Pd(II) Inhibition during Hexacyanoferrate(III) Oxidation of Sugars: A Kinetic Study

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ABSTRACT

An inhibition effect of PdCl₂ on the rate of oxidation of sugars, by alkaline hexacyano-ferrate(III) has been observed. The order of reactions in hexacyanoferrate(III) and OH⁻ is zero and unity, respectively, while that in sugars decreases from unity at higher sugar concentration. The kinetic data and spectrophotometric evidence support the formation of $\{Pd^{II} - (sugar)\}$ and $\{Pd^{II} - sugar)_2\}$ complexes and their resistance to react with $Fe(CN)_6^{3-}$. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Like other platinum group metals Pd(II) has also been observed to act as a homogeneous catalyst during various redox reactions [1-5]. However during alkaline hexacyanoferrate(III) oxidation of sugars an inhibition effect of palladium(II) on the rate of oxidation has been observed. Therefore, in the present communication, we report the detailed kinetics of oxidation of sugars by alkaline hexacyanoferrate(III) in presence of palladium(II) chloride. A spectrophotometric evidence in support of Pd(II) complexes of sugars has been observed.

EXPERIMENTAL

The reagents employed were glucose, fructose, xylose, galactose, arabinose, maltose and lactose (all AR grade), palladous chloride (Ranbaxy AR grade). Potassium ferricyanide and sodium hydroxide were of BDH, AR grade. Other reagents used were of AR grade. All the solutions were prepared in doubly distilled water.

The stock solution of palladous chloride $(22.5 \times 10^{-3} \text{ mol dm}^{-3})$ was prepared by dissolving the sample in dilute HCl $(1.0 \times 10^{-2} \text{ mol dm}^{-3})$ and was stored in black coated bottles to prevent photochemical decomposition. The reaction vessels were also coated with black varnish to avoid any photochemical effect.

Appropriate quantities of the solutions of potassium ferricyanide, alkali, and palladous chloride were taken in 100 ml Jena glass vessel. The requisite amount of double distilled water was added, so that the total volume of reaction mixture would become 50 ml after adding the substrate solution. The reaction mixture was now placed in a water thermostat maintained at a desired temperature within the range $\pm 0.1^{\circ}$ C. The reaction mixture was allowed to attain the temperature of the bath. The reaction was started by adding the requisite amount of sugar solution, placed separately in the same bath, to the reaction

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vessel. The rates were measured by monitoring the absorbance due to hexacyanoferrate(III) as a function of time at 420 nm on a spectronic-20 spectrophotometer (MILTON ROY & COMP.). The absorbance due to hexacyanoferrate(II) and the catalyst was negligible at this wavelength. The concentration of hexacyanoferrate(III) was kept below 5.0×10^{-4} M in order to be within the Beer's Law limit. The rate constants were found to be reproducible to within $\pm 5\%$ in replicate runs.

Stoichiometry

The reaction mixtures containing a known excess of $[Fe(CN)_6^{3-}]$ over [sugar] were kept in the presence of alkali at 40°C for 72 h. Estimation of unreacted $[Fe(CN)_6^{3-}]$ showed that one mole of aldopentose or aldohexose consumes nearly two moles of ferricyanide. The results, in general, may be represented by the following stoichiometric equation,

CHO

$$H - C - OH + 2OH^{-} + 2Fe(CN)_{6}^{3-} \longrightarrow$$

$$R$$

$$2Fe(CN)_{6}^{4-} + H_{2}O + H - C - OH$$

$$R$$

$$R$$

The presence of corresponding aldonic acid as the product was detected by spot tests [6]. In the case of lactose and maltose more than two moles [4 to 6] of ferricyanide were consumed. The results are in agreement with the earlier studies [7-9].

However in the presence of palladium(II) a deviation in the above stoichiometric results (nearly a 1:1 stoichiometry between sugars and $Fe(CN)_6^{3-}$ was observed, which may be due to formation of palladium(II) complexes of sugars and their resistance to react with ferricyanide ion.

Pd(II) Complexes of Sugars

The ability of platinum group metals to form complexes with organic substrates coupled with the feasibility of sugars to form complexes with metal ions [10] is reported in literature. The spectrophotometric evidence for the formation of palladous chloride complexes of sugars in alkaline medium has been observed. In a set of experiments, the solutions were prepared by taking the constant amounts of palladium chloride $(1.125 \times 10^{-3} \text{ mol } \text{dm}^{-3})$ and NaOH $(0.25 \times 10^{-3} \text{ mol dm}^{-3})$ and varying amount of sugars. The absorbances of these solutions were obtained at 400 nm (λ_{max} of the complex). Figure 1, in which the results of Pd(II)-galactose complexes are reported, indicates the formation of more than one complexes between sugars and palladous chloride. The formation of 1:1 and 1:2 complexes of palladous chloride with aminoalcohols has been confirmed by Ardon plots [11] in our earlier studies [1,2].



Figure 1 A plot of (Absorbance) vs. [Galactose] keeping $[PdCl_2] = 2.25 \times 10^{-3} \text{ mol dm}^{-3}$ and $[NaOH] = 2.5 \times 10^4 \text{ mol dm}^{-3}$.

The same method has been used to confirm the complexes between palladium and sugars during the present investigations.

According to Ardon [11] for a general equilibrium

$$M + nS \rightleftharpoons MSn$$
 (a)

between two metal species M and MSn having different extinction coefficients, an equation has been derived as,

$$\frac{1}{\Delta A} = \frac{1}{\left[S\right]^{n}} \frac{1}{\Delta E^{[M]} \operatorname{Total}^{K}} + \frac{1}{\Delta E^{[M]} \operatorname{Total}}$$
(b)

where K is the equilibrium constant, ΔE is the difference in extinction coefficients between two metal species, $[M]_{Total}$ is the total concentration of metal species, and ΔA is the difference in absorbances of solution containing no S and one that contains a certain concentration of S which is represented by [S].

Equation (b) is valid provided that the amount of S tied up in the complex is negligible in comparison to the initial concentration of S or it is subtracted from the initial concentration of S. According to the above equation a plot of $1/\Delta A$ vs. 1/[S] should give a straight line with intercept in the case of a 1:1 complex formation between M and S. However, in the case of 1:2 M-S complex, a plot of $1/\Delta A$ vs. $1/[\text{S}]^2$ should yield a straight line. The intercept divided by the slope of this straight line gives the value of K.

In the present investigation the amount of sugars tied up in the complex was subtracted from the initial sugar concentration. Figures 2 and 3 were plotted assuming 1:1 complex and 1:2 complex, respectively. It can be seen that the 1:2 complex plot [Fig. 3] is a straight line while the 1:1 complex plot [Fig. 2] is a curved line. This confirms a 1:2 complex between palladium(II) and sugar at higher sugar concentration. Apparent formation constants (K) for 1:2 complex between Pd(II) and sugars obtained with the help of intercept and slopes were 1.6, 1.5, 2.8 and 2.0×10^5 in case of glucose, fructose, xylose, and galactose, respectively. Similar results have been obtained in the case of other sugars studied. These results suggest the formation of 1:1 and 1:2 complexes of Pd(II) with sugars at lower and higher concentrations of sugar, respectively.

KINETIC RESULTS

The reactions were studied at different initial concentrations of reactants. Absorbance vs. time plots were



Figure 2 Plots of $1/\Delta A$ vs. 1/[S] where S represents ([Sugar_{initial} - [Sugar]_{tied up in complex}). (A) Glucose: (B) Fructose; (C) Xylose; and (D) Galactose.

found to be good straight lines upto 85% of the reactions and therefore, the pseudo-zero-order rate constants in hexacyanoferrate(III) (k_{obs}) were evaluated from the slopes of these straight lines. The observed rate k_{obs} remained nearly the same at various $[Fe(CN)_{6}^{3-}]_{o}$ (Table I) which further confirmed an independent nature of rate with respect to hexacyanoferrate(III).

Plots of k_{obs} vs. [substrate] deviated from linearity at higher sugar concentrations [Fig. 4] suggesting that the order of reaction in substrate decreases at higher substrate concentration.

The effect of $[OH^-]$ on the oxidation rate was studied at fixed ionic strength maintained by NaClO₄ ($\mu = .03 \text{ mol dm}^{-3}$ for glucose, galactose, maltose, lactose, and arabinose, .05 mol dm⁻³ for fructose and .075 mol dm⁻³ for xylose). The amount of NaOH required to neutralize HCl in the catalyst was taken into account. The plots of k_{obs} vs. $[OH^-]$ [Fig. 5] were linear passing through the origin, suggesting first-order dependence of rate with respect to OH⁻. The effect of PdCl₂ lead to decrease in the observed rate constants. A plot of k_{obs} vs. $[PdCl_2]$ was linear with a negative slope and an lintercept [Fig. 6].

Addition of hexacyanoferrate(II) and sodium per chlorate upto $(5.0 \times 10^{-4} \text{ mol } \text{dm}^{-3} \text{ and } 0.2 \text{ mol } \text{dm}^{-3}$, respectively) had no effect on the reaction rate. The chloride ion effect on the rate of reaction (stud-



Figure 3 Plots of $1/\Delta A$ vs. $1/[S]^2$. Other conditions same as Figure 2.

ied by the successive addition of sodium chloride) also had negligible effect on the rate of oxidation in each case.

The rates were also studied at 35, 40, 45, and 50°C and the activation parameters calculated from Eyring plot are reported in Table II.

Successive addition of methanol into the reaction mixture retarded the observed rate constant (k_{obs}) e.g., for addition of Nil, 5, 10, 20, 30, and 40% (v/v) methanol the rate constants were, 5.0, 4.6, 4.0, 3.6, 3.3 and 3.0×10^{-7} mol dm⁻³ s⁻¹, respectively in the case of glucose when [Fe(CN)₆³⁻] = 5.0×10^{-4} mol dm⁻³, [PdCl₂] = 2.25×10^{-7} mol dm⁻³, [OH⁻] =

 3.0×10^{-2} mol dm⁻³, and at 35°C. The blank runs in the absence of glucose were also examined and no reaction was observed under the present experimental conditions.

DISCUSSION

The earlier studies [7,8] on the uncatalyzed oxidation of sugars by alkaline hexacyanoferrate(III) have shown a first-order dependence of the rate with respect to each sugar and OH^- and a zero-order dependence on the oxidant, $Fe(CN)_{6}^{5-}$, concentration. The

Table I Effect of [Fe(CN)³⁻] on Rate Constants at 35°C

1.	\sim	107	(-1

	$k_{\rm obs} imes 10^7 ({ m mol} { m dm}^{-3} { m s}^{-1})$						
$[Fe(CN)_{6}^{3-}] \times 10^{4}$ mol dm ⁻³	Glucose A	Fructose B	Xylose C	Galactose D	Maltose E	Lactose F	Arabinose G
2.5	2.08	1.58	1.66	1.75		3.33	1.45
3.0	2.08	1.58	-	1.70	~	_	-
3.5	2.08	1.58	1.66	1.79	4.85	3.50	1.45
4.0	2.08	1.50	1.66	1.79	4.80	3.55	1.45
5.0	1.66	1.58	1.70	1.83	4.80	3.50	1.45
	(3.08)	(2.85)	(2.60)	(2.90)	(5.60)	(4.50)	(1.70)
6.0	1.58	1.33	1.58	1.87	4.85	3.65	1.41

 $[PdCl_2] = 2.25 \times 10^{-7} \text{ mol dm}^{-3} \text{ and } [Sugar] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}.$

 $[OH^{-1}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ for A, D, E, F, and G, 2.0×10^{-3} for B and $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ for C.

In parentheses are the k_{obs} values obtained for different sugars with $[PdCl_2] = 0$.



Figure 4 Plots of k_{obs} vs. [sugar] at 35°C. [Fe(CN) $_{6}^{3-1}$] = 5.0 × 10⁻⁴ mol dm⁻³, [PdCl₂] = 2.25 × 10⁻⁷ mol dm⁻³, and [NaOH] = 1.0 × 10⁻² mol dm⁻³ for (A), (D), (E), (F), and (G) and = 2.0 × 10⁻³ mol dm⁻³ for (B) and 5.0 × 10⁻³ mol dm⁻³ for (C). (A) Glucose; (B) Fructose; (C) Xy-lose; (D) Galactose; (E) Maltose; (F) Lactose; and (G) Arabinose.



Figure 5 Plots of k_{obs} vs. [OH⁻] at 35°C. [Fe(CN)₆³⁻] = 5.0×10^{-4} mol dm⁻³, [sugar] = 5.0×10^{-3} mol dm⁻³, and [PdCl₂] = 2.25×10^{-7} mol dm⁻³. Other conditions same as in Figure 4.



Figure 6 Plots of k_{obs} vs. [PdCl₂] at 35°C. All other concentrations same as in Figures 4 and 5.

mechanism has been proposed via formation of an intermediate Enediol of sugars (in presence of OH^-) in a slow step and its subsequent reaction with ferricyanide to give the product (corresponding aldonic acid) in fast step. The formation of 1:1 and 1:2 complexes of Pd(II) chloride with sugars at lower and higher concentration of sugars, respectively, is also indicated by spectrophotometric results during the present investigations.

The decrease in the order of reaction in substrate at higher sugar concentration and retarding effect of palladium(II) on the rate of disappearance of ferricyanide clearly indicate that the palladium complexes of sugars are resistant to react with hexacyanoferrate(III). The same value of ΔG^{\neq} (Table II) suggests a common mechanism for the oxidation of these reducing sugars.

On the basis of the above facts the mechanism for the oxidation of sugars by hexacyanoferrate(III) in the presence of Pd(II) may be proposed as follows:

H
|
C - OH
|| + Fe(CN)₆³⁻
$$\xrightarrow{k_2}$$

C - OH
|
R (enediol)

 $Fe(CN)_6^{4-}$ + other reaction products (fast) (2)

$$S + Pd^{II} \xleftarrow{K_3} X$$
 (fast) (3)

$$X + S \xleftarrow{K_4} Y$$
 (fast) (4)

R represents — CHOHCHOHCH₂OH in the case of xylose and arabinose; — CHOH(CHOH)₂CH₂OH in the case of glucose, fructose, and galactose, and — CHOHCHCHOHCH₂OH in the case of maltose $\Box_{-}O_{-}R^{1}$

and lactose where R^1 is nonreducing glucose and galactose unit of maltose and lactose, respectively. (C_4 of R is attached to C_1 of cyclic structure of R^1).

In alkaline medium, $PdCl_2$ has been shown [5,12] to exist as $[Pd(OH)Cl_3]^{2-}$ and $[Pd(OH)_2Cl_2]^{2-}$ at lower and higher alkali concentrations, respectively. Under the present experimental conditions, $[Pd(OH)_2Cl_2]^{2-}$ may be considered as the reacting species of $PdCl_2$. Therefore, the formation of (X) and (Y) may be represented as,

Substrate	E _{act} (kJ mol ⁻¹)	$\frac{\Delta S^{\neq}}{(\mathbf{J}\mathbf{K}^{-1} \operatorname{mol}^{-1})}$	$\frac{\Delta H^{\neq}}{(\text{kJ mol}^{-1})}$	$\frac{\Delta G^{\neq}}{(\text{kJ mol}^{-1})}$
Glucose	32.6 ± 0.1	- 270.0 ± 1.0	29.5 ± 0.5	113.5 ± 1.0
Fructose	68.9 ± 0.1	-151.5 ± 1.0	66.5 ± 0.5	113.5 ± 1.0
Galactose	103.5 ± 0.1	-39.5 ± 0.5	100.5 ± 0.5	112.5 ± 1.0
Xylose	91.9 ± 0.1	-41.5 ± 0.5	83.5 ± 0.5	111.0 ± 1.0
Arabinose	95.7 ± 0.1	-65.5 ± 0.5	93.0 ± 0.5	113.0 ± 1.0
Lactose	80.4 ± 0.1	-107.5 ± 0.5	77.5 ± 0.5	111.5 ± 1.0
Maltose	88.0 ± 0.1	-80.5 ± 0.5	85.5 ± 0.5	111.0 ± 1.0

Table II Activation Parameters

$$H - C = O$$

$$H - C - OH + [Pd(OH)_{2}Cl_{2}]^{2} \longrightarrow$$

$$R$$
(S)
$$\begin{bmatrix} OH \\ H - C - O - Pd(OH)Cl_{2} \\ H - C - OH \\ R \end{bmatrix}^{2}$$
(X)
$$(S) + (X) \longrightarrow \begin{bmatrix} OH \\ H - C - O - Pd - O - C - H \\ H - C - OH \\ C - OH \\$$

Involvement of a neutral molecule in a rate determining step is supported by a negligible effect of ionic strength (addition of Sodium perchlorate) on the rate of reaction. Interaction of a neutral molecule with a negatively charged ion (OH⁻), i.e., step (1) is, further, indicated by the observed positive dielectric effect.

According to the above mechanism the rate of disappearance of $Fe(CN)_6^{3-}$ may be given as,

$$-\frac{d[\operatorname{Fe}(\operatorname{CN})_{6}^{3-}]}{dt} = \frac{k_{1}k_{2}[\operatorname{S}][\operatorname{OH}^{-}][\operatorname{Fe}(\operatorname{CN})_{6}^{3-}]}{k_{-1} + k_{2}[\operatorname{Fe}(\operatorname{CN})_{6}^{3-}]}$$
(5)

since step (2) is fast, $k_2[Fe(CN)^{3-}] \gg k_{-1}$ may be taken as a suitable approximation and therefore eq. (5) becomes,

$$\frac{d[Fe(CN)_{6}^{3-}]}{dt} = k_1[S][OH^-]$$
(6)

Now the total concentration of sugar, i.e., $[S]_T$ at any time may be given as,

$$[S]_{T} = [S] + [X] + [Y]$$
(7)

where

$$[X] = K_{2}[S] [Pd^{II}]$$
 from step (3)

and

$$[Y] = K_{3}K_{4}[S]^{2} [Pd^{II}]$$
 from step (3) and (4).

Thus finding the concentration of [S] in terms of total concentration of sugar, i.e., $[S]_T$ and substituting it in eq. (6), the rate law becomes,

$$\frac{d[\operatorname{Fe}(\operatorname{CN})_{6}^{3-}]}{dt} = \frac{k_{1}[S]_{T}[\operatorname{OH}^{-}]}{1 + K_{3}[\operatorname{Pd}^{II}]\{1 + K_{4}[S]\}}$$
(8)

Rate law (8) is in agreement with the experimental results, i.e., first-order and zero-order dependence of the rate with respect to OH^- and oxidant, respectively; retarding the effect of Pd^{II} on the rate of reaction [Fig. 6] and a decreasing of order of reaction in sugar at higher sugar concentrations [Fig. 4].

However at low sugar concentrations, when 1:2 complex does not exist, $K_4 = 0$ and therefore, the rate law (8) may be taken as,

$$-\frac{d[Fe(CN)_{6}^{3-}]}{dt} = \frac{k_{1}[S]_{T}[OH^{-}]}{1+K_{3}[Pd^{II}]}$$
(9)

The rate law (9) suggests a first-order dependence of the rate with respect to sugar at low sugar concentrations which has also been observed experimentally [Fig. 4].

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