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Kinetics and mechanism of Pd(II) catalysed oxidation of D-arabinose, D-xylose and D-galactose by *N*-bromosuccinimide in acidic solution

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Abstract

The kinetics of Pd(II) catalysed oxidation of Ara, Xyl and Gal by *N*-bromosuccinimide (NBS) in acidic medium has been studied using $Hg(OAc)_2$ as a scavenger for the Br^- ion. The reaction data show that first-order kinetics in each pentose and hexose at low concentrations tend to zero-order at high concentrations. First-order kinetics with respect to NBS and Pd(II) and inverse fractional order, i.e., decreasing effect of $[H^+]$ and $[Cl^-]$, were observed, whereas ionic strength, $Hg(OAc)_2$ and succinimide did not influence the oxidation rate. Various activation parameters have been calculated and recorded. The corresponding acids, arabonic, xylonic and galactonic, were identified as the main oxidation products of the reactions. On the basis of the experimental findings, a suitable mechanism has been proposed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Mechanism; Pd(II) catalysis; Acidic medium; Oxidation; Reducing sugars; *N*-bromosuccinimide

1. Introduction

N-Bromosuccinimide (NBS) has been used as an oxidising and halogenating agent in the quantitative estimation of a large number of compounds. Various investigations on oxidation kinetics involving NBS and esters [1], alcohols [2,3], ketones [4–6], polyhydric alcohols [7] and glycol [8] have been reported. Although the oxidative capacity of NBS has been examined in several uncatalysed and catalysed reactions in acidic media, it appears from the literature that no attempt has so far been made to explore the catalytic potential of Pd(II) in NBS oxidation. It is known that NBS oxidation of organic compound is complicated by parallel bromine oxidation. However, bromine oxidation is obviated by using Hg(II) [1]. The oxidation of sugars [9–12] by alkaline NBS solution has also been reported, but no study has examined the role of Pd(II) chloride as a catalyst in NBS oxidation of sugars. This prompted the authors to perform the present work, which constitutes an investigation of the kinetics and mechanism of Pd(II) catalysed oxidation of reducing sugars like Ara, Xyl and Gal by NBS in acidic medium.

2. Experimental

Materials.—NBS solution was always made up fresh and stored in a black-coated flask to prevent photochemical deterioration. It was prepared from E. Merck grade recrystallised material dissolved in double-distilled water. The prepared solution was then standardised

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against sodium thiosulphate solution using starch as an indicator. Aqueous solutions of Ara, Xyl and Gal (AR grade) were also prepared fresh each day. A solution of Pd(II) chloride (Qualigens Chemical India Ltd.) was prepared in HCl of known strength. The overall strength of HCl was maintained at 1.00×10^{-3} M and the strength of Pd(II) chloride was 5.64×10^{-3} M. An aq standard solution of mercuric acetate (E. Merck), acidified with acetic acid and 20% perchloric acid diluted with water, was standardised through acid–base titration.

Method.—The reactants, i.e., NBS, $Hg(OAc)_2$, $HClO_4$ and Pd(II), were mixed in a black-coated conical flask and equilibrated for ca. 30 min at 40 °C. The sugar solution at 40 °C was then rapidly poured into the reaction mixture and the reaction was started by vigorous shaking of the reaction mixture and its progress followed by measuring unconsumed NBS iodometrically.

3. Results and discussion

The kinetics of the oxidation of sugars were investigated at several initial concentrations of the reactants. The rate of reaction in each kinetic run was determined by the slope of the tangent drawn at a fixed concentration of NBS. The effect of NBS variation on the reaction rate $(-dc/dt)$ has been determined by the formula

$$k_1 = (-dc/dt)/[\mathrm{NBS}]$$

A close perusal of the results indicates that the rate of reaction $(-dc/dt)$ is almost directly proportional to the concentration of NBS. The first-order kinetics with respect to NBS are also verified by the constant values of k_1 obtained at various initial concentrations of NBS (Table 1).

Table 1
Effect of variation of [NBS] on reaction rate at 40 °C

$[\mathrm{NBS}] \times 10^4$ M[a]	$k_1 \times 10^5$ (s^{-1})		
	Ara	Xyl	Gal
4.00	5.66	6.75	5.25
6.00	5.45	6.00	5.83
8.00	5.00	6.66	5.92
10.00	5.16	7.01	5.65
16.00	5.33	6.50	4.83
20.00	5.03	6.02	4.83

[a] Solution conditions: 2.00×10^{-3} M perchloric acid, 5.00×10^{-3} M mercuric acetate, 19.74×10^{-6} M palladous chloride, 5.00×10^{-2} M (Ara and Gal), 10.00×10^{-2} M (Xyl).

A plot of $(-dc/dt)$ versus [sugar] shows that first-order kinetics with respect to sugars in their lower range of concentration shifts to zero-order in the higher range of their concentrations (Fig. 1). A $\log k_1$ versus $\log[\mathrm{Pd(II)}]$ plot gives a straight line with a slope near unity (1.02, 0.92 and 0.94 in Ara, Xyl and Gal, respectively), which confirms the first-order dependence of the reactions on Pd(II) chloride (Fig. 2). The order of reaction with respect to hydrogen ions (obtained from perchloric acid) was determined as -0.38 for Ara, -0.34 for Xyl and -0.13 for Gal from the slope of the plot between $\log k_1$ and $\log[\mathrm{H}]^+$ (Fig. 3).

The results of Table 2 indicate the negative effect of the addition of KCl and the zero effect of the addition of succinimide (NHS) on the rate constant. The reactions were studied at different temperatures and the rate constants at 35, 40, 45 and 50 °C used to calculate E_a, $\Delta S^{\#}$ and $\Delta G^{\#}$ in the oxidation of Ara, Xyl and Gal as 6.86, 10.49 and 12.20 kcal/mol, respectively, -30.18, -17.62 and -10.77

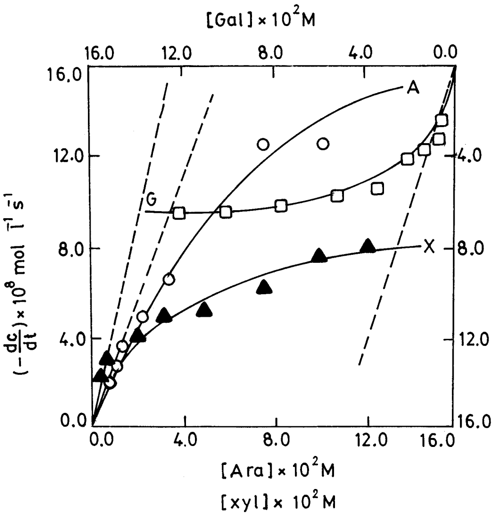


Fig. 1. Plots of $(-dc/dt)$ vs. [substrate] at 40 °C. $[\mathrm{NBS}] = 10.00 \times 10^{-4}$ M, $[HClO_4] = 2.00 \times 10^{-3}$ M, $[PdCl_2] = 19.74 \times 10^{-6}$ M, $[Hg(OAc)_2] = 1.25 \times 10^{-3}$ M; A, Ara; X, Xyl; G, Gal.

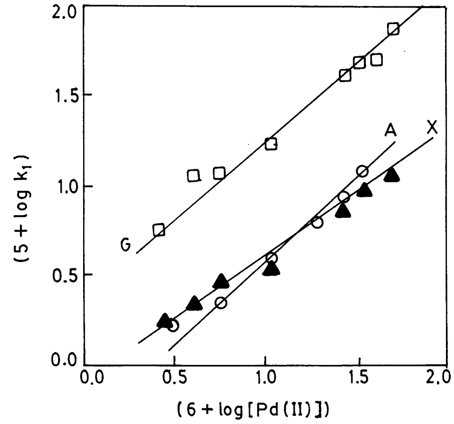


Fig. 2. Plots of log [Pd(II)] vs. log k_1 at 40 °C. [NBS] = 10.00 × 10^{-4} M, [$HClO_4$] = 2.00 × 10^{-3} M, [$Hg(OAc)_2$] = 1.25 × 10^{-3} M, [substrate] = 5.00 × 10^{-2} M (for Ara and Gal), 10.00 × 10^{-2} M (for Xyl); A, Ara; X, Xyl; G, Gal.

eu, respectively, and 15.55, 15.30 and 15.21 kcal/mol, respectively. Mercuric acetate was found to have a limited role as a bromide ion scavenger.

On the basis of the above experimental findings, a probable scheme (Scheme 1) is proposed for the oxidation of Ara, Xyl and Gal. The kinetic data led the authors to assume that HOBr and $[PbCl_4]^{2-}$ are reactive species of NBS and palladous chloride, respectively.

The rate of oxidation of the title substrate may be expressed in terms of loss of [NBS] as

$$-\mathrm{d}[\mathrm{NBS}]/\mathrm{d}t = k_d[C_3][S] \qquad (1)$$

Considering steps (i)–(iii) of Scheme 1 and on applying a steady state approximation to [C_2] and [C_3], the rate equation (Eq. (1)) may be expressed finally as Eq. (2) with suitable approximations.

$$-\frac{\mathrm{d}[NBS]}{\mathrm{d}t} = \frac{kk_2k_3[\mathrm{PdCl_4}]^{2-}[\mathrm{NBS}][\mathrm{RCHO}]}{k_3[\mathrm{H}^+] + kk_{-2}[\mathrm{RCHO}][\mathrm{Cl}^-] + k_3} \qquad (2)$$

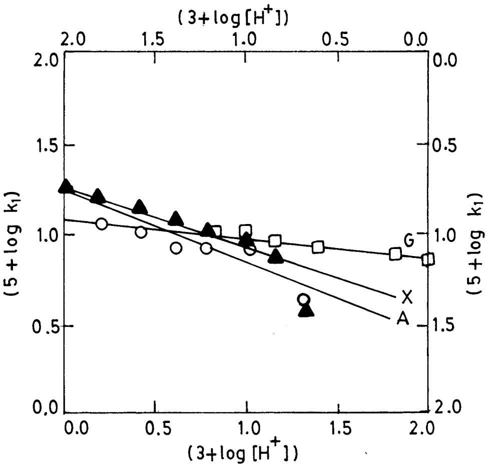


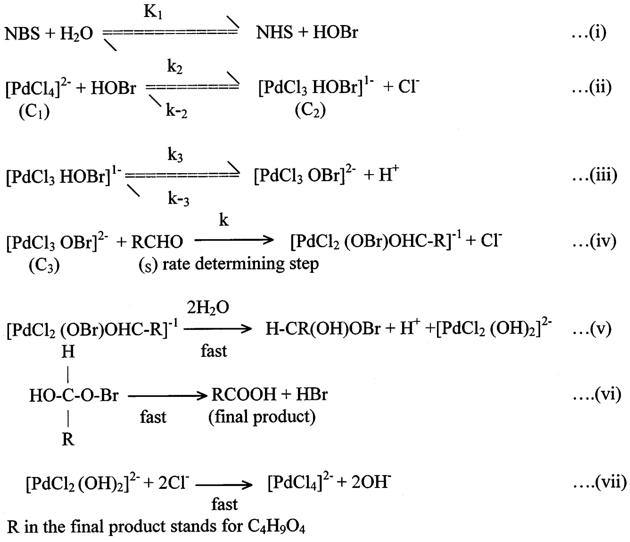
Fig. 3. Plots of log [H^+] vs. log k_1 at 40 °C. [NBS] = 10.00 × 10^{-4} M, [$PdCl_2$] = 19.74 × 10^{-6} M, [$Hg(OAc)_2$] = 1.25 × 10^{-3} M, [substrate] = 5.00 × 10^{-2} M (for Ara and Xyl), 10.00 × 10^{-2} M (for Gal); A, Ara; X, Xyl; G, Gal.

Table 2
Effect of addition of KCl and succinimide [NHS] on rate constant at 40 °C

[KCl] × 10^2 M	[NHS] × 10^4 M	k_1[a] × 10^5 (s^{-1})		
		Ara	Xyl	Gal
1.42		11.92	10.00	11.74
2.42		11.40	9.64	10.00
3.42		10.95		9.47
5.42		10.52	9.29	9.29
7.42			8.76	8.78
9.42		10.02	9.36	7.89
15.42	3.34	5.36	6.73	5.51
15.42	5.00	5.24	6.31	5.72
15.42	10.00	5.23	6.55	5.89
15.42	20.00	5.26	6.33	5.78
15.42	30.00	5.30	6.58	5.76

[a] Solution conditions: 10.00 × 10^{-4} M *N*-bromosuccinimide, 19.74 × 10^{-6} M palladous chloride, 2.00 × 10^{-3} M perchloric acid, 1.25 × 10^{-3} M mercuric acetate, 5.00 × 10^{-2} M (Ara and Gal), 10.00 × 10^{-2} M (Xyl).

The negligible effect of succinimide concentration on the rate of reaction is obvious, as it does not appear in the rate law (Eq. (2)). The



Scheme 1.

proposed mechanism is well supported by the value of the energy of activation parameters. A high positive value of free energy of activation ($\Delta G^{\#}$) indicates that the transition state is highly solvated, while a negative value of entropy of activation ($\Delta S^{\#}$) suggests the formation of an activated complex with a reduction in the degree of freedom of reacting molecules.

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