

Mechanism of Ir(III)-catalysed and Hg(II)-co-catalysed oxidation of reducing sugars by *N*-bromoacetamide in acidic medium

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ABSTRACT: The kinetics of Ir(III)-catalysed and Hg(II)-co-catalysed oxidation of D-glucose (Glu) and D-fructose (Fru) by *N*-bromoacetamide (NBA) were studied in acidic medium. The reactions follow identical kinetics, being zero order in each sugar concentration. The experimental results show a first-order dependence on NBA and Ir(III) at low concentrations, but tending towards zeroth order at higher concentrations. A negative effect of variation of $[H^+]$, $[Cl^-]$ and $[NHA]$ was observed whereas the ionic strength (*I*) of the medium has no influence on oxidation rate. The important feature of the reaction is that it follows a second-order dependence on mercury(II) ion concentration at low concentrations, but it tends towards first order at higher concentrations. Various activation parameters were calculated and recorded. The corresponding acids were identified as the main oxidation products of the reaction. On the basis of the experimental findings, a suitable mechanism consistent with the observed kinetics was proposed. A comparative study was also made between the kinetic results of the present investigation and those of Ru(III)- and Pd(II)-catalysed oxidations of reducing sugars. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: kinetics; oxidation; mechanism; reducing sugars; Ir(III)-catalysis; Hg(II)-co-catalysis; *N*-bromoacetamide

INTRODUCTION

Recently, considerable attention has been focused on the diverse nature of the chemistry of *N*-halo compounds^{1–5} owing to their ability to act as a source of halogenonium cations, hypohalite species and nitrogen anions which act as both bases and nucleophiles. *N*-Bromoacetamide (NBA) has been widely used as an oxidizing and halogenating agent in preparative organic chemistry. Oxidation with NBA as an oxidant with some primary alcohols,⁶ dimethyl sulphoxide,⁷ some aliphatic ketones^{8,9} and cyclic ketones,¹⁰ and as a substrate in acidic–alkaline media have been reported. Recent studies in oxidation of sugar by chloramine-T,^{11,12} *N*-bromosuccinimide¹³ and NBA¹⁴ prompted us to undertake the present work on the investigation of the kinetics and mechanism of Ir(III)-catalysed oxidation of reducing sugars [D-glucose (Glu) and D-fructose (Fru)] by NBA in acidic medium.

EXPERIMENTAL

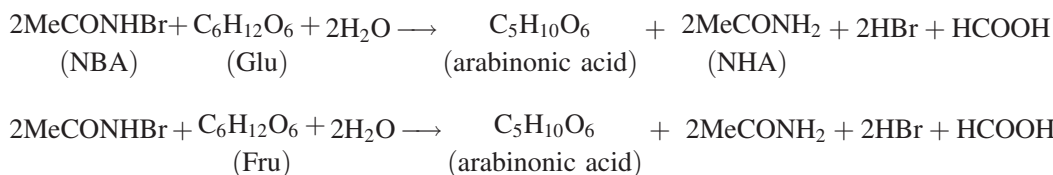
All reagents were of the highest purity available. NBA (Fluka A-G grade) solution was always freshly prepared and its strength was checked iodimetrically. Solutions of sugars (Glaxo and Merck) were freshly prepared by weighing the samples. Mercuric acetate, acetamide, KCl, perchloric acid and sodium perchlorate solutions were prepared from samples obtained from Merck. A solution of the catalyst IrCl₃ was prepared by dissolving the sample in HCl of known strength.

The reactants, i.e. NBA, Hg(OAc)₂, HClO₄, KCl and Ir(III), were mixed in a black-coated conical flask and thermostatted at 308 K for thermal equilibrium. A measured amount of sugar solution, also equilibrated at the same temperature, was rapidly added to the reaction mixture. The progress of the reaction was monitored by measuring the unconsumed NBA iodometrically.

STOICHIOMETRY AND PRODUCT ANALYSIS

Various sets of reactions were performed with different [NBA]:[sugar] ratios under kinetic conditions for 48 h. Determination of unconsumed NBA revealed that for the oxidation of each mole of sugar 2 mol of NBA were required. The stoichiometric equations are as follows:

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The products were found to be identical under both stoichiometric and kinetic conditions and also by thin-layer chromatography. Identification of major reaction product i.e. arabinonic acid, was further verified by paper chromatography.¹⁵

RESULTS

The kinetics of the oxidation of sugars was investigated at several initial concentrations of the reactants. Figure 1 shows the nature of the reaction. The initial rate of reaction in each run was determined by the slope of the tangent drawn at a fixed concentration of NBA, except for studies of NBA variation, where the slope of the tangent was drawn at fixed time. Considering NBA, reducing sugar, hydrogen ions, iridium(III) chloride and Hg(II) as the main reactants, the general form of rate equation for the reaction can be written as

$$\text{rate} = k[\text{NBA}]^\alpha [\text{sugar}]^\beta [\text{H}^+]^\gamma [\text{Ir(III)}]^\delta [\text{Hg(II)}]^\theta \quad (1)$$

In order to determine the experimental rate law, a series of experiments with varying initial concentrations of NBA were performed at constant concentration of all other reactants and at constant temperature. Throughout the variation of NBA, the concentration of NBA was kept much lower than that of sugar and H^+ ions. Under this condition, since the concentrations of other reactants except NBA will essentially be constant, the rate law (1)

becomes

$$\text{rate} = J[\text{NBA}]^\alpha \quad (2)$$

where J , the apparent rate constant, $= k[\text{sugar}]^\beta [\text{H}^+]^\gamma [\text{Ir(III)}]^\delta [\text{Hg(II)}]^\theta$

The results obtained with NBA variation are summarized in Table 1. It is clear that almost constant values of the apparent rate constant (J) are observed up to $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ concentration of NBA with a slight decrease at higher concentrations. This indicates that the order of reaction with respect to NBA is unity up to its $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ and thereafter it tends towards zeroth order. Since in the determination of the order of reaction with respect to all other reactants the experiments were performed with a $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ concentration of NBA, throughout the study the order of reaction with respect to NBA has been taken as unity. Under pseudo-first-order conditions, the concentration of sugar was varied from 1.00×10^{-2} to $10.00 \times 10^{-2} \text{ mol dm}^{-3}$ (Table 1). Zero-order kinetics with respect to [sugar] are evident from the very similar values of J . A linear increase in the apparent first-order rate constant was observed with increase in Ir(III) chloride concentration throughout its variation, except at very high concentrations where a slight deviation from first-order kinetics was noted. This result was further verified by the plot of $\log J$ vs $\log [\text{Ir(III)}]$ (Fig. 2), where slope of the plot gives less than unity order in [Ir(III)] for both the reducing sugars [0.88 (Glu) and 0.80 (Fru)]. The order of reaction with respect to hydrogen ions (obtained from

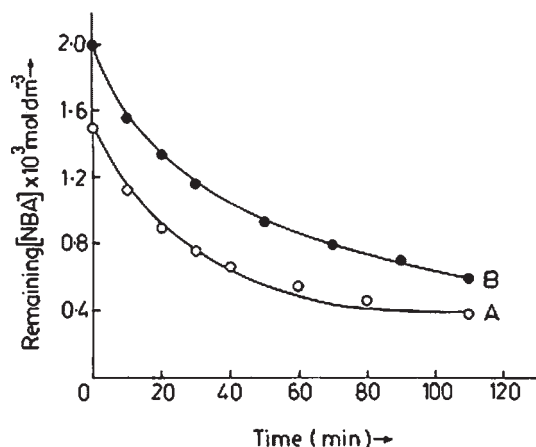


Figure 1. Plot between remaining [NBA] and time at 308 K. [Sugar] = 1.00×10^{-2} , [Ir(III)] = 3.34×10^{-5} , [Hg(OAc)₂] = 5.00×10^{-3} , [HClO₄] = 2.50×10^{-2} , [KCl] = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$. (A) Glu; (B) Fru

Table 1. Effect of [reactants] on the rate constant at 308 K^a

[NBA] $\times 10^3$ (mol dm ⁻³)	[Sugar] $\times 10^2$ (mol dm ⁻³)	$J \times 10^4$ (s ⁻¹)	
		Glu	Fru
0.50(a)	1.00	5.33	5.25
0.75(a)	1.00	5.08	4.93
1.00(a)	1.00	5.16	4.76
1.50(a)	1.00	4.56	4.21
2.00(a)	1.00	3.80	3.86
2.50(a)	1.00	3.56	3.46
1.00	12.00(b)	2.03	3.95
1.00	2.00(b)	2.07	3.44
1.00	4.00(b)	2.03	3.85
1.00	6.00(b)	1.86	3.84
1.00	8.00(b)	1.96	3.72
1.00	10.00(b)	1.83	3.62

^a [Ir(III)] = 3.34×10^{-5} , [HClO₄] = 2.50×10^{-2} , [KCl] = 2.00×10^{-3} , [Hg(OAc)₂] = (a) 5.00×10^{-3} and (b) $2.00 \times 10^{-3} \text{ mol dm}^{-3}$.

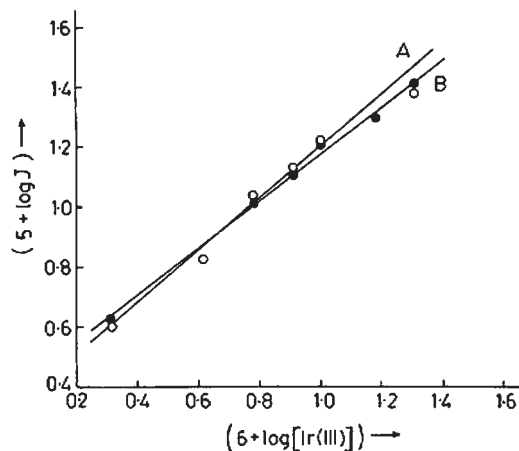


Figure 2. Plot of $\log J$ versus $\log [\text{Ir(III)}]$ at 308 K. $[\text{NBA}] = 1.00 \times 10^{-3}$, $[\text{sugar}] = 1.00 \times 10^{-2}$, $[\text{Hg(OAc)}_2] = 3.00 \times 10^{-3}$ (A) and 4.00×10^{-3} (B), $[\text{HClO}_4] = 2.50 \times 10^{-2}$, $[\text{KCl}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$. (A) Glu; (B) Fru

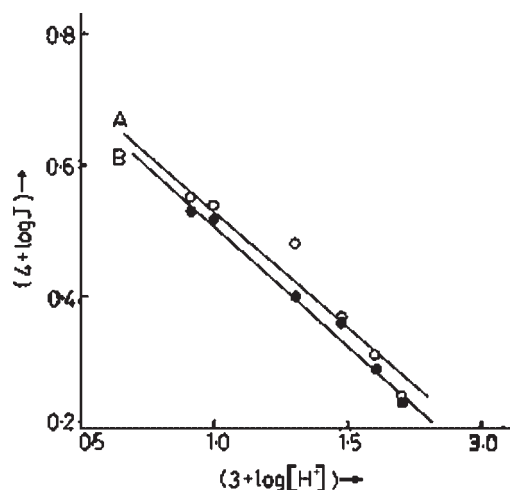


Figure 3. Plot of $\log J$ versus $\log [\text{H}^+]$ at 308 K. $[\text{NBA}] = 1.00 \times 10^{-3}$, $[\text{sugar}] = 1.00 \times 10^{-2}$, $[\text{Ir(III)}] = 3.34 \times 10^{-5}$, $[\text{Hg(OAc)}_2] = 2.00 \times 10^{-3}$, $[\text{KCl}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$. (A) Glu; (B) Fru

perchloric acid) was determined as -0.35 (Glu) and -0.35 (Fru) from the slope of the plot of $\log J$ vs $\log [\text{H}^+]$ (Fig. 3).

Successive addition of Hg(OAc)_2 to the reaction mixture increases the J (Table 2), which is observed to be directly proportional to $[\text{Hg(II)}]^2$ at low concentrations, indicating a second-order reaction with respect to $[\text{Hg(II)}]$. On moving from low to higher concentration of Hg(II) , a possible shift in order from two to one was observed. The possible change in order with respect to Hg(II) from two to one is also supported by the plot of $\log J$ vs $\log [\text{Hg(II)}]$, where the order in the case of glucose and fructose was found to be 1.40 and 1.36, respectively. Since the clarification of the role of acetamide (NHA) and Cl^- ions is significant in ascertaining the reactive species of NBA and Ir(III)chloride , the effects of variations in NBA and Cl^- concentrations on the apparent rate constant were also studied (Table 2).

Table 2. Effect of addition of $[\text{Hg(OAc)}_2]$, $[\text{NHA}]$ and $[\text{Cl}^-]$ on the rate constant at 308 K^a

$[\text{Hg(OAc)}_2] \times 10^3$ (mol dm^{-3})	$[\text{NHA}] \times 10^4$ (mol dm^{-3})	$[\text{Cl}^-] \times 10^3$ (mol dm^{-3})	$J \times 10^4 \text{ (s}^{-1}\text{)}$	
			Glu	Fru
1.00(a)	—	2.00	0.88	0.95
2.00(a)	—	2.00	2.65	3.38
2.50(a)	—	2.00	5.09	5.72
3.00(a)	—	2.00	6.85	6.24
4.00(a)	—	2.00	9.54	9.04
5.00(a)	—	2.00	11.55	—
5.00	2(b)	2.00	3.41	2.57
5.00	4(b)	2.00	3.03	2.42
5.00	10(b)	2.00	2.24	1.59
5.00	15(b)	2.00	1.98	1.42
5.00	20(b)	2.00	1.77	1.31
2.00	—	2.00(a)	2.65	—
2.00	—	4.00(a)	1.50	1.42
2.00	—	6.00(a)	1.25	1.15
2.00	—	8.00(a)	1.00	1.05
2.00	—	10.00(a)	0.80	0.99

^a $[\text{NBA}] = 1.00 \times 10^{-3}$, $[\text{sugar}] = 1.00 \times 10^{-2}$, $[\text{Ir(III)}] = (\text{a}) 3.34 \times 10^{-5}$ and $(\text{b}) 2.00 \times 10^{-5}$, $[\text{HClO}_4] = (\text{a, b}) 2.50 \times 10^{-2} \text{ mol dm}^{-3}$.

The results clearly indicate that with increase in concentration of NBA and Cl^- ions, there is a decrease in the apparent first-order rate constant. The order with respect to NBA was found to be -0.28 (Glu) and -0.32 (Fru) from the slope of the plot of $\log J$ vs $\log [\text{NBA}]$. Similarly, the order with respect to chloride ions was -0.62 (Glu) and -0.48 (Fru). Variations in the ionic strength of the medium had an insignificant effect on the apparent first-order rate constant.

On the basis of the observed values of α , β , γ , δ and θ in $[\text{NBA}]^\alpha$, $[\text{sugar}]^\beta$, $[\text{H}^+]^\gamma$, $[\text{Ir(III)}]^\delta$ and $[\text{Hg(II)}]^\theta$, the experimental rate law for the oxidation of both reducing sugars, Glu and Fru, can be written as Eqns (3) and (4), respectively:

$$\text{rate} = k[\text{NBA}][\text{H}^+]^{-0.35}[\text{Ir(III)}]^{0.88}[\text{Hg(II)}]^{1.40} \quad (3)$$

$$\text{rate} = k[\text{NBA}][\text{H}^+]^{-0.36}[\text{Ir(III)}]^{0.80}[\text{Hg(II)}]^{1.36} \quad (4)$$

When the effects of additions of NBA and Cl^- on the rate of reaction are also taken into consideration, the rate laws (3) and (4) will become

$$\begin{aligned} \text{rate} = k[\text{NBA}][\text{H}^+]^{-0.35}[\text{Ir(II)}]^{0.88}[\text{Hg(II)}]^{1.40} \\ \times [\text{NHA}]^{-0.28}[\text{Cl}^-]^{-0.62} \end{aligned} \quad (5)$$

$$\begin{aligned} \text{rate} = k[\text{NBA}][\text{H}^+]^{-0.36}[\text{Ir(II)}]^{0.80}[\text{Hg(II)}]^{1.36} \\ \times [\text{NHA}]^{-0.32}[\text{Cl}^-]^{-0.48} \end{aligned} \quad (6)$$

The reactions were studied in the temperature range 303–318 K and the values of activation parameters such as energy of activation (E_a), entropy of activation ($\Delta S^\ddagger$) and enthalpy of activation ($\Delta H^\ddagger$) at 308 K are given in Table 3. The identical kinetic results for the oxidation of

as product. In order to eliminate the possibility of parallel Br_2 oxidation and to ensure pure NBA oxidation, Hg(II) was used throughout the investigation by maintaining its concentration either equal to or higher than that of NBA.

Considering the reactive species of Ir(III) and NBA and with the help of above experimental findings, the probable mechanism shown in Scheme 1 is proposed.

On the basis of the mechanism in Scheme 1, the rate in terms of decrease in concentration of NBA can be expressed as

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = 2k_5[\text{C}_4][\text{Hg(II)}] \quad (19)$$

where 2 indicates the number of moles of NBA consumed

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{2k_5K_1K_2K_3K_4[\text{NBA}][\text{Ir(III)}]_T[\text{Hg(II)}]^2}{[\text{NHA}][\text{H}^+](\text{[Cl}^-] + K_2) + K_1K_2K_3K_4[\text{NBA}][\text{Hg(II)}]} \quad (28)$$

per mole of sugar. On applying the law of chemical equilibrium to steps (12)–(15), we obtain the equations

$$K_1 = \frac{[\text{NHA}][\text{HOBr}]}{[\text{NBA}]} \quad (20)$$

$$K_2 = \frac{[\text{C}_2][\text{Cl}^-]}{[\text{C}_1]} \quad (21)$$

$$K_3 = \frac{[\text{C}_3][\text{H}^+]}{[\text{Hg(II)}][\text{HOBr}]} \quad (22)$$

$$K_4 = \frac{[\text{C}_4]}{[\text{C}_2][\text{C}_3]} \quad (23)$$

From Eqns (20)–(23), we can obtain

$$[\text{C}_4] = \frac{K_1K_2K_3K_4[\text{C}_1][\text{NBA}][\text{Hg(II)}]}{[\text{NHA}][\text{H}^+][\text{Cl}^-]} \quad (24)$$

Substituting the value of $[\text{C}_4]$ from Eqn (24) in Eqn (19), we have

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{2k_5K_1K_2K_3K_4[\text{C}_1][\text{NBA}][\text{Hg(II)}]^2}{[\text{NHA}][\text{H}^+][\text{Cl}^-]} \quad (25)$$

According to Scheme 1, the total concentration of Ir(III) can be expressed as

$$[\text{Ir(III)}]_T = [\text{C}_1] + [\text{C}_2] + [\text{C}_4] \quad (26)$$

On substituting the values of $[\text{C}_2]$ and $[\text{C}_4]$ from Eqns (21) and (24) in Eqn (26), we obtain

$$[\text{C}_1] = \frac{[\text{Ir(III)}]_T[\text{NHA}][\text{H}^+][\text{Cl}^-]}{[\text{NHA}][\text{H}^+](\text{[Cl}^-] + K_2) + K_1K_2K_3K_4[\text{NBA}][\text{Hg(II)}]} \quad (27)$$

From Eqns (25) and (27), the final rate law can be written as

According to Eqn (28), when a plot was constructed between $[\text{Ir(III)}]_T \times [\text{Hg(II)}]/\text{rate}$ and $1/[\text{Hg(II)}]$ or $[\text{Cl}^-]$, a straight line having an intercept on the y-axis was obtained for both reducing sugars. From the intercepts and slopes of the straight lines, the value of K_2 was calculated as $2.68 \times 10^{-4}\text{M}$ (Glu) and $3.02 \times 10^{-4}\text{M}$ (Fru) at 35°C . With these values of K_2 and $[\text{Cl}^-]$ used in our experiments $[(2.00\text{--}10.00) \times 10^{-3}\text{mol dm}^{-3}]$, the inequality $[\text{Cl}^-] \gg K_2$ can be assumed as valid and hence Eqn (28) will be reduced to

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{2k_5K_1K_2K_3K_4[\text{NBA}][\text{Ir(III)}]_T[\text{Hg(II)}]^2}{[\text{NHA}][\text{H}^+][\text{Cl}^-] + K_1K_2K_3K_4[\text{NBA}][\text{Hg(II)}]} \quad (29)$$

The total concentration of NBA can be expressed as

$$[\text{NBA}]_T = [\text{NBA}] + [\text{HOBr}] + [\text{C}_3] + [\text{C}_4] \quad (30)$$

On substituting the values of $[\text{HOBr}]$, $[\text{C}_3]$ and $[\text{C}_4]$ from Eqns (20), (22) and (24) in Eqn (30) and on assuming the inequalities $[\text{Cl}^-] \gg K_2$ and $[\text{NHA}][\text{H}^+][\text{Cl}^-] \gg K_1K_2K_3K_4[\text{NBA}][\text{Hg(II)}]$, we have

$$[\text{NBA}] = \frac{[\text{NBA}]_T[\text{NHA}][\text{H}^+][\text{Cl}^-]}{[\text{NHA}][\text{Cl}^-][\text{H}^+] + K_1[\text{H}^+][\text{Cl}^-] + K_1K_3[\text{Hg(II)}][\text{Cl}^-] + K_1K_2K_3K_4[\text{Ir(III)}]_T[\text{Hg(II)}]} \quad (31)$$

Considering Eqns (29) and (31), the final rate law can be obtained as

$$\text{rate} = -\frac{d[\text{NBA}]}{dt} = \frac{2k_5K_1K_2K_3K_4[\text{NBA}]_T[\text{Ir(III)}]_T[\text{Hg(II)}]^2}{[\text{NHA}][\text{Cl}^-][\text{H}^+] + K_1[\text{H}^+][\text{Cl}^-] + K_1K_3[\text{Hg(II)}][\text{Cl}^-] + K_1K_2K_3K_4[\text{Ir(III)}]_T[\text{Hg(II)}] + K_1K_2K_3K_4[\text{NBA}]_T[\text{Hg(II)}]} \quad (32)$$

Significant values of the terms $K_1K_2K_3K_4[\text{Ir(III)}][\text{Hg(II)}]$ and $K_1K_2K_3K_4[\text{Hg(II)}][\text{NBA}]_T$ at very high concentrations of Hg(II), NBA, Ir(III) and $[\text{Cl}^-]$ and at very low concentrations of H^+ and NHA in the denominator of rate law (32) clearly demonstrate that order of reaction with respect to Hg(II) is much less than two, whereas in NBA and Ir(III) it is less than one. It also explains the negative fractional order in Cl^- , H^+ ions and NHA. Negligible values of $K_1K_2K_3K_4[\text{Ir(III)}][\text{Hg(II)}]$ and $K_1K_2K_3K_4[\text{Hg(II)}][\text{NBA}]_T$ at very low concentrations of Hg(II), NBA and Ir(III) and at very high concentrations of H^+ , Cl^- and NHA clearly support the nearly second-order kinetics with respect to Hg(II), first-order kinetics with respect to both NBA and Ir(III), the negative fractional order in both H^+ and NHA and inverse order in Cl^- ions. Since experiments on the variation of chloride ion concentration were performed at moderate and constant concentrations of all other reactants, the order with respect to $[\text{Cl}^-]$ was found to be -0.62 (Glu) and -0.43 (Fru) instead of -1.00 as indicated by the rate law (32) at low concentrations of Hg(II), NBA and Ir(III) and at high concentrations of H^+ and NHA. In this way, we find that there is great resemblance between the derived rate law (32) and the experimental rate laws (5) and (6) based on the kinetic observations.

Equation (32) can also be written as.

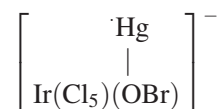
$$\frac{1}{\text{rate}} = \frac{[\text{NHA}][\text{Cl}^-][\text{H}^+]}{2k_5a[\text{NBA}]_T[\text{Ir(III)}]_T[\text{Hg(II)}]^2} + \frac{[\text{H}^+][\text{Cl}^-]}{2k_5b[\text{NBA}]_T[\text{Ir(III)}]_T[\text{Hg(II)}]^2} + \frac{[\text{Cl}^-]}{2k_5c[\text{NBA}]_T[\text{Ir(III)}]_T[\text{Hg(II)}]} + \frac{1}{2k_5[\text{NBA}]_T[\text{Hg(II)}]} + \frac{1}{2k_5[\text{Ir(III)}]_T[\text{Hg(II)}]} \quad (33)$$

where $a = K_1K_2K_3K_4$, $b = K_2K_3K_4$ and $c = K_2K_4$.

According to Eqn (33), if a plot is made of $1/\text{rate}$ versus $1/[\text{NBA}]_T$, $[\text{Cl}^-]$ or $[\text{NHA}]$, then a straight line having positive intercept on the y-axis should be obtained. When $1/\text{rate}$ values are plotted against $1/[\text{NBA}]_T$, $[\text{Cl}^-]$ and $[\text{NHA}]$, straight lines with positive intercepts on the y-axis were obtained, which proves the validity of rate Eqn (32) and hence the proposed mechanism. Linear plots with positive intercepts on the $1/\text{rate}$ axis clearly demonstrate the retarding effect of [NBA] and decreasing effect of $[\text{Cl}^-]$ and [NHA] on the rate. Owing to the rate equation being complicated, it was not possible to calculate individual constants shown in the mechanistic steps.

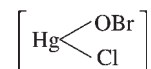
In the present study of the oxidation of reducing sugars by NBA in the presence of Ir(III) as a homogeneous catalyst, the activated state will be less polar caused by

the reactants

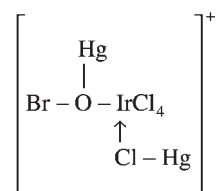


and Hg^{2+} ions. The positive entropy of activation observed in the oxidation of Glu and Fru is due to desolvation of the activated state rather than the reactants. The same order of the frequency factor for both reducing sugars also indicates the operation of a single mechanism in the Ir(III)-catalysed oxidation of the sugars by NBA in the presence of perchloric acid.

Efforts were also made to compare the findings in this work with results already reported^{13,14} for the Pd(II)-catalysed oxidation of D-arabinose (Ara), D-xylose (Xyl) and D-galactose (Gal) by NBS and with Ru(III) and Hg(II) co-catalysed oxidation of D-galactose (Gal) and D-ribose (Rib) by NBA. The observed second-order kinetics with respect to Hg(II) at low concentrations and first-order kinetics at higher concentrations clearly distinguish the present investigation from the other two where the order with respect to $[\text{Hg(II)}]$ was found to be either first tending towards zeroth¹⁴ or zeroth order¹³ throughout $[\text{Hg(II)}]$ variations. On the basis of zeroth order in $[\text{Hg(II)}]$, it is concluded that the role of Hg(II) is limited only up to its function as a Br^- ion scavenger in the Pd(II)-catalysed oxidation of reducing sugars. In contrast to this finding, the reported first-order kinetics which tend to zeroth order at higher $[\text{Hg(II)}]$ in the Ru(III)-catalysed oxidation led the authors to assume that the role of Hg(II) is not limited up to its function as a Br^- ion scavenger but that it also takes part in the reaction prior to the rate-determining step. The proposed reaction path¹⁴ shows the interaction of Hg(II) with the reactive species of NBA, i.e. HOBr, to form the complex $[\text{Hg} \leftarrow \text{OBr}]^+$ which ultimately reacts in the form of



with the complex $[\text{RuCl}_5\text{S}]^{2-}$ as most reactive oxidizing species in the rate-determining step. In Scheme 1, Hg(II), in addition to its role as a Br^- ion scavenger, reacts with HOBr, the reactive species of NBA, to form the complex $[\text{Hg}-\text{OBr}]^+$ showing a resemblance to the Ru(III)-catalysed oxidation¹⁴ but its further involvement in the rate-determining step to form the transient complex C_5 , i.e.



clearly distinguishes the present study from the other two studies reported earlier.^{13,14}

The present study differs entirely from the other two studies^{13,14} with respect of the order in [sugar]. The fractional positive effect of sugar concentration on the rate in both cases supports the contention that the sugar molecule with its active participation in the reaction forms a complex with the catalyst in one case¹⁴ and interacts with the most reactive species $[\text{PdCl}_3\text{OBr}]^{2-}$ in the other.¹³

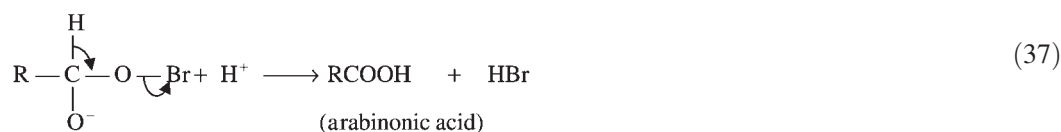
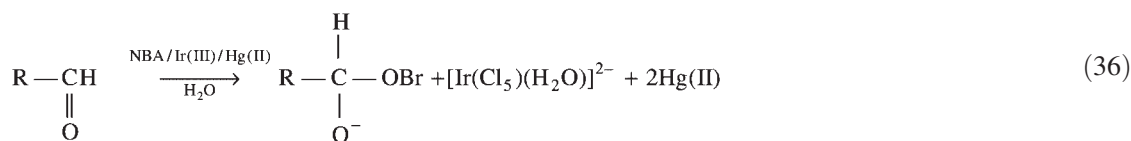
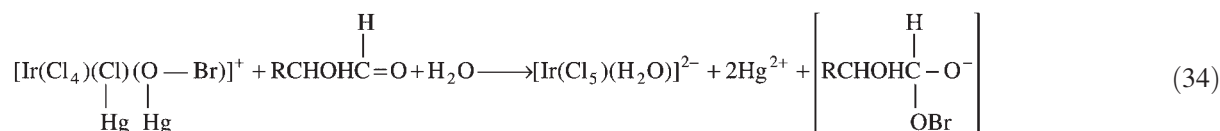
The observed zero effect of sugar concentration can be viewed in a different way by negating the possibility of the formation of an active complex between the reactive species of Ir(III) and the reducing sugar. The negative effect of $[\text{Cl}^-]$ on the rate constant of the reaction led us to assume that the species $[\text{IrCl}_5(\text{H}_2\text{O})]^{2-}$ is the reactive species of Ir(III) in the present investigation, whereas on the basis of positive effect of the chloride ion, $[\text{RuCl}_6]^{3-}$ is reported to be the true reactive species of ruthenium(III) chloride in the NBA oxidation of Gal and Rib. $[\text{PdCl}_4]^{2-}$, being the lone species in the solution of PdCl_2 and HCl , has been taken as the reactive species of PdCl_2 in NBS oxidation of reducing sugars.¹³ The inverse fractional order in [acetamide] was the basis for considering HOBr as the reactive species of NBA in both Ir(III)- and Ru(III)-catalysed oxidation of reducing sugars, but in Pd(II)-catalysed oxidation it is only the

kinetic data which led the authors to assume that HOBr is the reactive species of NBS. Needless to say, the oxidation rate is unaffected by the addition of succinimide. In this way it can be concluded that HOBr is the reactive species of both NBA and NBS in the Ru(III)-, Ir(III)- and Pd(II)-catalysed oxidation of reducing sugars. A decreasing effect of $[\text{H}^+]$ was observed in all three catalysed reactions. The change in order of with respect to $[\text{Ir(III)}]$ from first to zeroth at higher concentrations of Ir(III) shows that Ir(III) participants in the reaction in a different way to Ru(III) and Pd(II), where first-order kinetics were observed throughout their concentration variation.

The positive entropy of activation observed in both Ru(III)- and Ir(III)-catalysed oxidation of reducing sugars by NBA indicates that the activated state will be less polar than the reactants whereas the negative entropy of activation in the case of Pd(II) shows that the activated complex would be more extensively solvated than the reactant species.

The reaction scheme for the Ir(III) and Hg(II) co-catalysed oxidation of reducing sugars by NBA is shown in Scheme 2. This reaction scheme corresponds to the oxidation of D-glucose, and earlier steps have already been given Scheme 1.

DA similar mechanism can be drawn for the oxidation of fructose.



Scheme 2

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