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Pd(II) Inhibition of Glucose Oxidation by KMnO_4 in Alkaline Medium: A Kinetic Study

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ABSTRACT

The kinetics of PdCl_2 inhibition of glucose oxidation by Potassium Permanganate in alkaline medium was investigated at λ_{max} 525 nm. The oxidation reaction followed pseudo-first order kinetics: $[\text{glucose}]_0 > [\text{KMnO}_4]_0$ using a double beam Schmadzu-1800 UV/Visible spectrophotometer. A decrease in absorbance values of reaction mixtures with time were obtained and evaluated. The results showed zero order dependence to $[\text{KMnO}_4]$, first order dependence each to $[\text{glucose}]$ and $[\text{OH}^-]$, inverse unity order to $[\text{Pd}^{\text{II}}]$ and no ionic strength effect was observed. Activated parameters for ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger were $29.78 \text{ kJ mol}^{-1}$, $-0.21 \text{ kJ K}^{-1} \text{ mol}^{-1}$ and $92.36 \text{ kJ mol}^{-1}$, respectively. The Ardon equation revealed the formation of 1:1 and 1:2 Pd(II)-glucose complexes at low and high concentrations of glucose, respectively.

KEYWORDS: Palladium(II) Chloride, glucose, potassium permanganate, inhibition.

1. INTRODUCTION

Catalytic effects of metals on the oxidation of sugars have not received much attention. However, palladium (II) inhibition of sugar oxidation in hexacyanoferrate (III) has been reported.¹ Ru (III)-catalyzed oxidation of sugars in acidic and alkaline media was also investigated.² Furthermore, Ir (III) catalysis of sugar oxidation has received great attention.^{3,4} The oxidation of some aldoses and amino sugars by potassium bromate in hydrochloric acid medium has been reported to proceed via the intermediate formation of bromate esters followed by the breaking down of the esters to yield products, and hydrogen ions catalyzed the reaction.⁵ Oxidation of glucose and Arabinose mixtures over $\text{Au}/\text{Al}_2\text{O}_3$ has been reported.⁶ Mechanisms of sugar oxidation in alkaline and acidic media has received great attention.^{7,8,9} However, the mechanism of the catalytic effect of transition metals on sugar oxidation needs serious appraisal which prompted this research. This research seek to investigate the mechanism of Pd(II) inhibition of glucose oxidation by Potassium Permanganate in alkaline medium.

2. MATERIALS AND METHODS

2.1. Materials

D-glucose (reductant, Merck, Germany) and KMnO_4 (oxidant, Merck, India) were used. All other reagents were of analytical grade. Distilled water was used as solvent.

2.2. Kinetic runs

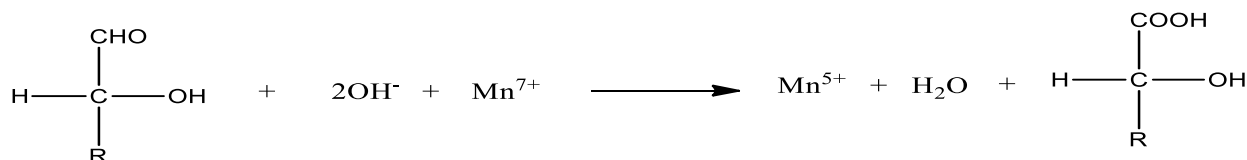
Each kinetic run was performed under pseudo-first-order kinetics using \geq tenfold excess $[\text{glucose}]$ over $[\text{KMnO}_4]$. A mixture containing the requisite amount of all the reactants (except potassium permanganate) was thermally equilibrated at the desired temperature and rapidly added to a known amount of the oxidant solution (pre-equilibrated at the same temperature). Decrease in absorbance of manganese (VII) with time at 525 nm using a double-beam Schmadzu-1800 UV/visible spectrophotometer equipped with a thermo-regulated cell compartment and spectral data processing facilities was monitored. The pseudo-first-order constants (k_{obs}) were obtained from the slope of log (absorbance) versus time plots.

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2.3. Stoichiometry

The reaction mixtures of known excesses of [glucose] over [KMnO₄] were kept in the presence of sodium hydroxide at 298 K for 3 days. Estimated unreacted [KMnO₄] revealed that one mole of glucose consumed one mole of potassium permanganate.



2.4. Pd (II) Complexes of Sugar

In this kinetic study, the absorbance of solutions at fixed [Pd(II)] 1.20 x 10⁻³ M and [NaOH] 1 x 10⁻³ M and varying 5 x 10⁻⁴ M ≤ [glucose] ≤ 1.30 X 10⁻² M were taken at 400 nm (λ_{max} of the complex) and change in absorbance with [glucose] is shown in Figure 1.

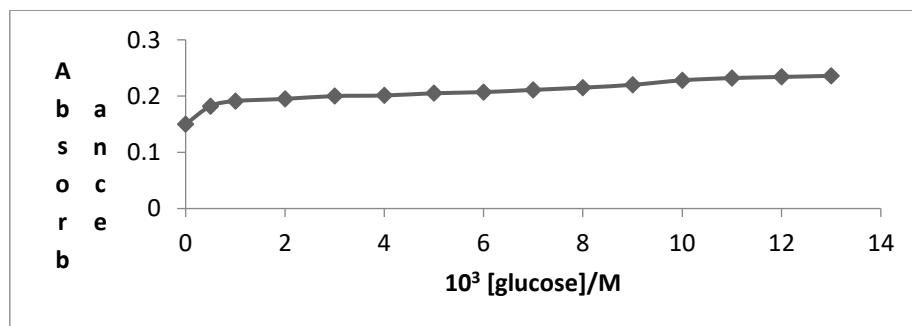


Figure 1. A plot of Absorbance vs [glucose]

From general equilibrium equation¹⁰



$$\frac{1}{\Delta A} = \frac{1}{[\text{S}]^n} \frac{1}{\Delta E^{[\text{M}]_{\text{Total}} K} + \frac{1}{\Delta E^{[\text{M}]_{\text{Total}}}} \quad (2)$$

Herein, the amount of glucose tied up in the complex is negligible in comparison to the initial concentration of S. Therefore, a plot of $\frac{1}{\Delta A}$ Vs $\frac{1}{[\text{S}]}$ gave a straight line with intercept suggesting 1:1 complex formation between M and S at low concentrations of glucose.

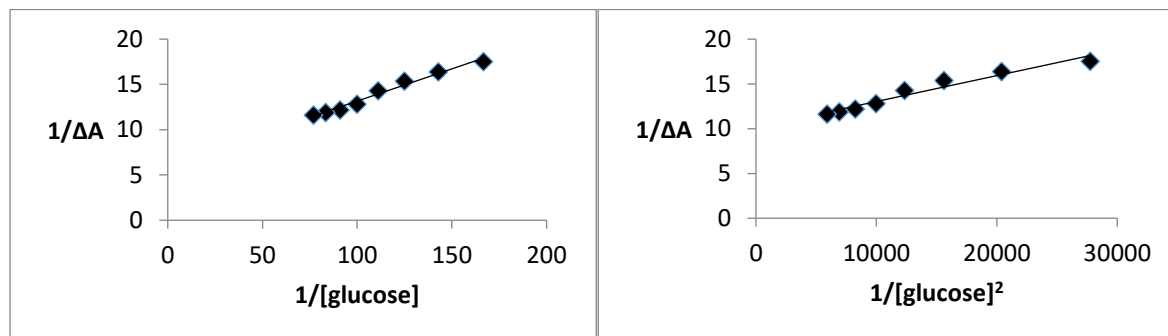


Figure 2. Plot of $\frac{1}{\Delta A}$ Vs $\frac{1}{[\text{S}]}$

Figure 3. Plot of $\frac{1}{\Delta A}$ vs $\frac{1}{[\text{S}]^2}$

Furthermore, a plot of $\frac{1}{\Delta A}$ vs $\frac{1}{[S]^2}$ gave a straight line with an intercept, suggesting a 1:2 metal-sugar complex formation at higher glucose concentration and the apparent equilibrium constant (K) obtained from the intercept and slope was 3.50.

3. RESULTS AND DISCUSSION

3.1. Kinetic Results

The kinetic results showed relatively constant k_{obs} with $[KMnO_4]$, indicating no dependence on the oxidant concentrations. However, the observed rate constant increased with increase in $[glucose]$ as shown in Figure 4.

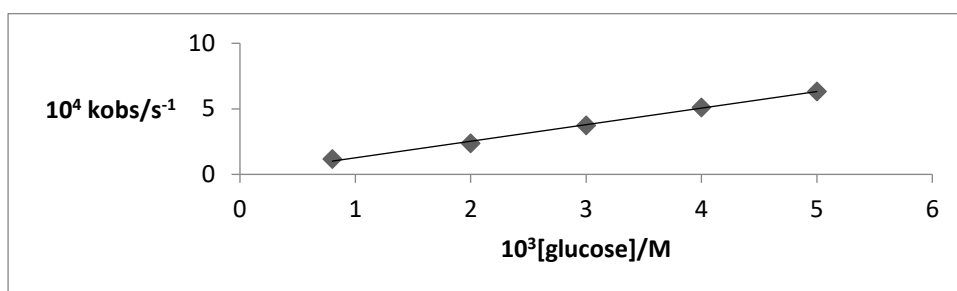


Figure 4. Plot of k_{obs} versus $[glucose]$

The order of reaction with respect to $[glucose]$ obtained from $\log k_{obs}$ versus $\log [glucose]$ gave one, suggesting a first order kinetics with respect to $[glucose]$. There was an increase in pseudo first order rate constant with increase in $[OH^-]$ as shown in figure 5, and the order with respect to $[OH^-]$ was obtained to be one.

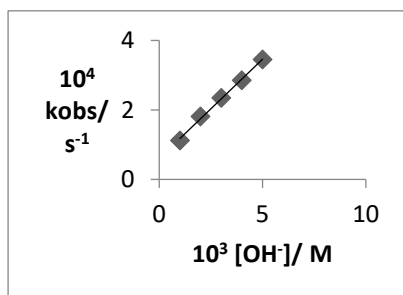


Figure 5. Plot of k_{obs} versus $[OH^-]$

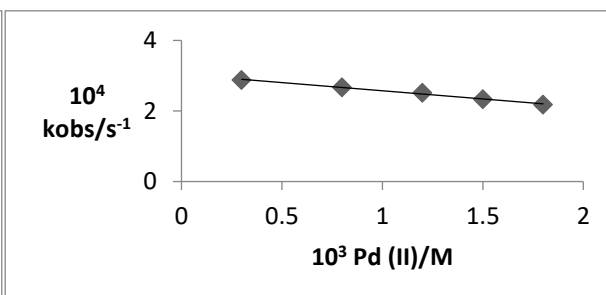


Figure 6. Plot of k_{obs} versus $[Pd(II)]$

A plot of k_{obs} versus $[Pd(II)]$ was linear with negative slope with an intercept as shown in figure 6.

Activation parameters were obtained from Eyring's plot from temperature dependent study as shown in Table 1.

$$\ln\left(\frac{k}{T}\right) = \frac{-\Delta H^\ddagger}{RT} + \ln\left(\frac{K'}{h}\right) + \left(\frac{\Delta S^\ddagger}{R}\right)$$

$$\text{where } \ln\left(\frac{K'}{h}\right) = 23.76$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

k = rate constant; T = Temperature; ΔH^\ddagger = Enthalpy of Activation; ΔS^\ddagger = Entropy of Activation; ΔG^\ddagger = Free Gibb's Energy of Activation; R = Molar gas constant; k' = Boltzmann constant; h = Planck's constant.

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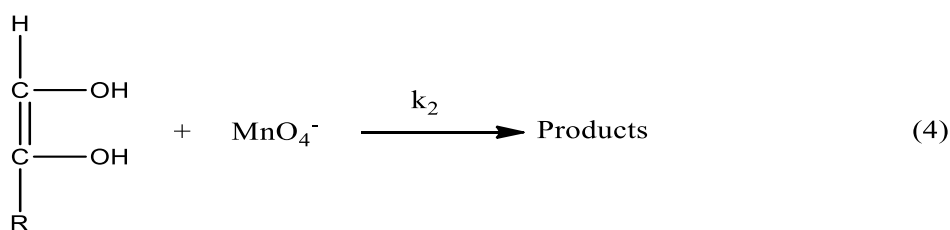
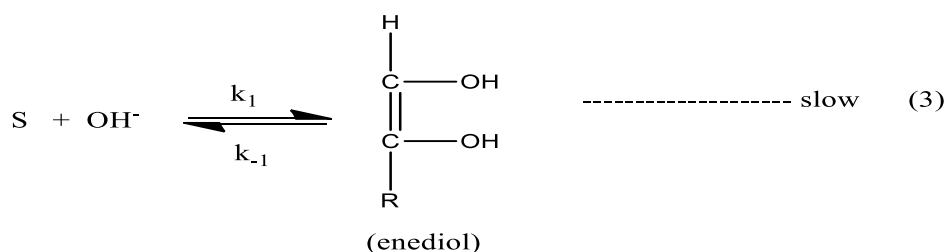
Table 1. Activation parameters

Substrate	ΔH^\ddagger /kJ mol ⁻¹	$-\Delta S^\ddagger$ /kJ K ⁻¹ mol ⁻¹	ΔG^\ddagger /kJ mol ⁻¹
Glucose	29.78	0.21	92.36

[KMnO₄] 3 x 10⁻⁵ M, [glucose] 3 x 10⁻³ M, [OH⁻] 1 x 10⁻³ M, [Pd(II)] 1.20 x 10⁻³ M, μ 0.05 M

3.2. Discussion

The un-catalyzed oxidation of sugars by alkaline permanganate showed first order dependent each to [OH⁻] and [glucose] and zero order with respect to [KMnO₄].⁸ Furthermore, this study revealed no change in *k*_{obs} with increase in ionic strength of the reaction mixtures. Consequently, a plot of log *k*_{obs} versus √*I* gave straight line with Z_AZ_B equals to zero, suggesting that ionic strength did not affect the oxidation reaction, thereby revealing the presence of a neutral molecule in the rate determining step. The mechanism involved the formation of an intermediate enediol of sugars in alkaline medium which subsequently react with potassium permanganate to give the product and palladium(II) chloride formed complexes with glucose in the course of the reaction.



(enediol)



Based on the kinetic results obtained in this research, the mechanism reported herein followed that which was earlier reported.¹ The complexes are represented as (X) and (Y). In this study, the formation of 1:1 and 1:2 complexes of Pd (II) chloride with glucose at lower and higher concentrations of glucose respectively were confirmed. The decrease in the pseudo first order rate constants with increase in Pd (II) on the oxidation reaction shows that palladium complex resisted the oxidation reaction.

The mechanism of inhibition was proposed as follows:

$$\frac{-d[MnO_4^-]}{dt} = \frac{k_1 k_2 [S][OH^-][MnO_4^-]}{k_{-1} + k_2 [MnO_4^-]} \quad (7)$$

$$k_2 [MnO_4^-] \gg k_{-1}$$



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$$\frac{-d[\text{MnO}_4^-]}{dt} = k_1[\text{S}][\text{OH}^-] \quad (8)$$

$$[\text{S}]_T = [\text{S}] + [\text{X}] + [\text{Y}] \quad (9)$$

$$[\text{X}] = K_3[\text{S}][\text{Pd}^{II}]$$

$$[\text{Y}] = K_3K_4[\text{S}]^2[\text{Pd}^{II}]$$

$$[\text{S}]_T = [\text{S}] + K_4[\text{S}][\text{Pd}^{II}] + K_3K_4[\text{S}]^2[\text{Pd}^{II}]$$

$$[\text{S}]_T = [\text{S}](1 + K_3[\text{Pd}^{II}] + K_3K_4[\text{S}][\text{Pd}^{II}])$$

$$[\text{S}] = \frac{[\text{S}]_T}{1 + K_3[\text{Pd}^{II}] + K_3K_4[\text{S}][\text{Pd}^{II}]}$$

Substituting in equation (8)

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{k_1[\text{S}]_T[\text{OH}^-]}{1 + K_3[\text{Pd}^{II}] + K_3K_4[\text{S}][\text{Pd}^{II}]} \quad (10)$$

Rate law (10) reveals first order and zero order dependence of the rate with respect to $[\text{OH}^-]$ and $[\text{KMnO}_4]$ respectively which is in consonance with the experimental results. It also showed the inhibition effect of $\text{Pd}(\text{II})$ on the oxidation reaction. Furthermore, at low [glucose], when 1:1 complex is predominant $K_4 = 0$. Therefore, the rate law can be expressed as:

$$\frac{-d[\text{MnO}_4^-]}{dt} = \frac{K_1[\text{S}]_T[\text{OH}^-]}{1 + K_3[\text{Pd}^{II}]} \quad (11)$$

4. CONCLUSION

$\text{Pd}(\text{II})$ inhibited the oxidation of glucose by potassium permanganate in alkaline medium. 1:1 and 1:2 $\text{Pd}(\text{II})$ -glucose complexes were obtained via Ardon plots at lower and higher concentrations of glucose, respectively. The reaction was zero order to $[\text{KMnO}_4]$, first order each to [glucose] and $[\text{OH}^-]$ and inverse first order to $[\text{Pd}(\text{II})]$ and an independent ionic strength effect was observed.

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