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Pd(II)-catalysed and Hg(II)-co-catalysed oxidation of D-glucose and D-fructose by N-bromoacetamide in the presence of perchloric acid: a kinetic and mechanistic study

Ashok Kumar Singh,* Jaya Srivastava, Shahla Rahmani and Vineeta Singh

Department of Chemistry, University of Allahabad, Allahabad 211002, India Received 28 June 2005; accepted 4 November 2005

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Abstract—The kinetics of Pd(II)-catalysed and Hg(II)-co-catalysed oxidation of D-glucose (Glc) and D-fructose (Fru) by *N*-bromoacetamide (NBA) in the presence of perchloric acid using mercury(II) acetate as a scavenger for Br^- ions have been studied. The results show first-order kinetics with respect to NBA at low concentrations, tending to zero order at high concentrations. First-order kinetics with respect to Pd(II) and inverse fractional order in Cl⁻ ions throughout their variation have also been noted. The observed direct proportionality between the first-order rate constant (k_1) and the reducing sugar concentration shows departure from the straight line only at very higher concentration of sugar. Addition of acetamide (NHA) decreases the first-order rate constant while the oxidation rate is not influenced by the change in the ionic strength (μ) of the medium. Variation of [Hg(OAc)₂] shows a positive effect on the rate of reaction. The observed negative effect in H⁺ at lower concentrations tends to an insignificant effect at its higher concentrations. The first-order rate constant decreases with an increase in the dielectric constant of the medium. The various activation parameters have also been evaluated. The products of the reactions were identified as arabinonic acid and formic acid for both the hexoses. A plausible mechanism involving HOBr as the reactive oxidising species, Hg(II) as co-catalyst, and [PdCl₃·S]⁻¹ as the reactive Pd(II)–sugar complex in the rate-controlling step is proposed.

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1. Introduction

N-Haloimides have attained a distinguished place among oxidising agents for their specific oxidising character. Amongst them, *N*-bromoacetamide (NBA) has been widely used as an oxidising and brominating reagent¹ in preparative organic chemistry, as well as an analytical reagent to determine the concentration of various organic and inorganic compounds. Recently, considerable attention has been focused on the diverse nature of the chemistry of *N*-halo compounds owing to their ability to act as a source of halogenonium cations, hypohalite species and nitrogen anions that act as both bases and nucleophiles. NBA as an oxidant has been used for some uncatalysed^{2,3} processes. The kinetics of redox reactions incorporating certain transition metal ions, viz., Os(VIII),^{4,6} Ru(III),^{5,7} Ru(VIII)⁸ and Ir(III)^{9,10} as homogeneous catalysts have been extensively investigated. Reactions involving Pd(II)^{11,12} have received limited attention. In view of scant work on the mode of NBA oxidation with biologically important substrates like carbohydrates, there seems to be much exciting chemistry in further probing the oxidative capacity of NBA in the oxidation of reducing sugars, particularly in the presence of Pd(II). Palladium chloride is the most important Pd(II) salt in the homogeneous catalytic chemistry of palladium. Because of the commercial importance of the reaction, the kinetics of the oxidation of ethylene by aqueous Pd(II) chloride were studied by Henry in 1964.¹³ Palladium(II) is a wellknown catalyst for several organic transformations. Some interesting results in the homogeneous catalysis of reactions of organic compounds, particularly the

^{*} Corresponding author. Tel.: +91 532 2640434; e-mail: ashokeks@ rediffmail.com

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successful commercial exploitation of the Wacker onestage process for the homogeneous catalytic oxidation of acetaldehyde in the presence of Pd(II) chloride have contributed to this interest. In the present paper, our main aim is to ascertain the oxidative mode of NBA with reducing sugars, the role of reducing sugars in the redox system, and to explore catalytic potential of Pd(II) with NBA as an oxidant.

2. Experimental

2.1. Materials

An aqueous solution of *N*-bromoacetamide (NBA) was prepared afresh each day by direct weighing, and its strength was checked by iodometric titration of active bromine. Aqueous solutions of glucose and fructose were also prepared fresh each day. The solution of PdCl₂ (Qualigen 'Glaxo' Chem.) was prepared in HCl of the known strength. The overall strength of HCl was maintained at 22.56×10^{-3} mol dm⁻³, and the strength of PdCl₂ was 5.64×10^{-3} mol dm⁻³. All other reagents, namely Hg(OAc)₂, NaClO₄, HClO₄, acetamide (NHA) and KCl were prepared from samples obtained from E. Merck. All the solutions were prepared with double-distilled water.

2.2. Kinetic measurements

The requisite volumes of standard solutions of NBA, Pd(II), $HClO_4$, $Hg(OAc)_2$, KCl, NHA and $NaClO_4$ were taken in a black-coated reaction vessel and equilibrated at 40 °C. A measured volume of sugar solution, also equilibrated separately at the same temperature, was poured into the reaction vessel, and the reaction was started by vigorous shaking of the reaction mixture. The progress of the reaction was monitored iodometrically by estimating the amount of the remaining NBA at regular time intervals.

2.3. Stoichiometry and product analysis

Various sets of experiments were performed with different [NBA]/[sugar] ratios under kinetic conditions for 72 h. Determination of unconsumed NBA revealed that for the oxidation of each mole of sugar 2 mol of NBA were required. Accordingly, the following stoichiometric equations could be formulated: The products were found to be identical under both stoichiometric and kinetic conditions and also by a spot test¹⁴ and thin-layer chromatography (TLC). Although arabinonic acid, which is a strong reducing agent, is formed in the reaction, the possibility of its further oxidation by NBA under our experimental conditions is completely ruled out.

3. Results and discussion

3.1. Kinetics

A kinetic study of oxidation of Glc and Fru by NBA in the presence of Pd(II) as catalyst and Hg(OAc)₂ as the Br⁻ ion scavenger under the conditions [sugar] \gg [N-BA] was made in perchloric acid at several reactant concentrations. The value of the initial rate in each kinetic run was calculated from the slope of the tangent of plot of unconsumed [NBA] versus time at fixed [NBA] except in [NBA] variation when a tangent has been drawn at a fixed time. The value of the first-order rate constant (k_1) in each kinetic run was calculated as

$$k_1 = \frac{(-\mathrm{d}c/\mathrm{d}t)}{[\mathrm{NBA}]}$$

The first-order dependence of the reaction on NBA at its lower concentration tends to zero order at its higher concentrations as demonstrated by the plot of -dc/dtversus [NBA] (Fig. 1). This result is further verified by



Figure 1. $[PdCl_2] = 28.20 \times 10^{-6} \text{ mol } dm^{-3}$, $[sugar] = 2.50 \times 10^{-2} \text{ mol } dm^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol } dm^{-3}$ (Fru), $[HClO_4] = 13.33 \times 10^{-3} \text{ mol } dm^{-3}$, $[Hg(OAc)_2] = 3.00 \times 10^{-3} \text{ mol } dm^{-3}$, $[KCl] = 4.00 \times 10^{-4} \text{ mol } dm^{-3}$, $[NHA] = 3.50 \times 10^{-3} \text{ mol } dm^{-3}$, $\mu = 3.50 \times 10^{-2} \text{ mol } dm^{-3}$.

Table 1. Effect of variation of [NBA] and [sugar] on the first-order rate constant (k_1) at 40 °C^a

$[NBA] \times 10^4 \text{ (mol dm}^{-3}\text{)}$	$[sugar] \times 10^2 \text{ (mol dm}^{-3}\text{)}$	$k_1 \times 10^5$ (s ⁻¹)	
		Glc	Fru
2.50	2.50 ^{Glc} /2.00 ^{Fru}	4.78	5.54
3.75	2.50 ^{Glc} /2.00 ^{Fru}	4.92	5.54
5.00	$2.50^{Glc}/2.00^{Fru}$	4.88	5.70
6.25	2.50 ^{Glc} /2.00 ^{Fru}	4.91	5.32
7.50	$2.50^{\rm Glc}/2.00^{\rm Fru}$	4.95	5.33
8.75	2.00 ^{Fru}		5.39
10.00	$2.50^{Glc}/2.00^{Fru}$	4.92	5.45
12.50	2.50 ^{Glc} /2.00 ^{Fru}	4.77	5.32
15.00	2.50 ^{Glc} /2.00 ^{Fru}	4.28	5.37
17.50	$2.50^{Glc}/2.00^{Fru}$	3.93	5.09
20.00	2.50 ^{Glc} /2.00 ^{Fru}	3.62	4.63
22.50	$2.50^{Glc}/2.00^{Fru}$	3.30	4.38
8.33 ^{Glc} /10.00 ^{Fru}	1.00	1.33	2.25
8.33 ^{Glc} /10.00 ^{Fru}	1.25	2.29	
8.33 ^{Glc} /10.00 ^{Fru}	1.50		3.47
8.33 ^{Glc} /10.00 ^{Fru}	1.66	2.66	
8.33 ^{Glc} /10.00 ^{Fru}	2.00	3.51	5.00
8.33 ^{Glc} /10.00 ^{Fru}	2.50	4.55	5.18
8.33 ^{Glc} /10.00 ^{Fru}	3.00	4.85	6.02
8.33 ^{Glc} /10.00 ^{Fru}	3.33	5.55	_
8.33 ^{Glc} /10.00 ^{Fru}	4.00	6.25	7.94
8.33 ^{Glc} /10.00 ^{Fru}	4.50		9.12
8.33 ^{Glc} /10.00 ^{Fru}	5.00	7.25	10.96
8.33 ^{Glc} /10.00 ^{Fru}	6.00	8.90	12.95
8.33 ^{Glc} /10.00 ^{Fru}	7.00	_	13.98
8.33 ^{Glc} /10.00 ^{Fru}	8.00	9.35	14.25
8.33 ^{Glc} /10.00 ^{Fru}	10.00	9.75	14.95

^a Conditions: $[PdCl_2] = 28.20 \times 10^{-6} \text{ mol dm}^{-3}$, $[Hg(OAc)_2]$ (Glc and Fru) in [NBA] variation and $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ (Glc and Fru), $[KCl] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc and Fru), $[NHA] = 3.50 \times 10^{-3} \text{ mol dm}^{-3}$ (Glc and Fru) for [NBA] variation and $9.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc), $11.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), and $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc and Fru).



Figure 2. [NBA] = $8.33 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol dm}^{-3}$, [HClO₄] = $13.33 \times 10^{-3} \text{ mol dm}^{-3}$, [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$, [KCl] = $4.00 \times 10^{-4} \text{ mol dm}^{-3}$, [NHA] = $9.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc), $11.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$.

the constant values of the first-order rate constant, k_1 , in the lower range of [NBA] and decreasing values of k_1 in the higher range of [NBA] (Table 1). Since throughout the study the concentration of NBA was fixed in its lower concentration range, for the purpose of calculation of the first-order rate constant, k_1 , the order with respect to [NBA], has been taken as unity. Figure 2 shows first-order kinetics with respect to each sugar at lower concentration, but the reaction tends to zero order at higher concentrations of sugar. The plots of k_1 against [Pd(II)] were linear passing through origin, suggesting first-order dependence of the rate of reaction on the [Pd(II)]. At the same time, it also shows that the reaction does not proceed with measurable velocity in the absence of Pd(II) (Table 2, Fig. 3). The reactions

Table 2. Comparison of observed rates in the variation of [PdCl₂] with the calculated rates^a

$[PdCl_2] \times 10^6 \text{ (mol dm}^{-3})$	$-dc/dt \times 10^8 \pmod{dm^{-3} s^{-1}}$							
	D-Glucose			D-Fructose				
	Experimental	Calculated ^b	Calculated ^c	Experimental	Calculated ^b	Calculated ^c		
5.64	0.85	0.85	0.82	1.05	0.96	0.99		
11.28	2.08	1.70	1.61	2.02	1.92	1.98		
16.92	2.78	2.54	2.38	2.78	2.82	2.98		
22.56	3.72	3.38	3.15	4.04	3.84	3.98		
28.20	4.13	4.23	4.29	5.18	4.79	4.98		
31.02	4.97	4.65	4.68	5.80	5.27	5.48		
33.84	5.53	5.08	5.43	6.66	5.75	5.49		
39.48	6.23	5.92	6.18	7.40	6.71	6.99		
45.12	7.40	6.77	6.94	8.07	7.62	7.99		
50.76	8.33	7.62	7.92	9.25	8.63	9.00		
56.40			_	10.24	9.59	10.01		
62.04	_	_	_	11.11	10.35	11.02		

^a Conditions: [NBA] = 8.33×10^{-4} mol dm⁻³ (Glc) and 10.00×10^{-4} mol dm⁻³ (Fru), [sugar] = 2.50×10^{-2} mol dm⁻³ (Glc) and 2.00×10^{-2} mol dm⁻³ (Glc) and 11.11×10^{-4} mol dm⁻³ (Glc) and Fru), [KCl] = 4.00×10^{-4} mol dm⁻³ (Glc) and Fru), [NHA] = 9.11×10^{-4} mol dm⁻³ (Glc) and 11.11×10^{-4} mol dm⁻³ (Fru), $\mu = 3.50 \times 10^{-2}$ mol dm⁻³ (Glc and Fru), and t = 40 °C.

^b Calculated on the basis of rate law (14).

^c Calculated with the help of multiple regression analysis.



Figure 3. [NBA] = $8.33 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol } \text{dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol } \text{dm}^{-3}$ (Fru), [HClO₄] = $13.33 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [KCl] = $4.00 \times 10^{-4} \text{ mol } \text{dm}^{-3}$, [NHA] = $9.11 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ (Glc) and $11.11 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ (Fru), $\mu = 3.50 \times 10^{-2} \text{ mol } \text{dm}^{-3}$.

follow negative fractional order in $[H^+]$ up to nearly 8.00×10^{-3} mol dm⁻³, but thereafter with the increase in concentration of H⁺ ions, no significant change in the first-order rate constant (k_1) was observed (Table 3, Fig. 4). An increasing effect of $[Hg(OAc)_2]$ on the rate constant of the reaction was observed (Table 4) as indicating the involvement of Hg(II) as co-catalyst in addition to its role as a Br⁻ ion scavenger.^{2,15,16} Successive addition of acetamide (NHA) (Table 5) and Cl⁻ (Fig. 5) shows a negative effect on the rates of reaction

Table 3. Effect of variation of [HClO₄] and [KCl] on the first-order rate constant (k_1) at 40 °C^a

$[\text{HClO}_4] \times 10^3 \text{ (mol dm}^{-3})$	$[\text{KCl}] \times 10^4 \text{ (mol dm}^{-3}\text{)}$	$k_1 \times 10^5 (\mathrm{s}^{-1})$	
		Glc	Fru
1.00	4.00	21.38	22.15
2.00	4.00	13.80	14.29
3.00	4.00	12.47	10.84
4.00	4.00	8.81	9.13
5.00	4.00	7.50	
6.00	4.00	6.76	7.01
7.00	4.00	6.10	
8.00	4.00	5.62	5.82
9.00	4.00	5.43	
10.00	4.00	5.34	5.54
12.00	4.00	5.16	5.35
13.33	2.40	6.12	6.05
13.33	3.40	5.23	5.35
13.33	4.40	4.68	4.85
13.33	5.40	4.44	4.25
13.33	6.40	4.08	3.75
13.33	7.40	3.66	3.65

^a Conditions: [NBA] = $8.33 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol dm}^{-3}$ (Glc and Fru), [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ (Glc and Fru), [NHA] = $9.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $11.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), and $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc and Fru).



Figure 4. [NBA] = $8.33 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol dm}^{-3}$, [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$, [NHA] = $9.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $11.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), [KCl] = $4.00 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$.

in oxidation of both Glc and Fru. Change in ionic strength of the medium did not bring about any change in the rate of reaction. Change in dielectric constant of the medium showed that on increasing the dielectric constant of the medium, the rates were decreased.

The reactions were studied in the temperature range of 303–318 K, and the values of activation parameters such as energy of activation (E_a), entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and Gibbs free energy of activation ($\Delta G^{\#}$) at 313 K are given in Table 6. The identical kinetics results obtained for the oxidation of Glc and Fru suggest that the reactions follow a common mechanism.

3.2. Test for free radicals

To test for the presence of free radicals in the reaction, a reaction mixture containing acrylamide was kept for 24 h in an inert atmosphere. When the reaction mixture was diluted with methanol, the formation of a precipitate was not seen. This suggests that there is no possibility of formation of free radicals in the reaction.

3.3. Suggested mechanism

It has been reported¹⁷ earlier by several workers that NBA in acidic medium exists in the following equilibria:

$$CH_{3}CONHBr + H_{2}O \implies CH_{3}CONH_{2} + HOBr$$
(NBA)
(NHA)
(i)

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

Table 4.	Comparison	of	observed	rates in	1 the	variation	of [Hg(OAc)2]	with	the c	alculated	rates ^a
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$[Hg(OAc)_2] \times 10^3 \text{ (mol dm}^{-3})$	$(-dc/dt) \times 10^8 \text{ (mol dm}^{-3} \text{ s}^{-1})$							
		D-Glucose		D-Fructose				
	Experimental	Calculated ^b	Calculated ^c	Experimental	Calculated ^b	Calculated ^c		
0.90	3.32	3.42	3.35	_	_			
1.00	3.64	3.66	3.52	_				
1.11	3.75	3.91	3.69	4.89	4.38	4.62		
1.50	4.92	4.66	4.27	5.45	5.40	5.54		
1.75	_	_	_	6.90	5.97	6.07		
2.00	5.35	5.39	4.89	7.17	6.48	6.56		
2.25	_		_	7.63	6.94	7.03		
2.50	_	_	_	8.05	7.36	7.48		
3.00	5.95	6.41	5.92	8.45	8.09	8.33		
3.50	_	_	_	9.46	8.71	9.11		
4.00	7.05	7.07	6.78	10.25	9.24	9.86		
5.00	7.45	7.54	7.53	10.96	10.10	11.23		
6.00	8.04	7.92	8.21	12.05	10.77	12.50		
7.00	8.52	8.16	8.83	12.35	11.31	13.69		

^a Conditions: [NBA] = 8.33×10^{-4} mol dm⁻³ (Glc) and 10.00×10^{-4} mol dm⁻³ (Fru), [sugar] = 2.50×10^{-2} mol dm⁻³ (Glc) and 2.00×10^{-2} mol dm⁻³ (Fru), [PdCl₂] = 28.20×10^{-6} mol dm⁻³ (Glc and Fru), [HClO₄] = 13.33×10^{-3} mol dm⁻³ (Glc and Fru), [KCl] = 4.00×10^{-4} mol dm⁻³ (Glc and Fru), [NHA] = 9.11×10^{-4} mol dm⁻³ (Glc) and 11.11×10^{-4} mol dm⁻³ (Fru), $\mu = 3.50 \times 10^{-2}$ mol dm⁻³ (Glc and Fru), [Glc and Fru), $\mu = 3.50 \times 10^{-2}$ mol dm⁻³ (Glc and Fru), $\mu = 3$

^bCalculated on the basis of rate law (14).

^cCalculated with the help of multiple regression analysis.

Table 5. Comparison of observed rates in the variation of [NHA] with the calculated rates^a

$[NHA] \times 10^3 \text{ (mol dm}^{-3}\text{)}$						
	D-Glucose			D-Fructose		
	Experimental	Calculated ^b	Calculated ^e	Experimental	Calculated ^b	Calculated ^c
1.00	3.95	4.14	3.86	5.24	4.88	5.21
2.00	3.70	3.56	3.05	4.50	4.05	3.89
4.00	2.52	2.78	2.45	3.02	3.02	2.91
6.00	2.19	2.28	2.16	2.67	2.41	2.46
8.00	1.99	1.93	1.97	2.05	2.03	2.18
10.00	1.66	1.68	1.83	1.85	1.72	1.98

^a Conditions: [NBA] = $8.33 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol dm}^{-3}$ (Glc and Fru), [HClO₄] = $13.33 \times 10^{-3} \text{ mol dm}^{-3}$ (Glc and Fru), [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ (Glc and Fru), [KCl] = $4.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc and Fru), $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc and Fru), and t = 40 °C.

^b Calculated on the basis of rate law (14).

^c Calculated with the help of multiple regression analysis.

or

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

$$(CH_{3}CONH_{2}Br)^{+} + H_{2}O \rightleftharpoons CH_{3}CONH_{2} + (H_{2}OBr)^{+}$$
(iv)

Perusal of the above equilibria (i–iv) shows that there can be four possible reactive species, that is, NBA itself, HOBr, $(CH_3CONH_2Br)^+$ and $(H_2OBr)^+$. In the light of the kinetic observations, especially the inverse fractional order in [NHA], HOBr can be assumed to be the main reactive species of NBA for the present investigation. Such an observation has also been noted in the reported²³ NBS oxidation of arabinose, xylose and galactose in acidic medium. But the mechanistic pathways are different for NBA and NBS oxidations of reducing sugars. HOBr, the reactive species in both NBA and NBS oxidations, participates in the reaction in an entirely different way. In the reported NBS oxidation, $PdCl_4^{2-}$, the reactive species of palladium(II) chloride, combines with HOBr, the reactive species of NBS, to form a complex of the type $[PdCl_3 \cdot HOBr]^{1-}$, which interacts with the sugar molecule in the form of $[PdCl_3 \cdot OBr]^{2-}$ in the rate-determining step. Contrary to this, in the present investigation $PdCl_4^{2-}$ first forms a complex with a sugar molecule with a composition of $[PdCl_3 \cdot S]^{1-}$. This complex in the rate-determining



Figure 5. [NBA] = $8.33 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and 10.00×10^{-4} mol dm⁻³ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol dm}^{-3}$, [HClO₄] = $13.33 \times 10^{-3} \text{ mol dm}^{-3}$, [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$, [NHA] = $9.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $11.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$.

step combines with HOBr and Hg(II) to form a most reactive activated complex, of the composition $\lceil PdCl_3 \cdot S \cdot OBr \rceil$

 $|_{\rm Hg}$. In this case Hg(II), which is used in the

reaction as a scavenger for Br^- ions also acts as co-catalyst. However, in NBS oxidation mercury(II) acetate was found to have a limited role as a Br^- ion scavenger only.

It is reported¹⁸ that Pd(II) chloride is rather insoluble in aqueous solution but does dissolve in the presence of Cl⁻ ion as PdCl₃(H₂O)⁻ and PdCl₄²⁻. The equilibrium constants corresponding to the following equilibria have been determined by several workers, and all are in fair agreement with a value of $\log \beta_4$ between 11 and 12 at 25 °C.

$$Pd^{2+} + Cl^{-} \stackrel{K_{1}}{\rightleftharpoons} PdCl^{+}$$
(v)

$$PdCl^{+} + Cl^{-} \stackrel{\kappa_{2}}{\rightleftharpoons} PdCl_{2}$$
 (vi)

$$PdCl_2 + Cl^{-} \stackrel{\kappa_3}{\rightleftharpoons} PdCl_3^{-}$$
(vii)

$$PdCl_{3}^{-} + Cl^{-} \stackrel{\kappa_{4}}{\rightleftharpoons} PdCl_{4}^{2-}$$
(viii)

Elding has studied both the stability constants and rates of reaction and determined values of $\log K_1$ to $\log K_4$ and also of $\log \beta_4$. β_4 , is the equilibrium constant for the following equilibrium:

$$Pd^{2+} + 4Cl^{-} \stackrel{\beta_4}{\rightleftharpoons} PdCl_4^{2-}$$
(ix)

In most of the studies, using Pd(II) as the homogeneous catalyst, it has been employed in the form of Pd(II) chloride. Pd(II) chloride, when dissolved in hydrochloric acid, exists in the form of $(PdCl_4)^{2-}$ as represented by equilibrium¹⁹ (viii). The existence of Pd(II) chloride exclusively in the form of $(PdCl_4)^{2-}$ is also supported by Ayres,²⁰ who has observed that when a reaction ratio of 2:1 for sodium chloride (Cl⁻ ion) to palladium(II) chloride is maintained, the result is the formation of well-known tetrachloropalladate(II), $(PdCl_4)^{2-}$. From the UV spectrum of the solution containing Pd(II) chloride, H^+ and Cl^- ions, it is clear that there are two peaks, one at 240 and the other at 215 nm (Fig. 6, Panel A, line 1). The peak observed at 240 nm can be considered as due to the presence of $(PdCl_4)^{2-1}$ in the solution, whereas the peak observed at 215 nm can be considered as due to the presence of $PdCl_3(H_2O)^-$ in solution. On the basis of values of k_h determined at various ionic strengths, it is reported²¹ that the hydrolysis of $(PdCl_4)^{2-}$ takes place according to the following equilibrium:

$$PdCl_4^{2-} + H_2O \stackrel{\kappa_h}{\rightleftharpoons} PdCl_3(H_2O)^- + Cl^- \qquad (x)$$

When spectra for Pd(II), H⁺, Cl⁻, sugar and NBA solutions and Pd(II), H⁺, Cl⁻, sugar, NBA and Hg(II) solutions were collected, it has been found, as will be discussed in detail below, that the additional peak at 215 nm completely disappears, and the species (PdCl₃·S)⁻ observed at 240 nm combines with the reactive species of NBA to form another complex, (PdCl₃·S·OBr)²⁻, which subsequently combines with $\lceil PdCl_3 \cdot S \cdot OBr \rceil$

Hg(II) to form a complex of the type | . In Hg

both the cases, an increase in absorbance was noted (Fig. 6). This spectral information led us to conclude that the species $PdCl_3(H_2O)^-$ initially observed in the solution is converted into $(PdCl_4)^{2-}$ with the formation $\begin{bmatrix} PdCl_3 \cdot S \cdot OBr \end{bmatrix}$

the basis of this, it is reasonable to assume that $(PdCl_4)^{2-}$ is the reactive species of Pd(II) chloride in the oxidation of Glc and Fru by NBA in the presence of perchloric acid.

Table 6. Activation parameters of Pd(II)-catalysed oxidation of D-glucose and D-fructose by NBA in acidic media^a

Reducing sugars	$E_{\rm a} ({\rm kJ} {\rm mol}^{-1})$	$k \;(\mathrm{mol}^{-1} \;\mathrm{dm}^3 \mathrm{s}^{-1})$	$\Delta S^{\#} (\mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1})$	$\Delta H^{\#} (\text{kJ mol}^{-1})$	$\Delta G^{\#} (\text{kJ mol}^{-1})$	$A \ (\mathrm{mol}^{-1} \ \mathrm{dm}^3 \ \mathrm{s}^{-1})$
D-Glucose	91.83	1.21	29.89	89.16	79.79	$21.44 \times 10^{14} \\ 2.63 \times 10^{14}$
D-Fructose	86.96	1.38	12.37	83.47	70.02	

^a Conditions: t = 40 °C.



Figure 6. (1) [NBA] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (2) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$, (3) [Hg(OAc)₂] = $1.00 \times 10^{-3} \text{ mol m}^{-3}$] $10^{-3} \text{ mol dm}^{-3}, (3) [Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}, [H^+] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}, [CI^-] = 4.00 \times 10^{-3} \text{ mol dm}^{-3} [sugar] = 0.2 \text{ mol dm}^{-3},$ (4) $[Pd(II)] = 5.64 \times 10^{-4} \text{ mol } dm^{-3}, \quad [H^+] = 2.25 \times 10^{-3} \text{ mol } dm^{-3},$ $[Cl^{-}] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}, [sugar] = 0.2 \text{ mol dm}^{-3},$ [NBA] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, (5) $[Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$, $[H^+] =$ $2.25 \times 10^{-3} \text{ mol dm}^{-3}$, $[Cl^{-}] = 4.00 \times 10^{-3} \text{ mol dm}^{-3},$ [sugar] = $0.2 \text{ mol } \text{dm}^{-3}$ [NBA] = $1.33 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, (6) [Pd(II)] = $5.64 \times 10^{-4} \text{ mol } \text{dm}^{-3}$, [H⁺] = $2.25 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{m}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{m}^{-3}$, [Cl⁻] = $4.00 \times 10^{-3} \text{ mol } \text{m}^{-3}$] , $[H^+] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}$, $10^{-3} \text{ mol dm}^{-3}$, [sugar] = 0.2 mol dm^{-3} [NBA] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ $[Hg(II)] = 1.25 \times 10^{-3} \text{ mol dm}^{-3}, (7) [Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}$ $[H^+] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}, [Cl^-] = 4.00 \times 10^{-3} \text{ mol dm}^{-3}, [sugar] =$ $[NBA] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}, [Hg(II)] = 1.67 \times 10^{-3} \text{ mol m}^{-3}, [Hg(II)] = 1.67$ 0.2 mol dm^{-3} $\begin{array}{c} 10^{-3} \text{ mol dm}^{-3}, \quad (8) \quad [Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}, \quad [H^+] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}, \quad (9) \quad [Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}, \quad [H^+] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}, \quad (9) \quad [Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}, \quad [H^+] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}, \quad (9) \quad [Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}, \quad [H^+] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}, \quad (9) \quad [Pd(II)] = 5.64 \times 10^{-4} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-4} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3}, \quad (10^{-3} \text{ mol dm}^{-3}) = 10^{-3} \text{ mol dm}^{-3} \text{ mol dm}^{-3} = 10^{-3} \text{ mol d$ $mol dm^{-3}$, $[sugar] = 1.00 \times 10^{-2} mol dm^{-3}$.

It is reported^{22a,12} that Pd(II) forms a complex with allyl alcohol/reducing sugar. In order to verify the existence of a Pd(II)-sugar complex and the formation of other probable complexes, several experiments were performed to collect the UV spectra at room temperature of Pd(II) chloride, H⁺ and Cl⁻ solutions, Pd(II), H⁺, Cl⁻ and sugar solutions, Pd(II), H⁺, Cl⁻, sugar and NBA solutions and Pd(II), H⁺, Cl⁻, sugar, NBA and Hg(II) solutions (Fig. 6). When spectra for Pd(II) chloride with two different solutions of Cl⁻ ions were collected, it was found that with the increase in concentration of Cl⁻ ions there was a significant increase in absorbance from 2.55 to 2.64 at 240 nm (Fig. 6, Panel B, lines 8 and 9), whereas there was an insignificant increase in absorbance at 215 nm. The peak observed at 215 nm, in addition to the peak observed at 240 nm is due to the presence of $PdCl_3(H_2O)^-$ in the solution of Pd(II) chloride, Cl^- ions and H^+ ions. When a sugar solution of two different concentrations was added to the solution of Pd(II), Cl⁻ and H⁺ ions, it was observed that with the increase in concentration of sugar there is an increase in absorbance from 2.64 to 2.68 and 2.77 at 240 nm (Fig. 6, Panel B, lines 9, 10 and 3, respectively). This increase in absorbance with the increase in sugar concentration is due to more and more formation of a complex between reactive species of Pd(II), that is, $(PdCl_4)^{2-}$ and a sugar molecule according to equilibrium (xi)

$$[PdCl_4]^{2-} + S \rightleftharpoons [PdCl_3 \cdot S]^- + Cl^-$$
(xi)

The formation of [Pd(II)-sugar] complexes also finds support from the observed negative effect of Cl^- ion concentrations on the first-order rate constant of the reaction.

Further, when NBA solutions of concentrations 1.00×10^{-3} and 1.33×10^{-3} mol dm⁻³ were added to the solution of Pd(II), Cl⁻, H⁺ and reducing sugar, it was again observed that with the increase in [NBA] there is an increase in absorbance from 2.77 to 2.91 and 2.94 nm with a shift in λ_{max} value towards longer wavelength (248 nm) (Fig. 6, Panel B, line 10, Panel A, lines 4 and 5, respectively). This increase in absorbance can be considered as due to the formation of a complex between (PdCl₃.S)⁻ and the reactive species of NBA according to equilibrium (xii)

$$[PdCl_3 \cdot S]^- + HOBr \rightleftharpoons [PdCl_3 \cdot S \cdot OBr]^{2-} + H^+$$
 (xii)

When Hg(II) solutions of concentrations 1.25×10^{-3} and 1.66×10^{-3} mol dm⁻³ were added to the solution of Pd(II), Cl⁻, H⁺, reducing sugar and NBA, it was very clearly observed that with the addition of Hg(II) solution there was an increase in absorbance from 2.91 to 3.06 and 3.27 at 258 nm (Fig. 6, Panel A, lines 4, 6 and 7, respectively). The increase in absorbance with a shift in λ_{max} towards longer wavelength can be considered as due to formation of a new complex, $\lceil PdCl_3 \cdot S \cdot OBr \rceil$

 $|_{Hg}$, which is the result of the combination

of the complex $(PdCl_3 \cdot S \cdot OBr)^{2-}$ and the reactant Hg^{2+} according to equilibrium (xiii)

On the basis of the above discussion made for the reactive species of NBA and Pd(II) chloride, spectral information collected for the possible formation of complex or complexes in the reaction and kinetic information about the effect of [NBA], [substrate], [Pd(II)], $[H^+]$, [Hg(II)], $[Cl^-]$, [acetamide], μ and dielectric constant (*D*) of the medium on the rate of reaction, the reactions shown in Scheme 1 may be proposed.

$$\begin{array}{c} \text{CH}_{3}\text{CONHBr} + \text{H}_{2}\text{O} & \underbrace{K_{1}}_{\text{(NBA)}} & \text{CH}_{3}\text{CONH}_{2} + \text{HOBr} & (\text{I}) \\ \text{(NHA)} & (\text{NHA}) \end{array}$$

$$[PdCl_4]^2 + S \xrightarrow{k_2} [PdCl_3 \cdot S]^- + Cl^-$$
(II)
(C₁) (C₂)

$$[PdCl_3 \cdot S]^- + Hg^{2+} + HOBr \xrightarrow{k_3} \begin{bmatrix} PdCl_3 \cdot S \cdot OBr \\ I \\ Hg \end{bmatrix} + H^+$$
(III)

$$\begin{bmatrix} PdCl_3 \cdot S \cdot OBr \\ I \\ Hg \end{bmatrix} + H_2O \xrightarrow[determining step]{(C_3)} H_2O \xrightarrow[determining step]{(C_3)} H_2O[]^- + R - C - C - C - C - C + Hg^{2+} (IV)$$

$$H_2O \xrightarrow[determining step]{(C_3)} H_2O[]^- + R - C - C - C - C - C - C + Hg^{2+} (IV)$$

$$H_2O \xrightarrow[determining step]{(C_3)} H_2O[]^- + H_2O[]^- + Hg^{2+} (IV)$$

where S stands for the sugar molecule and R stands for C4H9O4 for both Glc and Fru

$$\begin{array}{ccc} R-C-H & \xrightarrow{NBA/Pd(II)/Hg(II)} & OH \\ I \\ O & H^{+} & I \\ O & O-Br \end{array}$$
(VI)

$$\begin{array}{c} OH \\ R - C - O - Br \\ H \\ H \\ O \\ (Arabinonic acid) \end{array} \xrightarrow{R - C - OH + HBr} (VII)$$

$$[PdCl_{3}(H_{2}O)]^{-} + Cl^{-} \longrightarrow [PdCl_{4}]^{2-} + H_{2}O$$
(VIII)

Scheme 1.

On the basis of the above mechanism, the rate in terms of disappearance of NBA can be expressed as

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

On applying the law of chemical equilibrium to step (I) and steady-state approximation to steps (II) and (III), the rate law in terms of concentration of reaction components can be derived as change in the first-order rate constant, k_1 , with the increase in the concentration of H⁺ ions (Fig. 4). Since for the observed order with respect to [NBA], [sugar], [Pd(II)], [Hg(II)], [Cl⁻], [NHA] and for the effect of μ and dielectric constant (*D*) of the medium on the rate of reaction, the concentration of H⁺ has been fixed at 13.33×10^{-3} M where no effect of [H⁺] on the rate of reaction was observed; hence, the proposed mechanism needs modification. With zero order in [H⁺], step (III)

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

The above rate law is well in accordance with the observed order with respect to each reactant (except in the higher range of $[H^+]$) taking part in the reaction. In the present investigation, although the negative effect of $[H^+]$ in Glc and Fru is observed but in the higher range $(10.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ and above})$, there is almost no

of Scheme 1 can be considered as an irreversible step, and under this condition, steps (III) and (IV) of Scheme 1 will be shown as follows.

On the basis of (1) the reactions in Scheme 1, where reaction step (III) is taken as irreversible and is the rate-determining step, and (2) the stoichiometric equa-

$$\begin{bmatrix} PdCl_{3} \cdot S]^{-} + Hg^{2+} + HOBr \xrightarrow{k_{3}}_{\text{slow and rate-determining step}} \begin{bmatrix} PdCl_{3} \cdot S \cdot OBr \\ I \\ Hg \end{bmatrix} + H^{+}$$
(III)
$$\begin{bmatrix} PdCl_{3} \cdot S \cdot OBr \\ I \\ Hg \end{bmatrix} + H_{2}O \xrightarrow{\text{fast}} \begin{bmatrix} PdCl_{3}(H_{2}O)]^{-} + R - C - C - O^{-} + Hg^{2+} \\ I \\ OH OBr \end{bmatrix}$$
(IV)

tions for both Glc and Fru, the rate in terms of decrease in concentration of NBA, can be expressed as follows:

rate =
$$-\frac{d[NBA]}{dt} = 2k_3[C_2][Hg(II)][HOBr]$$
 (3)

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

$$[\text{HOBr}] = \frac{K_1[\text{NBA}]}{[\text{NHA}]} \tag{4}$$

On applying steady-state approximation to [C₂], we get

$$O = \frac{d[C_2]}{dt}$$

= $k_2[C_1][S] - k_{-2}[C_2][Cl^-] - k_3[C_2][Hg(II)][HOBr]$

or
$$[C_2] = \frac{k_2[C_1][S]}{k_{-2}[Cl^-] + k_3[Hg(II)][HOBr]}$$
 (5)

From Eqs. 4 and 5, we obtain Eq. 6

$$[C_2] = \frac{k_2[C_1][S][NHA]}{k_{-2}[CI^-][NHA] + K_1k_3[Hg(II)][NBA]}$$
(6)

From Eqs. 3, 4 and 6, we obtain Eq. 7

$$rate = -\frac{d[NBA]}{dt}$$
$$= \frac{2K_1k_2k_3[Hg(II)][S][NBA][C_1]}{k_{-2}[CI^-][NHA] + K_1k_3[Hg(II)][NBA]}$$
(7)

According to the proposed mechanism, the total concentration of Pd(II), that is, $[Pd(II)]_T$ can be expressed as

$$[Pd(II)]_{T} = [C_{1}] + [C_{2}]$$
(8)

On substituting the value of $[C_2]$ from Eq. 6 to Eq. 8, we obtain Eq. 9

$$[C_{1}] = \frac{(k_{-2}[Cl^{-}][NHA] + K_{1}k_{3}[Hg(II)])[Pd(II)]_{T}}{k_{-2}[Cl^{-}][NHA] + K_{1}k_{3}[Hg(II)][NBA] + k_{2}[S][NHA]}$$
(9)

On putting the value of $[C_1]$ from Eq. 9 to Eq. 7, we have Eq. 10

$$rate = -\frac{d[NBA]}{dt}$$
$$= \frac{2K_1k_2k_3[Hg(II)][S][NBA][Pd(II)]_T}{k_{-2}[CI^-][NHA] + K_1k_3[Hg(II)][NBA] + k_2[S][NHA]}$$
(10)

Total concentration of NBA, that is, $[NBA]_T$ can be expressed as Eq. 11

$$[NBA]_{T} = [NBA] + [HOBr]$$
(11)

On substituting the value of [HOBr] from Eq. 4 to Eq. 11, we get Eq. 12

$$[NBA] = \frac{[NBA]_{T}[NHA]}{[NHA] + K_{1}}$$
(12)

On putting the value of [NBA] from Eq. 12 to Eq. 10, the final rate law can be obtained as Eq. 13

$$rate = -\frac{d[NBA]}{dt}$$
$$= \frac{2K_1k_2k_3[S][Hg(II)]_T[NBA]_T[Pd(II)]_T}{(K_1 + [NHA])(k_{-2}[CI^-] + k_2[S]) + k_3K_1[NBA]_T[Hg(II)]}$$
(13)

The rate law (13) is in complete agreement with our experimental findings hence, the proposed mechanism can be assumed as a valid one.

If $k_2[S] \gg k_{-2}[Cl^-]$, then under this condition Eq. 13, will be reduced to Eq. 14

rate =
$$-\frac{d[NBA]}{dt}$$

= $\frac{2K_1k_2k_3[S][Hg(II)]_T[Pd(II)]_T[NBA]_T}{k_2K_1[S] + k_2[S][NHA] + k_3K_1[NBA]_T[Hg(II)]}$ (14)

On the other hand, if the inequality $k_{-2}[Cl^-] \gg k_2[S]$ is assumed as a valid one, then under this condition Eq. 13 will be reduced to Eq. 15

$$rate = -\frac{d[NBA]}{dt} = \frac{2K_1k_2k_3[S][Hg(II)][NBA]_T[Pd(II)]_T}{K_1k_{-2}[Cl^-] + k_{-2}[Cl^-][NHA] + k_3K_1[NBA]_T[Hg(II)]}$$
(15)

Eq. 14 can also be written as Eq. 16

$$\frac{[Pd(II)]_{T}}{rate} = \frac{1}{2k_{3}[Hg(II)][NBA]_{T}} + \frac{[NHA]}{2k_{3}K_{1}[Hg(II)][NBA]_{T}} + \frac{1}{2k_{2}[S]}$$
(16)



Figure 7. [NBA] = $8.33 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol dm}^{-3}$, [HClO₄] = $13.33 \times 10^{-3} \text{ mol dm}^{-3}$, [KCl] = $4.00 \times 10^{-4} \text{ mol dm}^{-3}$, [NHA] = $9.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $11.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$.



Figure 8. [NBA] = $8.33 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol } \text{dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol } \text{dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol } \text{dm}^{-3}$, [HClO₄] = $13.33 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol } \text{dm}^{-3}$, [KCl] = $4.00 \times 10^{-4} \text{ mol } \text{dm}^{-3}$, $\mu = 3.50 \times 10^{-2} \text{ mol } \text{dm}^{-3}$.

and again Eq. 15 can also be written as Eq. 17

$$\frac{[Pd(II)_{T}]}{rate} = \frac{k_{-2}[CI^{-}]}{2k_{2}k_{3}[S][Hg(II)][NBA]_{T}} + \frac{k_{-2}[CI^{-}][NHA]}{2k_{3}k_{2}K_{1}[S][Hg(II)][NBA]_{T}} + \frac{1}{2k_{2}[S]}$$
(17)

According to Eq. 16, if a plot is made between [Pd(II)]_T/rate and 1/[Hg(II)] or [NHA], then a straight line having a positive intercept on [Pd(II)]_T/rate axis should be obtained. When [Pd(II)]_T/rate values are plotted against 1/[Hg(II)] and [NHA], straight lines with positive intercepts on $[Pd(II)]_T$ /rate axis were obtained (Figs. 7 and 8). This clearly proves the validity of rate law (14) and hence the proposed reaction Scheme 1. From the slopes and intercepts of straight lines the values of constants k_2 , k_3 and K_1 were calculated for both the reducing sugars and are presented in Table 7. Using the values of constants k_2 , k_3 and K_1 and the rate law (14), the initial rates of the reaction, that is, -d[NBA]/dt, have been calculated for the variation of each [Pd(II)], [Hg(II)] and [NHA] and found in close conformity with the observed rates of reaction (Tables 2, 4 and 5). This further confirms the validity of the rate law (14) and hence the proposed reaction Scheme 1 where step (III) has been treated as an irreversible step.

According to Eq. 17, when $[Pd(II)]_T$ /rate values are plotted against [NHA] for both reducing sugars, straight lines with positive intercepts on the $[Pd(II)]_T$ /rate axis were obtained (Fig. 8). From the slopes of the straight lines the value of k_{-2} for each reducing sugar has been calculated and is presented in Table 7.

Further when k_{-2} values obtained for the oxidation of Glc and Fru were utilised for calculating the rate of reaction according to Eq. 15, then the values of calculated reaction rates show close resemblance with the observed rates for the variation of [Cl⁻] and [sugar] at 40 °C. The values of calculated reaction rates at low concentration of sugar are found to be very close to the experimental rates of reaction because the rate law that has been used for the calculation of the rate of reaction is valid only for the condition where k_{-2} [Cl⁻] $\gg k_2$ [S].

Since the order of reaction with respect to [NBA] is unity in the range of low concentration of NBA, under these conditions the inequality ($[K_1 + [NHA])$) ($k_{-2}[Cl^-] + k_2[S]$) $\gg k_3 K_1[NBA]_T[Hg(II)]$ can also be assumed as valid one, and under these conditions the rate law (13) will be reduced to rate law (18)

$$rate = -\frac{d[NBA]}{dt}$$
$$= \frac{2K_1k_2k_3[S][Hg(II)][NBA]_T[Pd(II)]_T}{(K_1 + [NHA])(k_{-2}[Cl^-] + k_2[S])}$$
(18)

Table 7. Calculation of constants $(k_2, K_1, k_3 \text{ and } k_{-2})$ from the plots of $[Pd(II)]_T$ /rate versus 1/[Hg(II)] and $[Pd(II)_T$ /rate versus [NHA] for the Pd(II)-catalysed oxidation of D-glucose and D-fructose by NBA^a

Plots	Constants	D-Glucose	D-Fructose
$\frac{\left[Pd(II)\right]_{T}}{rate} \ versus \ \frac{1}{\left[Hg(II)\right]}$	$k_2 (\mathrm{dm^3mol^{-1}s^{-1}})$	7.27×10^{-2}	14.28×10^{-2}
$\frac{[Pd(II)]_{T}}{rate} \text{ versus } [NHA]$	$K_1 \pmod{\text{dm}^{-3}} \\ k_3 (\text{dm}^6 \text{ mol}^{-2} \text{s}^{-1}) \\ k_{-2} (\text{dm}^3 \text{ mol}^{-1} \text{s}^{-1})$	$2.66 \times 10^{-3} 1.63 \times 10^{3} 4.55$	2.41×10^{-3} 1.40×10^{3} 7.14

^a Conditions: see Table 4 for [Hg(II)] variation and Table 5 for [NHA] variation.

Eq. 18 is valid only at low concentration of NBA for the oxidation of both of the reducing sugars. Using Eq. 18 and utilising the values of constants determined earlier, the values of the rate of reaction for the low concentrations of NBA in the oxidation of Glc and Fru have been calculated and found to be in close agreement with the observed rates. This gives an additional support to the proposed reactions in Scheme 1.

3.4. Multiple regression analysis

Multiple regression analysis has also been used to calculate rates for the variation of each [Pd(II)], [Hg(II)] and [NHA], and in each case it has been found that the reaction rates calculated on the basis of equations of fitted model for D-glucose and D-fructose are in close agreement with observed rates and the rates calculated on the basis of the rate law (14). This proves the validity of rate law (14) and hence the proposed reactions in Scheme 1. Rate equations, the use of which was made to calculate rates on the basis of multiple regression analysis for D-glucose and D-fructose, are (19) and (20), respectively:

$$k' = [S]^{0.72} [Pd(II)]^{0.98} [Hg(II)]^{0.47} [NHA]^{-0.35} [CI^{-}]^{-0.40} (19)$$

$$k' = [S]^{0.78} [Pd(II)]^{1.01} [Hg(II)]^{0.58} [NHA]^{-0.42} [CI^{-}]^{-0.49} (20)$$

where $k' = -\frac{d[NBA]/dt}{[NBA]^{0.87}}$ for D-glucose and $k' = -\frac{d[NBA]/dt}{[NBA]^{0.89}}$ for D-fructose.

3.5. Entropy of activation and other activation parameters

Entropy of activation plays an important role in the case of reaction between ions or between an ion and a neutral molecule or a neutral molecule forming ions. When reaction takes place between two ions of opposite charges, their union will result in a lowering of the net charge, and due to this some frozen solvent molecules will be released with an increase of entropy. But on the other hand, when reaction takes place between two similarly charged species, the transition state will be a more highly charged ion, and due to this, more solvent molecules will be required than for the separate ions, leading would lead to a decrease in entropy. On the basis of this information, the observed positive entropy of activation in the oxidation of both Glc and Fru (Table 6) supports the rate-determining step (III) of the proposed reactions in Scheme 1 where reaction is taking place between two oppositely charged species $[PdCl_3 \cdot S]^{1-}$ and Hg^{2+} , which while interacting with $PdCl_3 \cdot S \cdot OBr$

HOBr form a neutral complex | A un Ho

$$|_{Hg}$$
 . A uniform



Figure 9. [NBA] = $8.33 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $10.00 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), [sugar] = $2.50 \times 10^{-2} \text{ mol dm}^{-3}$ (Glc) and $2.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Fru), [PdCl₂] = $28.20 \times 10^{-6} \text{ mol dm}^{-3}$, [HClO₄] = $13.33 \times 10^{-3} \text{ mol dm}^{-3}$, [Hg(OAc)₂] = $1.25 \times 10^{-3} \text{ mol dm}^{-3}$, [KCl] = $4.00 \times 10^{-4} \text{ mol dm}^{-3}$, [NHA] = $9.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Glc) and $11.11 \times 10^{-4} \text{ mol dm}^{-3}$ (Fru), $\mu = 3.50 \times 10^{-2} \text{ mol dm}^{-3}$.

mechanism for the oxidation of both Glc and Fru is obvious from the observed order of frequency factor, which is the same for both of the reducing sugars.

3.6. Calculation of the size of the activated complex (d_{AB})

In order to determine the effect of the dielectric constant (D) of the medium on the rate of reaction, the reaction has been studied with different dielectric constants for the medium at constant concentration of all other reactants and at a constant temperature of 40 °C. The change in dielectric constant of the medium has been made by the addition of ethanol to the reaction mixture. Although primary alcohols are oxidised by N-chlorosuccinimide, which is treated as strong oxidant, it is reported^{22b} that NBA or NBS fails to oxidise aliphatic primary alcohols. It is also reported¹⁷ that in the catalysed range of [H⁺] between 0.2 and 0.75 M, primary alcohols are oxidised by N-bromoacetamide. Before conducting experiments for the study of the effect of dielectric constant of the medium on the rate of reaction, we have performed experiments taking ethyl alcohol as an organic substrate instead of reducing sugars in the usual manner and found that ethyl alcohol under the conditions of our experiments (at or below 13.33×10^{-3} mol dm⁻³ H⁺ concentration) is not at all oxidised by NBA in the presence of Pd(II) as the homogeneous catalyst. The decrease in the first-order rate constant with the increase in dielectric constant of the medium is observed. Since in the rate-determining step of the mechanism (Scheme 1) proposed for the Pd(II)catalysed oxidation of Glc and Fru, the reaction is taking place between two ions, the calculation of d_{AB} (size of activated complex) has been made with the help of the following equation:

$$\log k = \log k_0 - \frac{Z_A Z_B e^2 N}{2.303(4\pi\varepsilon_0) d_{AB} RT} \times \frac{1}{D}$$
(21)

From the slopes of the straight lines obtained in $\log k$ versus 1/D plots (Fig. 9), the value of d_{AB} has been calculated and found as 6.10 and 5.01 Å for Glc and Fru, respectively. Positive slopes obtained for the oxidation of both Glc and Fru clearly support the interaction between two oppositely charged species resulting in the formation of an activated complex of the type $\lceil PdCl_3 \cdot S \cdot OBr \rceil$

| in the rate-determining step of the pro-Hg

posed reactions in Scheme 1.

3.7. Primary salt effect

The negligible effect of μ observed in Pd(II)-catalysed oxidation of Glc and Fru also supports the rate-determining step of Scheme 1, where reaction is taking place between two ions and a neutral molecule (step III).

3.8. Comparative studies

Efforts have also been made to compare the findings of this paper with the results reported^{10,23} for the Ir(III)catalysed oxidation of reducing sugars by NBA in the presence of perchloric acid and the Pd(II)-catalysed oxidation of reducing sugars by N-bromosuccinimide (NBS) in acidic solution. The present paper on the one hand shows similarity with Ir(III)-catalysed¹⁰ oxidation of reducing sugars being first to zero order with respect to [NBA] in each case, and on the other hand it differs in order with respect to [NBS], indicating first-order kinetics throughout the variation of [NBS] in the Pd(II)-catalysed²³ oxidation of reducing sugars by NBS in the presence of perchloric acid. In the present study order with respect to reducing sugar has been found to be first order at its lower concentration and zero order at its very high concentration, whereas in the reported Ir(III)-catalysed oxidation of reducing sugars by NBA, order with respect to reducing sugar was found to be zero, and as a result, participation of the reducing sugar molecule was not shown in the proposed mechanism before the rate-determining step. Due to order being fractionally positive, with respect to reducing sugar concentration in the Pd(II)-catalysed oxidation of reducing sugars by NBA or NBS, the participation of a reducing sugar molecule in or before the rate-determining step and its contribution to the reaction rate is in contrast to the Ir(III)-catalysed oxidation of reducing sugars where the derived rate law does not relate the rate of reaction with the concentration of reducing sugar.

The present study entirely differs with the other two studies^{10,23} as far as the order with respect to Hg(II) is concerned. In the Pd(II)-catalysed oxidation of D-glucose and D-fructose by NBA, order with respect to [Hg(II)] has been found to be fractionally positive,

whereas in the reported Ir(III)-catalysed oxidation of reducing sugars by NBA, it varies from two to one and in the Pd(II)-catalysed oxidation of reducing sugars by NBS, its role is limited to that of a Br⁻ ion scavenger only. First-order kinetics with respect to [Pd(II)] throughout its variation in the oxidation of D-glucose and D-fructose by NBA, as well as in the oxidation of reducing sugars by NBS, is certainly different from the first-order kinetics not usually observed at low concentration of Ir(III), which changes to zero-order kinetics at its high concentration in the oxidation of reducing sugars by NBA in the presence of perchloric acid. Although the reported negative fractional order in [H⁺] for the Pd(II)-catalysed oxidation of reducing sugars by NBS is similar to the observed negative fractional order at low concentration of H⁺, a distinguishing feature in the present study is that at very high $[H^+]$, almost no effect of $[H^+]$ on the rate of reaction is observed. Negative fractional order in Cl⁻ ions and negligible effect of μ on the rate of reaction were observed in the present case, as well as in the reported Pd(II)- and Ir(III)-catalvsed oxidation of reducing sugars.

Positive entropy of activation observed in the present case supports the interaction between two oppositely charged species in the rate-determining step and shows similarity with the reported Ir(III)-catalysed oxidation of reducing sugars by NBA. But this is in contrast to the negative entropy of activation observed in Pd(II)catalysed oxidation of reducing sugars by NBS. The distinct feature of the present study is that the proposed mechanism is consistent with kinetic data and is supported by the spectra collected for the formation of complexes during the course of reaction and also by multiple regression analysis.

References

- 1. Filler, R. Chem. Rev. 1963, 63, 21-43.
- Venkatasubramanian, N.; Thiagrajan, V. Can. J. Chem. 1969, 47, 694–697.
- Singh, B.; Singh, D.; Singh, A. K. Int. J. Chem. Kinet. 1988, 20, 501–571.
- 4. Perumal, S.; Alagummalae, S.; Selvraj, S.; Arumugan, N. *Tetrahedron* **1986**, *42*, 4867–4872.
- Singh, B.; Singh, D.; Bajpai, S.; Ashutosh, K. Transition Met. Chem. 1991, 16, 610–613.
- Agarwal, M. C.; Upadhyay, S. K. J. Sci. Ind. Res. 1983, 42, 508–517.
- Singh, A. K.; Singh, V.; Singh, A. K.; Gupta, N.; Singh, B. Carbohydr. Res. 2002, 337, 345–357.
- Singh, A. K.; Singh, A.; Gupta, R.; Saxena, M.; Singh, B. Transition Met. Chem. 1992, 17, 413–416.
- Saxena, M.; Gupta, R.; Singh, A.; Singh, B.; Singh, A. K. J. Mol. Catal. 1991, 65, 317–327.
- Singh, A. K.; Rahmani, S.; Singh, B.; Singh, R. K.; Singh, M. J. Phys. Org. Chem. 2004, 17, 249–256.
- 11. Gupta, N.; Chaurasia, N.; Singh, V. Oxid. Commun. 2000, 23, 42–49.

- Singh, A. K.; Singh, V.; Rahmani, S.; Singh, A. K.; Singh, B. J. Mol. Catal.: A Chem. 2003, 197, 91–100.
- 13. Henry, P. M. J. Am. Chem. Soc. 1964, 86, 3246-3250.
- Feigl, F. Spot Tests in Organic Analysis; Elsevier: New York, 1960, p 368.
 Bailar, J. C. The Chemistry of Coordination Compounds;
- Bailar, J. C. *The Chemistry of Coordination Compounds*; Reinhold: New York, 1956, p 4.
- Gopalkrishnan, G.; Rai, B. R.; Venkatasubramanian, N. Indian J. Chem. 1930, 19B, 293–296.
- 17. Mukherjee, J.; Benerjee, K. K. J. Org. Chem. 1981, 46, 2323–2326.
- Henry, P. M. In *Palladium(II)-Catalysed Oxidation of Hydrocarbons*; D. Reidal Publishing Company: Dordecht, 1980; Vol. 2, pp 11–12.
- (a) Schlanskaya, V. A.; Biryukov, A. A. Russ. J. Inorg. Chem. 1966, 11, 28; (b) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th ed.; Wiley: New York, 1989, p 1026; (c) Tikhonova, G. P.; Bovkovets, S. N. Russ. J. Inorg. Chem. 1973, 23, 813.
- 20. Ayres, G. H. Anal. Chem. 1953, 24, 1622-1623.
- 21. Moiseev, I. I.; Levanda, O. G.; Vargaftik, M. N. J. Am. Chem. Soc. 1974, 96, 1003–1007.
- (a) Hiremath, G. A.; Timmanagoudar, P. L.; Nandibewoor, S. T. J. Phys. Org. Chem. 1998, 11, 31–35; (b) Filler, R. Chem. Rev. 1963, 63, 21–44.
- 23. Singh, A. K.; Chopra, D.; Rahmani, S.; Singh, B. Carbohydr. Res. 1998, 314, 157–160.