

## **Oxidation of organic compounds by phenyl iodoso acetate (II). Kinetics and mechanism of oxidation of aldo-sugars**

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**Abstract.** Kinetics of oxidation of five aldo-sugars by phenyl iodoso acetate in aqueous acetic acid medium in presence of perchloric acid has been investigated. The reaction has first order dependence on both substrate and oxidant. The reaction is retarded by perchloric acid and has unit inverse dependence on acidity. Increase in acetic acid in the solvent composition decreases the rate. A suitable mechanism involving the complex formation between the oxidant and substrate is postulated which explains the observed kinetic data.

**Keywords.** Phenyl iodoso acetate; aldo-sugars; oxidation mechanism; kinetics.

### **1. Introduction**

Pati and Dev (1979) have recently reported the oxidation of cyclic ketones by phenyl iodoso acetate (PIA) in aqueous acetic acid medium both in the presence of perchloric acid and sulphuric acid separately. Oxidation of different sugars has been reported by Mehrotra and Amis (1974), Kumar and Mehrotra (1975), Singh (1970) and Pottenger and Johnson (1970) using different oxidants. A survey of literature shows no report on oxidation of sugars using PIA as an oxidant. In the present paper the kinetic data of oxidation of five sugars—D-glucose, D-arabinose, D-xylose, D-mannose and D-galactose—are presented.

### **2. Materials and methods**

All the organic substrates used were of extra pure variety (BDH/Merck/Fluka) AR grade. AnalaR grade acetic acid is purified by standard methods and solutions were prepared in conductivity water. PIA was prepared by the modified method of Boeseken and Schneider (1931). The reaction velocity was measured by the standard iodometric method [Pati and Dev (1979)].

### **3. Results and discussion**

The oxidation of the five sugars by PIA in aqueous acetic acid medium both in the presence of perchloric acid and sodium acetate has been studied separately

in detail from the kinetic point of view. The reaction has first order dependence on the oxidant as seen from the values of rate constants obtained with different initial oxidant concentrations (see table 1).

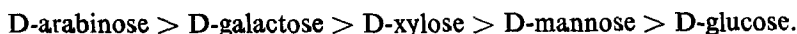
The plots of  $\log(b - x)$  versus time are linear indicating first order dependence on the oxidant concentrations. Vaidyanathan and Venkatasubramanian (1973) have also reported first order dependence on oxidant in their work on oxidation of  $\alpha$ -hydroxy acids and amides by PIA.

It is observed that there is a first order dependence on sugar concentration. The plot of  $\log k_1$  versus  $\log [\text{sugar}]$  (figure 1) is linear with unit slope indicating first order dependence of the reaction on substrate. The rate constants for different sugars at various initial substrate concentrations are given in table 2.

As the reaction has first order dependence on oxidant and substrate, it may be stated that the reaction follows the rate law :

$$-d[\text{PIA}]/dt = k_2 [\text{PIA}] [\text{sugar}].$$

From the rate constants given in table 2 it is seen that it is the highest for D-arabinose and lowest for D-glucose. In spite of small differences in the individual rates, it is observed that the order of reactivity is :



Such an order of reactivity has also been reported by Amis (1974) and Pottenge and Johnson (1970) in their work on oxidation of sugars.

Amis holds the view that these differences in rates of oxidation are not due to structural variation of sugars, for almost similar percentage of  $\alpha$  and  $\beta$  forms,

**Table 1.** Dependence of oxidant on the oxidation of sugars in aqueous acetic acid medium by PIA.

Substrate = 0.005 M, Acetic acid = 10% (V/V), Temp. : 35° C

Substrate	$10^3$ [oxidant] M	$10^2 \times k_1$ min <sup>-1</sup>	$k_2$ lit. mol <sup>-1</sup> min <sup>-1</sup>
D-galactose	0.5194	2.75	5.47
	0.7031	2.62	5.26
	0.9701	2.62	5.26
	1.864	2.63	5.27
D-xylose	0.5610	1.99	3.99
	0.7031	1.85	3.70
	1.010	2.00	4.17
	1.864	1.97	3.94
D-mannose	0.4897	0.72	1.45
	0.7241	0.76	1.52
	0.9736	0.74	1.47
	1.923	0.74	1.49

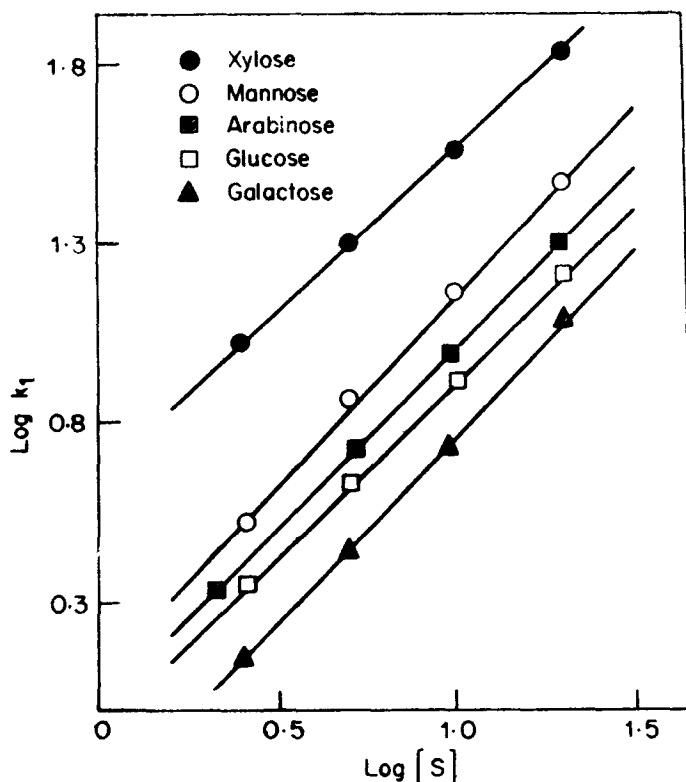


Figure 1.

and an identical orientation of hydrogen atoms at  $C_1$  and  $C_2$  atoms, present at the seat of the reaction, should have not only produced oxidation rates of the same order but also of the same magnitude. He suggests that the differences in rates are due to the differing concentration of the free aldehyde sugars present as intermediates in the dynamic equilibrium of mutarotation in aqueous solution.

### 3.1. Effect of acidity

The effect of change in concentration of perchloric acid on the reaction studied at different concentrations are given in table 3.

It is clear that there is a retarding effect on the reaction, the rate decreases with increase of acid concentration. The plots of  $\log k_1$  versus  $H_0$  and  $\log k_1$  versus  $\log H^+$  are linear with unit slope indicating inverse unit dependence on the acidity.

### 3.2. Effect of solvent

In order to determine the effect of change of solvent composition on the oxidation rate, the reaction has been studied at different compositions of acetic acid (table 4).

It is observed that increased proportion of water in the reaction mixture increases the rate of the reaction. Such a dependence on solvent has been reported by Dyall and Pausacker (1958) in their work on oxidation of benzpinacol by PIA,

**Table 2.** Dependence of substrate on the oxidation of sugars by PIA in aqueous acetic acid medium.

PIA = 0.0005 M, Acetic acid = 10% (V/V), Temp. : 35° C

Substrate	$10^3$ [Substrate] M	$10^3 k_1$ min <sup>-1</sup>	$k_2$ lit. mol <sup>-1</sup> min <sup>-1</sup>
D-arabinose	2.131	2.34	10.99
	5.196	5.33	10.26
	9.860	9.73	10.07
	19.65	20.1	10.27
D-galactose	2.556	1.41	5.52
	5.024	2.75	5.47
	9.550	5.23	5.47
	20.27	11.8	5.82
D-xylose	2.498	1.04	4.17
	4.998	1.99	3.99
	9.993	3.67	3.67
	19.320	6.65	3.52
D-mannose	2.571	3.35	1.30
	4.998	7.24	1.45
	10.07	14.45	1.43
	20.03	29.89	1.49
D-glucose	2.499	0.22	0.85
	5.082	0.50	0.85
	10.050	0.81	0.81
	19.960	1.60	0.81

**Table 3.** Effect of perchloric acid on oxidation of sugars by PIA in aqueous acetic acid medium.Substrate = 0.005 M,  
PIA = 0.0005 M,Acetic acid = 10% (V/V),  
Temp. : 35° C.

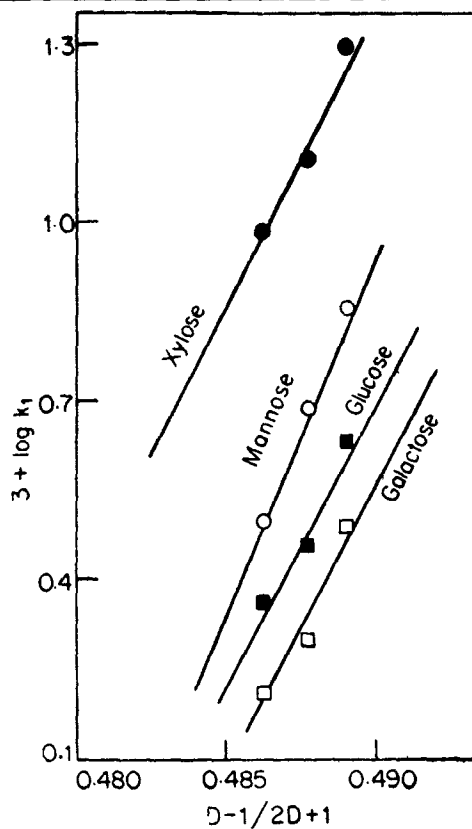
Sugars	$10^3 \times k_1$ min <sup>-1</sup> in HClO <sub>4</sub> at		
	0.05 M	0.1 M	0.2 M
D-arabinose	2.9	1.36	0.62
D-galactose	1.04	0.568	0.29
D-xylose	0.71	0.41	0.20
D-mannose	0.29	0.16	0.09
D-glucose	0.18	0.09	0.04

The observed dependence on solvent composition can be correlated with the dielectric constant of the medium. The reaction between sugar and PIA can be regarded as a dipole-dipole reaction. The plots of  $\log k_1$  versus  $D - 1/2D + 1$  (figure 2) are linear indicating applicability of Laidler and Amis approach for dipole-dipole reactions.

**Table 4.** Effect of solvent composition on oxidation of sugars by PIA.

Substrate = 0.005 M, PIA = 0.0005 M, Temp., = 35° C.

Sugars	$10^3 \times k_1 \text{ min}^{-1}$ in		
	10% aq. HOAc	20% aq. HOAc	30% aq. HOAc
D-arabinose	5.33	3.66	3.36
D-galactose	2.74	2.02	1.62
D-xylose	1.99	1.30	0.90
D-mannose	0.72	0.50	0.31
D-glucose	0.50	0.28	0.23



**Figure 2.**

### 3.3. Effect of sodium acetate

The effect of sodium acetate on the reaction has been studied following the kinetics of the reaction in the presence of different compositions of sodium acetate. It is observed that there is no change of reaction rate, indicating that addition of sodium acetate has no effect on the reaction.

### 3.4. Effect of temperature

The effect of temperature on the reaction has been determined by studying the reaction at three different temperatures, i.e., 30° C, 35° C and 40° C. The rate constants at different temperatures are given in table 5.

The Arrhenius activation parameters computed from these rate constants are given in table 6.

## 4. Mechanism

The kinetic data of the present study on oxidation of aldo-sugars by PIA point to a transition state involving one molecule of sugar and one molecule of PIA. The complex thus formed decomposes in a slow step to give the products. The sequence of the oxidation can be picturised as

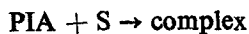


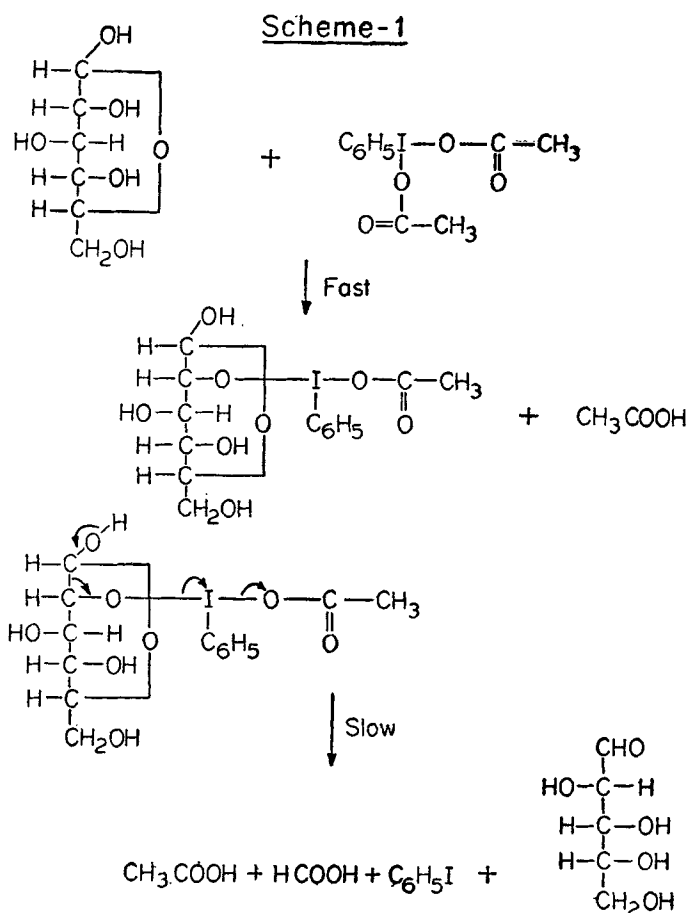
Table 5. Effect of temperature on oxidation of sugars by PIA in aqueous acetic acid medium.

Substrate = 0.005 M, PIA = 0.0005 M, Acetic acid = 10% (V/V).

Sugars	$10^3 \times k_1 \text{ min}^{-1}$ at		
	30° C	35° C	40° C
D-galactose	1.48	2.74	3.89
D-xylose	0.90	1.99	2.42

Table 6. Arrhenius parameters for the PIA oxidation of sugars.

Sugar	$E$ K.cal. mol <sup>-1</sup>	$\Delta H^\ddagger$ K.cal.mol <sup>-1</sup>	log A	$\Delta S^\ddagger$ Cal.mol <sup>-1</sup> degree <sup>-1</sup>
D-galactose	17.16	16.54	11.12	-9.69
D-xylose	15.29	14.67	9.66	-15.9



Such a complex formation between the oxidant and substrate has been reported by Mehrotra and Amis (1974) in the case of sugar oxidation by quinquivalent vanadium and tetravalent cerium in acid medium. The formation of PIA substrate complex has been earlier reported by Pausacker (1953) in the oxidation of 1 : 2 diols and Vaidyanathan and Venkatasubramanian (1973) in the oxidation of  $\alpha$ -hydroxy acids and amides by PIA. The reaction is considerably retarded by mineral acids; this observation also favours the formation of a complex between the substrate and PIA.

The non-formation of any polymers with acrylonitrile also clearly establishes the absence of free radical formation during PIA oxidation of sugars. This favours the mechanism postulated in scheme 1.

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