80 \times 10^{-3} \text{ mol dm}^{-3}$ (Man), $3.00 \times 10^{-3} \text{ mol dm}^{-3}$ (Mal); [Hg(OAc)₂] = $1.20 \times 10^{-3} \text{ mol dm}^{-3}$ (Man), $1.42 \times 10^{-3} \text{ mol dm}^{-3}$ (Mal).

first-order dependence of reaction on the catalyst and at the same time it also shows that reaction does not proceed with measurable velocity in the absence of Pd(II) (Fig. 4).

Table 2 shows the effect of successive addition of Hg(OAc)₂, Cl[−] and acetamide. A close examination of results in Table 2 revealed that the reaction rate is enhanced by the addition of Hg(OAc)₂, indicating the involvement of Hg(II) as co-catalyst in addition to its role as Br[−] ion scavenger [9,20,21]. Successive addition of chloride ion and acetamide (i.e. NBA as one of reaction products of NBA) to the reaction mixture shows decreasing effect on the rates of oxidation of both Man and Mal. Addition of NaClO₄ (to study the effect of ionic strength ' μ ') varied from 1.60×10^{-3} to $5.60 \times 10^{-3} \text{ mol dm}^{-3}$ for Man and 1.71×10^{-3} to $7.71 \times 10^{-3} \text{ mol dm}^{-3}$ for Mal in the reaction mixture showed an insignificant effect on the rate of oxidation, suggesting involvement of at least one neutral molecule in the rate determining step of the reaction. The reaction were studied at different temperatures and the rate constants measured at 35, 40, 45 and 50 °C led to compute activation parameters in the oxidation of reducing sugars (Table 3). The identical kinetic results obtained for the oxidation of both reducing sugars suggested that both the oxidation reactions follow a common mechanism.

5. Discussion

Various mononuclear complexes namely [PdLCl₃][−], [PdL₂Cl₂], [PdL₃Cl]⁺ and [PdL₄]²⁺ (where 'L' represents a legand like amine, phosphine, thioether, sulfide, etc.) are reported [23] in the literature. In most of the studies using Pd(II) as homogeneous catalyst, it has been employed in the form of Pd(II) chloride [22]. Palladium(II) chloride is rather insoluble in aqueous solution but is soluble in hydrochloric acid and exists [22,23] as [PdCl₄]^{2−}, according to the equilibrium (a) [24]:



The existence of PdCl₂ exclusively in the form of [PdCl₄]^{2−} is also supported by Ayres [25] who has observed that when a reaction ratio of 2:1 for sodium chloride (Cl[−] ion) to palladium(II) chloride is maintained, then this will result in the formation of the well-known tetrachloropalladate(II), [PdCl₄]^{2−}. Since throughout the experiments, ratio of Cl[−] ion to the palladium(II) chloride concentration, i.e. [Cl[−]]/[PdCl₂] was maintained more than 2, hence it is reasonable to assume that the species [PdCl₄]^{2−} is the sole palladium(II) species in HCl. Such species of palladium(II) chloride has also been reported in the oxidation of amino alcohols by chloromine-T [26], *N*-bromosuccinimide [27] and some sugars by *N*-bromosuccinimide [28] and *N*-bromoacetamide (NBA) [29].

In order to verify the existence of species [PdCl₄]^{2−} and possibility of [Pd(II)–sugar] complex formation under our experimental conditions, UV-spectra of PdCl₂ solution, sugar solution and palladium(II)chloride with different concentrations of sugar solution at 40 °C have been collected (Fig. 5). The single peak observed at 234 nm (2) in afore-said spectrum clearly supports the existence of lone species of palladium(II), i.e. [PdCl₄]^{2−} in the solution of PdCl₂ ($5.64 \times 10^{-4} \text{ mol dm}^{-3}$) and HCl ($1.8 \times 10^{-3} \text{ mol dm}^{-3}$), which can be assumed as the reactive species of PdCl₂ in the present investigation. The absorption spectra of palladium(II)chloride with three different concentrations of sugar solution, clearly indicate that the reactive species of palladium(II), i.e. [PdCl₄]^{2−} forms a complex with the sugar molecule, showing an increase in absorbance of pure palladium(II) chloride solution from 2.50 to

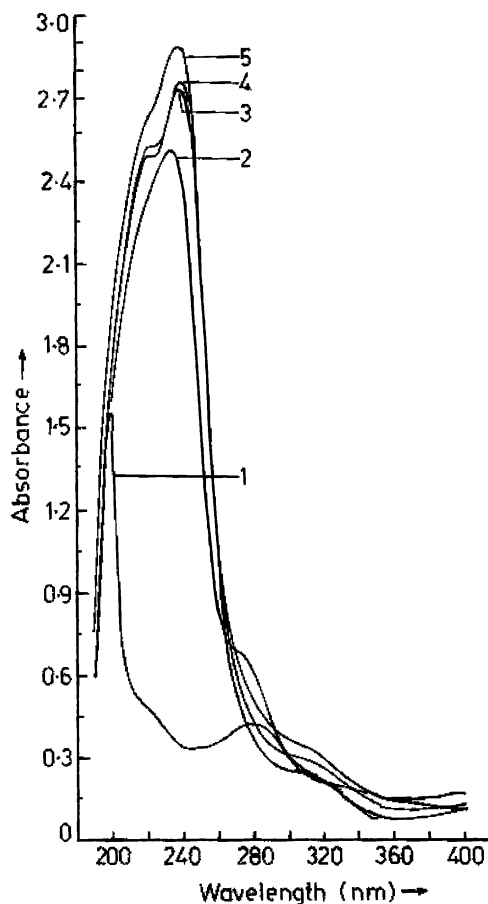
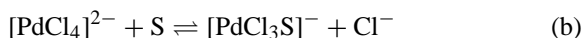


Fig. 5. Spectra of [Pd(II)] and sugar solutions recorded at 40 °C: (1) [sugar] = $5.00 \times 10^{-1} \text{ mol dm}^{-3}$, (2) [Pd(II)] = $5.64 \times 10^{-4} \text{ mol dm}^{-3}$ and [HCl] = $1.80 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Pd(II)] = $5.64 \times 10^{-4} \text{ mol dm}^{-3}$ and [sugar] = $5.00 \times 10^{-2} \text{ mol dm}^{-3}$, (4) [Pd(II)] = $5.64 \times 10^{-4} \text{ mol dm}^{-3}$ and [sugar] = $10.00 \times 10^{-2} \text{ mol dm}^{-3}$, (5) [Pd(II)] = $5.64 \times 10^{-4} \text{ mol dm}^{-3}$ and [sugar] = $20.00 \times 10^{-2} \text{ mol dm}^{-3}$.

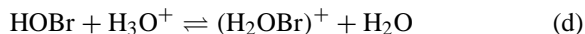
2.73 (3), 2.76 (4), and 2.88 (5). This increase in absorbance is due to the fact that with increase in sugar concentration, the equilibrium (b) between $[\text{PdCl}_4]^{2-}$ and a sugar molecule shifts towards the right with more and more formation of [Pd(II)–sugar] complex which becomes a sole factor for the increase in absorbance:



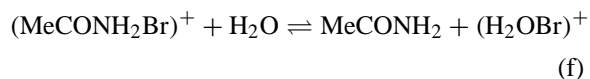
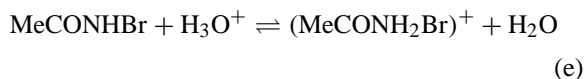
Above equilibrium (b), where formation of [Pd(II)–sugar] complex is indicated, is also supported

by the observed negative effect of chloride ion concentration on the rate of reaction.

It has been established that in acidic medium NBA [4–12] is found in following two sets of equilibria, which are indistinguishable in present case:

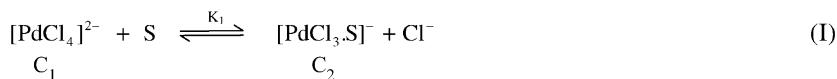


or

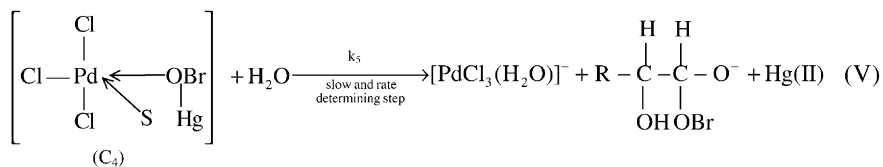
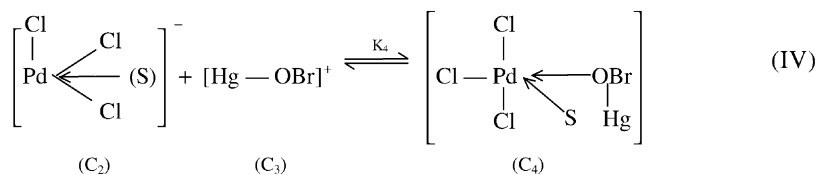
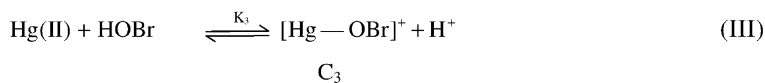
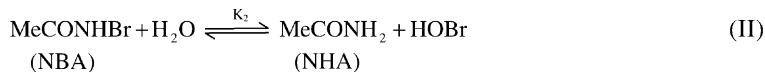


In the present investigation either or both of the two sets of equilibria (c and d) or (e and f) may be operative. Hence, there may be four possible reactive NBA species, i.e. NBA itself, HOBr, protonated NBA, i.e. $(\text{MeCONH}_2\text{Br})^+$ and cationic bromine, i.e. $(\text{H}_2\text{OBr})^+$. 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 steps c and f. When NBA or $(\text{MeCONH}_2\text{Br})^+$ is assumed as the reactive species, their derived rate laws fail to explain the negative effect of acetamide, hence neither of these species can be considered as reactive species. When $(\text{H}_2\text{OBr})^+$ is taken as the reactive species, the rate law obtained shows first-order kinetics with respect to $[\text{H}^+]$ contrary to our observed negative fractional order in $[\text{H}^+]$, 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.

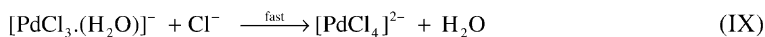
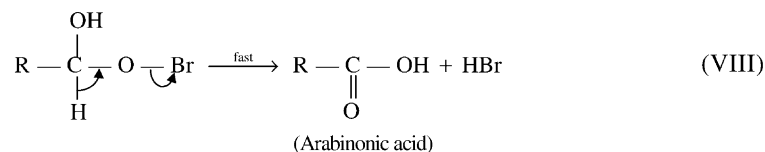
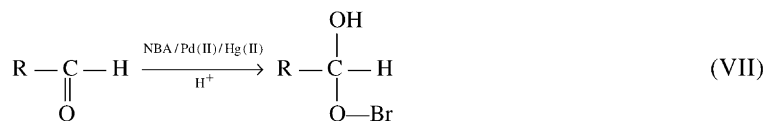
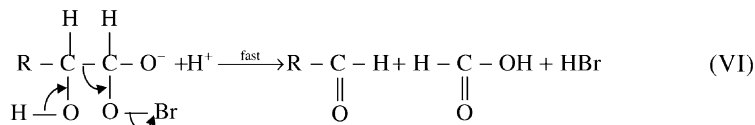
On the basis of above discussion and kinetic studies, a probable reaction path has been proposed for the Pd(II) and Hg(II) co-catalyzed oxidation of Man and Mal in acidic medium as Scheme 1.



where 'S' stands for Man and Glu (two molecules of Glucose are obtained by acidic hydrolysis of one molecule of maltose).



where R stands for $\text{C}_4\text{H}_9\text{O}_5$



Scheme 1.

On the basis of the reaction steps in Scheme 1 and stoichiometric equations for both mannose and maltose the rate of disappearance of [NBA] can be expressed as:

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = nk_5[\text{C}_4] \quad (1)$$

where $n = 2$ (for mannose) and $n = 4$ (for maltose).

On applying the law of chemical equilibrium to steps I–IV, we have Eqs. (2)–(5):

$$[\text{C}_2] = \frac{K_1[\text{C}_1][\text{S}]}{[\text{Cl}^-]} \quad (2)$$

$$[\text{HOBr}] = \frac{K_2[\text{NBA}]}{[\text{NHA}]} \quad (3)$$

$$[\text{C}_3] = \frac{K_3[\text{Hg(II)}][\text{HOBr}]}{[\text{H}^+]} \quad (4)$$

$$[\text{C}_4] = K_5[\text{C}_2][\text{C}_3] \quad (5)$$

From Eqs. (2)–(5) we obtain Eq. (6):

$$[\text{C}_4] = \frac{K_1 K_2 K_3 K_4 [\text{NBA}][\text{S}][\text{Hg(II)}][\text{C}_1]}{[\text{Cl}^-][\text{H}^+][\text{NHA}]} \quad (6)$$

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

$$[\text{Pd(II)}]_{\text{T}} = [\text{C}_1] + [\text{C}_2] + [\text{C}_4] \quad (7)$$

On substituting the values of $[\text{C}_2]$, and $[\text{C}_4]$ from Eqs. (2) and (6), respectively, to Eq. (7), we obtain Eq. (8):

$$[\text{C}_1] = \frac{[\text{Pd(II)}]_{\text{T}}[\text{Cl}^-][\text{H}^+][\text{NHA}]}{[\text{Cl}^-][\text{H}^+][\text{NHA}] + K_1[\text{S}][\text{H}^+][\text{NHA}] + K_1 K_2 K_3 K_4 [\text{S}][\text{Hg(II)}][\text{NBA}]} \quad (8)$$

On putting the value of $[\text{C}_1]$ from Eq. (8) to Eq. (6), we obtain Eq. (9):

$$[\text{C}_4] = \frac{K_1 K_2 K_3 K_4 [\text{NBA}][\text{S}][\text{Hg(II)}][\text{Pd(II)}]_{\text{T}}}{[\text{Cl}^-][\text{H}^+][\text{NHA}] + K_1[\text{S}][\text{H}^+][\text{NHA}] + K_1 K_2 K_3 K_4 [\text{S}][\text{Hg(II)}][\text{NBA}]} \quad (9)$$

On substituting the value of $[\text{C}_4]$ from Eq. (9) to Eq. (1), the final rate law can be obtained as Eq. (10):

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{nk_5 K_1 K_2 K_3 K_4 [\text{NBA}][\text{S}][\text{Pd(II)}]_{\text{T}}[\text{Hg(II)}]}{[\text{Cl}^-][\text{H}^+][\text{NHA}] + K_1[\text{S}][\text{H}^+][\text{NHA}] + K_1 K_2 K_3 K_4 [\text{S}][\text{Hg(II)}][\text{NBA}]} \quad (10)$$

The observed first-order kinetics with respect to $[\text{Pd(II)}]_{\text{T}}$ and less than unity order in $[\text{S}]$, $[\text{Hg(II)}]$ and $[\text{NBA}]$ are very well explained by the rate law (10). Negative fractional order in $[\text{H}^+]$, $[\text{NHA}]$ and $[\text{Cl}^-]$, as is evident from the presence of the term $K_1 K_2 K_3 K_4 [\text{Hg(II)}][\text{NBA}][\text{S}]$ in the denominator of rate law (10), is also in accordance with our experimental findings.

Eq. (10) can also be written as:

$$\frac{1}{\text{rate}} = \frac{[\text{NHA}][\text{H}^+][(\text{Cl}^-) + K_1[\text{S}]]}{nk_5 K_1 K_2 K_3 K_4 [\text{Pd(II)}]_{\text{T}} [\text{NBA}][\text{Hg(II)}][\text{S}]} + \frac{1}{nk_5 [\text{Pd(II)}]_{\text{T}}} \quad (11)$$

According to Eq. (11), if a plot is made between $(1/\text{rate})$ and $(1/[\text{NBA}])$ or $(1/[\text{Hg(II)}])$ or $[\text{H}^+]$ or $[\text{NHA}]$, then a straight line having positive intercept on $(1/\text{rate})$ axis should be obtained. When $(1/\text{rate})$ values are plotted against $(1/[\text{NBA}])$, $(1/[\text{Hg(II)}])$, $[\text{H}^+]$ and $[\text{NHA}]$ straight lines with positive intercepts on $(1/\text{rate})$ axis were obtained which prove the validity of the rate law (10) and hence the proposed mechanism. From the intercept of each plot of Figs. 6 and 7, the values of rate constant, k_5 have been calculated and

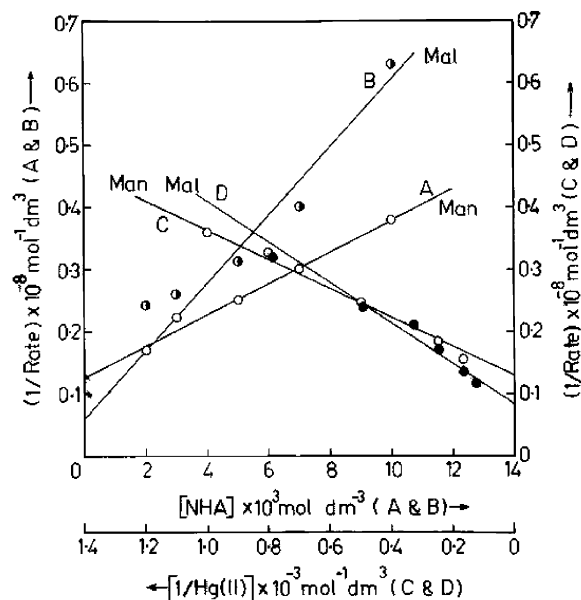


Fig. 6. Verification of rate law (10) under the conditions of Table 2 ((1/rate) vs. $(1/[\text{Hg(II)}])$ and $(1/\text{rate})$ vs. $[\text{NHA}]$): (A and C) mannose, (B and D) maltose.

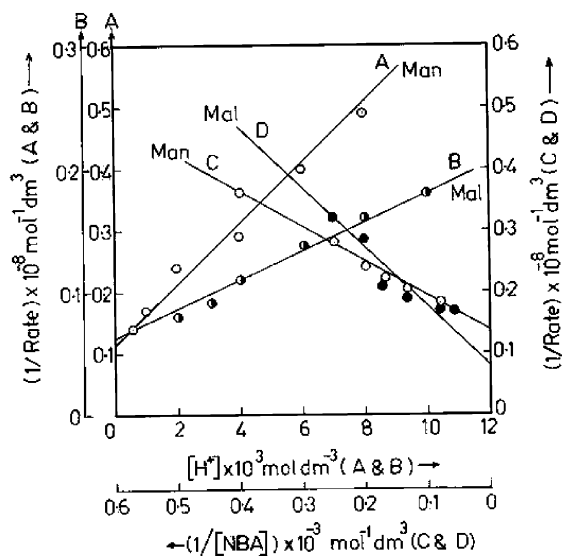


Fig. 7. Verification of rate law (10) under the conditions of Table 1 ((1/rate) vs. (1/[NBA])) and Fig. 3 ((1/rate) vs. $[H^+]$): (A and C) mannose, (B and D) maltose.

recorded in Table 4. The values of the rate constant k_5 obtained from four different methods, i.e. from variation in [NBA], $[Hg(II)]$, $[H^+]$ and [NHA] are quite close to each other. These results support the mechanism for the oxidation of reducing sugars. Due to complicated rate law it was not possible for us to calculate equilibrium constants shown in mechanistic steps. Linear plots with positive intercepts on (1/rate) axis clearly indicate the retarding effect of [NBA] and $[Hg(II)]$ and decreasing effect of $[H^+]$ and [NHA] on the rate of reaction.

Table 4
Calculation of k_5 values for plots of (1/rate) vs. (1/[NBA]) or (1/[Hg(II)]) or $[H^+]$ or [NHA]

Plots between	k_5 ($\times 10^2 \text{ s}^{-1}$)	
	Man	Mal
$\frac{1}{\text{rate}}$ and $\frac{1}{[NBA]}$	0.13	0.11
$\frac{1}{\text{rate}}$ and [NHA]	0.14	0.11
$\frac{1}{\text{rate}}$ and $\frac{1}{[Hg(II)]}$	0.14	0.10
$\frac{1}{\text{rate}}$ and $[H^+]$	0.15	0.14

In Pd(II) catalyzed oxidation of Man and Mal by *N*-bromoacetamide in the presence of perchloric acid, the activated state will be less polar caused by reactants $[PdCl_3S]^-$ and $[Hg-OBr]^+$. Positive entropy of activation in the oxidation of Man and Mal (Table 3) is due to desolvation of the activated state rather than reactants. 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 reducing sugars by NBA in presence of Pd(II) as homogeneous catalyst.

References

- [1] R. Filler, Chem. Rev. 63 (1963) 21–43.
- [2] B. Singh, A.K. Singh, V.K. Singh, A.K. Sisodia, M.B. Singh, J. Mol. Catal. 40 (1987) 49–56.
- [3] S. Gupta, V. Ali, S.K. Upadhyay, Transition Met. Chem. 13 (1988) 135.
- [4] J. Mukherjee, K.K. Banerji, J. Org. Chem. 46 (1981) 2323–2326.
- [5] M. Komal Reddy, C. Sanjeeva Reddy, E.V. Sundaram, Tetrahedron 41 (1985) 3071–3081.
- [6] B. Singh, R. Srivastava, Tetrahedron 42 (1986) 2749.
- [7] P.S. Radhakrishnamurthy, N.C. Sahu, Indian J. Chem. 20A (1981) 269.
- [8] B. Singh, R. Srivastava, Curr. Sci. 54 (1985) 415.
- [9] N. Venkatasubramanian, V. Thiagarajan, Can. J. Chem. 47 (1969) 694–697.
- [10] B. Singh, D. Singh, A.K. Singh, Int. J. Chem. Kinet. 20 (1988) 501.
- [11] M. Saxena, R. Gupta, A. Singh, A.K. Singh, J. Mol. Catal. 65 (1991) 317.
- [12] B. Singh, D. Singh, S. Bajpai, A. Kumar, Transition Met. Chem. 16 (1991) 610–613.
- [13] (a) S. Perumal, S. Alagumalai, S. Selvaraj, N. Arumugam, Tetrahedron 42 (1986) 4867; (b) M.C. Agrawal, S.K. Upadhyay, J. Sci. Ind. Res. 42 (1983) 508.
- [14] T.S. Vivekanandan, M.S. Ramachandran, Indian J. Chem. 22A (1983) 629.
- [15] S.P. Srinivasan, N.S. Gnanaprakasam, J. Indian Chem. Soc. LX (1983) 953.
- [16] K.S. Rangappa, M.P. Raghvendra, D.S. Mahadevappa, D.C. Gowda, Carbohydr. Res. 306 (1998) 57–67; K.S. Rangappa, H. Manjunathaswamy, M.P. Raghvendra, D.C. Gowda, Carbohydr. Res. 307 (1998) 253–262; K.S. Rangappa, M.P. Raghavendra, D.S. Mahadevappa, D.C. Gowda, J. Org. Chem. 63 (1998) 531–536.
- [17] M.Z. Barkat, M.F. Wahab Abdel, Anal. Chem. 26 (1954) 1973.
- [18] (a) F. Feigl, Spot Tests in Organic Analysis, Elsevier, New York, 1966; (b) R.D. Hartly, G.J. Lawson, J. Chromatogr. 4 (1960) 410–413.

- [19] A.I. Vogel, *Elementary Practical Organic Chemistry: Part III*, Longmans & Green, London, 1958, p. 53.
- [20] J.C. Bailar, *The Chemistry of Co-ordination Compounds*, Nostrand Reinhold (Van), New York, 1956, p. 4.
- [21] G. Gopalkrishnan, B.R. Rai, N. Venkatsubramanian, *Indian J. Chem.* 198 (1980) 293–296.
- [22] G.P. Tikhonova, S.N. Bovkovets, *Russ. J. Inorg. Chem.* 23 (1973) 813.
- [23] F.A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, 1988, p. 1026.
- [24] V.I. Schlenskaya, A.A. Biryukov, *Russ. J. Inorg. Chem.* 11 (1966) 28.
- [25] G.H. Ayres, *Anal. Chem.* 24 (1953) 1622–1627.
- [26] A. Shukla, S. Gupta, S.K. Upadhyay, *Int. J. Chem. Kinet.* 23 (1991) 279–288.
- [27] R. Saxena, A. Shukla, S.K. Upadhyay, *Transition Met. Chem.* 19 (1994) 91–94.
- [28] A.K. Singh, D. Chopra, S. Rahmani, B. Singh, *Carbohydr. Res.* 314 (1998) 157–160.
- [29] (a) N. Gupta, N. Chaurasia, V. Singh, A.K. Singh, *Oxid. Commun.* 23 (2000) 450–464;
(b) A.K. Singh, S. Rahmani, V.K. Singh, D. Kesarwani, B. Singh, *Indian J. Chem.* 40A (2001) 519–523.