

Kinetics and Mechanism of Cu (II) Inhibition Towards Oxidation of Simple Sugars by Hexacyanoferrate (III) Ion in Alkaline Buffer Solution.

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ABSTRACT

The kinetics and mechanism of copper (II) inhibition of oxidation of maltose and xylose by hexacyanoferrate (III) has been studied in alkaline medium. The rate of reaction was monitored spectrophotometrically under a wide range of experimental conditions. The reaction was found to be zero order in oxidant and first order in sugar concentration. But the order of reaction in sugar decreased from one to zero at higher sugar concentration. The rate of reaction decreased with increase in copper (II) concentration. The rate of reaction shows no significant dependence on the ionic strength of the medium. Base on the kinetic data obtained, the mechanism of this reaction has been proposed. The rate of reaction was found to be proportional to $\{k/(1+K_3[Cu^{2+}])\}$. Arrhenius activation energy and other thermodynamic activation parameters were evaluated and reported.

(Keywords: Cu (II), copper inhibition of oxidation, maltose, xylose, hexacyanoferrate (III), rate reaction)

INTRODUCTION

The biological, biochemical, and economic importance of carbohydrates, and especially monosaccharides and disaccharides, have been largely responsible for the great interest in the study of their bio- and physic-chemical properties and reactivity (1-4). These studies have included structure elucidation, chemical degradation and oxidation reactions.

Various transition metal ions, inorganic acids, complex ions as well as hydrogen peroxides and enzymes have been employed in a variety of oxidation studies in both acidic and alkaline media (5). Oxidation of sugars occurs under different conditions of pH, temperature, and ionic

strength giving products that depend on the reaction condition used.

The kinetics and mechanism of oxidation of monosaccharides and disaccharides have been studied in both acidic and alkaline media. The results show that the mechanism may depend on the nature of the oxidant and the substrate. Copper II ion has been widely used as a catalyst in both acidic and basic media. Copper II ion has been used to catalyze the oxidation of ascorbic acid by molecular oxygen (6). Pd II inhibition during the oxidation of some reducing sugars has been reported (7). In the present work, we intend to study the kinetics and mechanism of Cu (II) inhibition towards the oxidation of maltose and xylose in alkaline buffer solution.

EXPERIMENTAL

Chemical Reagents: The reagents were of analytical grade and were used without further purification. The stock solution of both oxidant and substrate were freshly prepared using distilled water.

Spectral Measurement: The absorption spectra of different concentrations of the hexacyanoferrate (III) ion were measured in the visible region between 340 and 460 nm; and kinetic data collected at 420 nm, the wavelength corresponding to maximum absorbance.

Kinetic Measurements: Each reactant solution was placed in a thermostated water bath for about 45 minutes to attain a temperature of 40°C. Appropriate quantities of the reagent solutions were mixed in a 250ml conical flask already placed in the thermostated water bath. The reaction rate was followed by measuring the decrease in absorbance at 420 nm, the reaction was completed when the hexacyanoferrate (III)

ion–sugar solution turned from yellow to colorless.

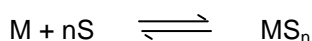
Iodine Water Test: When aqueous solution of iodine was added to various reaction mixtures, large quantities of iodine solution were consumed. This provides evidence for the formation of enediol intermediate.

RESULTS AND DISCUSSION

Effect of Substrate Concentration

The observed rate constants k_{obs} were determined at different initial concentrations of the sugars while maintaining constant other variables such as the concentration of the oxidant, copper (II) and sodium nitrate. The pH and temperature were also kept constant at 10.3 and 40°C respectively. The results presented in Table 1 show that the rate of oxidation increased as the concentration of sugar is increased. But with a careful look at Figure 1a, it can be shown that the order of reaction in sugar concentration decreased from unity to zero. This is due to the formation of complex between sugar and copper(II). This copper-sugar complex inhibits the disappearance of hexacyanoferrate (III) ion. The complex formation is confirmed by Ardon plot (7).

According to Ardon, for a general equilibrium:



between two metal species M and MS_n having different extinction coefficient, an equation has been derived as:

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

In these equations, K is the equilibrium constant, ΔE is the difference in extinction coefficient between the two metal species, $[M]_{Total}$ is the total concentration of the species, S is sugar, MS_n is metal-sugar complex and ΔA is the difference in absorbance of solution containing no sugar and one that contains certain concentration of sugar. According to the above equation, a plot of $1/\Delta A$ versus $1/[S]$ should give a straight line graph with an intercept in the case of a 1:1 complex formation between a metal M and substrate S. However, in the case of 1:2 M-S complex, a plot of $1/\Delta A$ versus $1/[S]^2$ should give a straight line graph. In this present work a plot of $1/\Delta A$ versus

$1/[S]^2$ give a straight line graph (Figure1b). This equation has been used by Pankai et al. to confirm the complex formation between palladium (II) and some reducing sugars. The result obtained in this present research agrees with their result (7).

Table 1: Variation of Rate Constant with the Sugar Concentration.

$10^{-2}[\text{sugar}] \text{ M}$	MALTOSE	XYLOSE
	$10^{-2}k_{obs} \text{ Ms}^{-1}$	$10^{-2}k_{obs} \text{ Ms}^{-1}$
1	0.89	0.58
2	1.89	1.17
3	2.44	1.72
4	2.53	2.20
5	2.84	2.34
6	2.49	2.56

$T=40^\circ\text{C}$, $[\text{sugar}]=2 \times 10^{-2} \text{ M}$, $\text{pH} = 10,3$, $[\text{Cu}^{2+}] = 8.0 \times 10^{-5}$, $[\text{NaNO}_3]=0.1 \text{ M}$

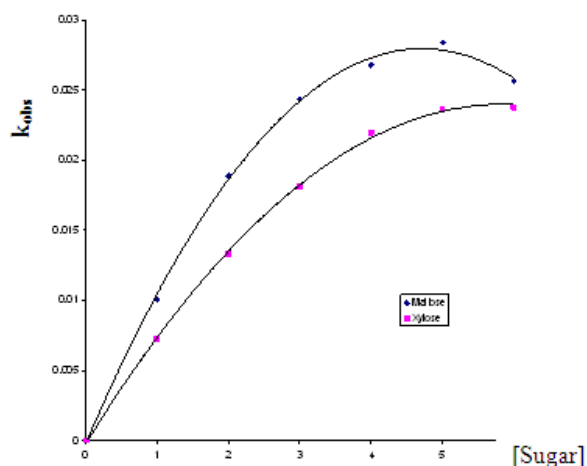


Figure 1a: k_{obs} versus Sugar Concentration.

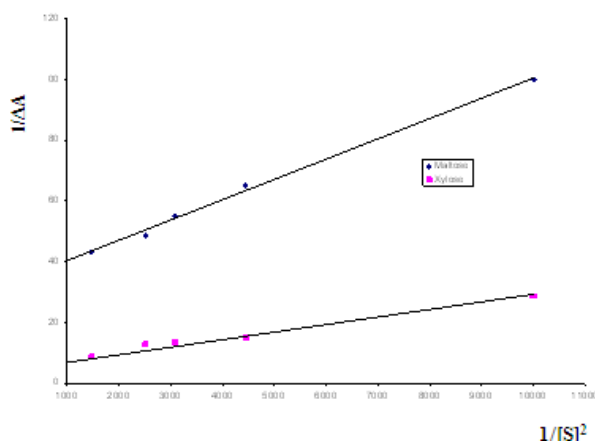


Figure 1b: Ardon Plot, $1/\Delta A$ versus $1/[S]^2$.

Effect of Hexacyanoferrate III Ion Concentration

The observed rate constants were measured at different initial concentration of hexacyanoferrate III ions but at constant concentration of sugar and copper (II). The reaction was carried out at constant temperature of 40°C, pH of 10.3. The ionic strength of the medium was also kept constant. The values of the k_{obs} were presented Table 2. The results show that the rate of oxidation of the sugars is independent of the initial concentration of the hexacyanoferrate III ion concentration. This result is in line with the literature reports (8-12).

Table 2: Variation of Rate Constant with Concentration of Oxidant.

$10^{-4}[\text{Fe}(\text{CN})_6^{3-}] \text{ M}$	MALTOSE	XYLOSE
	$10^{-2}k_{obs} \text{ Ms}^{-1}$	$10^{-2}k_{obs}, \text{Ms}^{-1}$
1	2.16	0.77
2	2.28	0.77
3	2.24	0.79
4	2.23	0.72
5	2.26	0.79
6	2.22	0.78

T=40°C, [sugar]=2X10⁻² M, pH = 10,3, [Cu²⁺]= 8.0X10⁻⁵, [NaNO₃]=0.1M

Effect of Ionic Strength

The reactions were studied at several initial concentrations of sodium nitrate but at constant concentration of sugar, hexacyanoferrate (III) ion, copper (II) and at constant temperature of 40°C and pH of 10.3. The results are presented in Table 3. According to the results, there is no significant difference in the value of the observed rate constant. This shows that the rate of oxidation did not depend on the ionic strength of the medium.

This result is in agreement with the work done by Venkata and Jaya in which they found that the rate of oxidation of some reducing sugars did not change with increasing or decreasing in ionic strength (13). This result shows that oxidation of maltose and xylose involves reaction between an ion and a neutral molecule at the rate-determining step (14).

Table 3: Variation of Rate Constant with Ionic Strength.

$10^{-1}[\text{NaNO}_3] \text{ M}$	MALTOSE	XYLOSE
	$10^{-2}k_{obs} \text{ Ms}^{-1}$	$10^{-2}k_{obs}, \text{Ms}^{-1}$
1	1.22	0.83
2	1.05	0.93
3	1.28	0.81
4	1.05	0.84
5	1.05	0.82
6	1.06	0.87

T=40°C, [Fe(CN)₆³⁻] = 2 X 10⁻⁴M, pH= 10.3
[Sugar]= 2X10⁻²M, [Cu²⁺]= 8.0X10⁻⁵M

Effect of Concentration of Copper (II) ion Concentration

The effect of different initial concentrations of copper (II) on the observed rate constant was investigated at constant concentration of sugar, oxidant, sodium nitrate, and constant temperature of 40°C and pH of 10.3. The results in Table 4 and Figure 2 show that the rates of oxidation of these sugars decreased with increase in the concentration of copper (II) ion in agreement with the work done by Pankai et al. where they discovered that the rate of reaction was inhibited by palladium (II) (7).

Table 4: Variation of Rate Constant with Copper (II) Ion Concentration.

$10^{-1}[\text{Cu}^{2+}] \text{ M}$	MALTOSE	XYLOSE
	$10^{-2}k_{obs} \text{ Ms}^{-1}$	$10^{-2}k_{obs}, \text{Ms}^{-1}$
1	1.29	1.00
2	1.22	0.85
3	1.18	0.76
4	0.95	0.69
5	0.92	0.64
6	0.84	0.60

T=40°C, [Fe(CN)₆³⁻] =2X10⁻⁴ M, [Sugar] = 1 X 10⁻²M, pH=10.3, [NaNO₃] = 0.1M

Effect of Temperature

Oxidation of the reducing sugar was carried out at different temperatures from 40 to 65°C. The Arrhenius parameters were evaluated from the natural logarithmic plot of the observed rate constant against the reciprocal of the temperature in degrees.

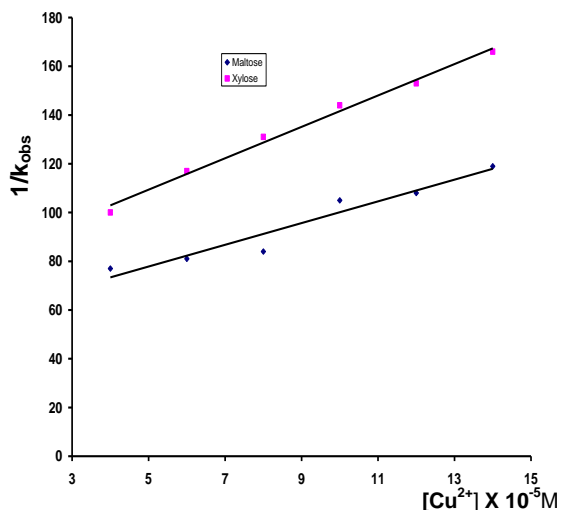


Figure 2: $1/k_{obs}$ versus Copper (II) Concentration.

The values of the Arrhenius activation energy E_a , for the oxidation of maltose and xylose obtained from the slope of the linear plot are $92.28 \text{ kJ mol}^{-1}$ and $106.86 \text{ kJ mol}^{-1}$ for maltose and xylose respectively (Figure 3). Other thermodynamic activation parameters were also calculated and recorded in Table 5. The positive values of entropy of activation for the reactions were due to the increase in entropy caused by desolvation of the activated complex than the reactants. This means that the activated complex formed by $\text{Fe}(\text{CN})_6^{3-}$ and enediol is less polar which brings about increase in translational freedom. (15), this result agrees with the result of Kalyan and Basu (16).

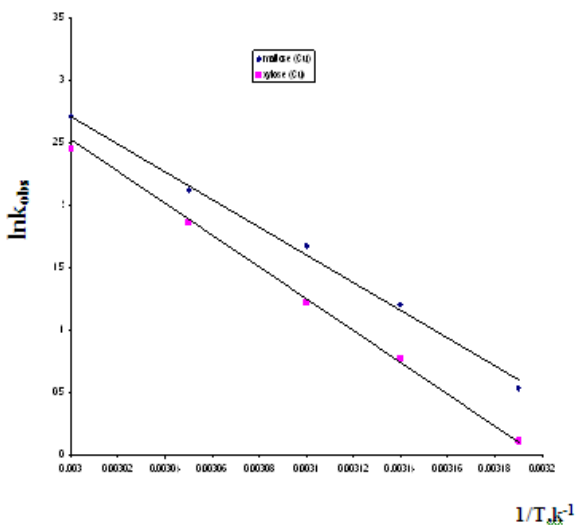


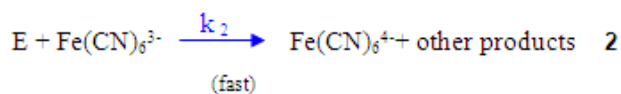
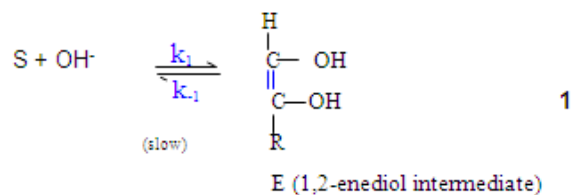
Figure 3: Arrhenius plot, $\ln k_{obs}$ versus $1/T$.

Table 5: Activation Energy and Thermodynamic Activation Parameters.

Parameter	Maltose	Xylose
$E_a \text{ KJmol}^{-1}$	92.28	106.17
$\Delta H^\ddagger \text{ KJ mol}^{-1}$	89.67	100.86
$\Delta S^\ddagger \text{ JK}^{-1} \text{ mol}^{-1}$	12.43	52.20
$\Delta G^\ddagger \text{ KJmol}^{-1}$	85.78	84.53

Reaction Mechanism and Rate Equation

In the oxidation of reducing sugars by copper (II) and iodine ion (8, 17), it has been shown that the reactions occur via the formation of an enediol intermediate and that the rate of enolisation is the same as the rate of oxidation. The similar values of free energy change (ΔG^\ddagger) obtained from this work indicate a common mechanism for the oxidation of these reducing sugars (7, 17). Also, the independency of rate of oxidation on the initial concentration of sodium nitrate for the reactions provides more evidence for common mechanism of oxidation for these sugars. The positive test with bromine water and spectra analysis provides additional evidence for the formation of enediol intermediate. Based on the above facts, the mechanism for the oxidation of sugar by hexacyanoferrate (III) ion may be proposed as follows:



According to the above mechanism, the rate of disappearance of hexacyanoferrate (III) is given by

$$\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{k_2 k_1 [\text{S}] [\text{OH}^-] [\text{Fe}(\text{CN})_6^{3-}]}{k_{-1} + k_2 [\text{Fe}(\text{CN})_6^{3-}]} \quad 3$$

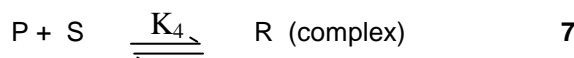
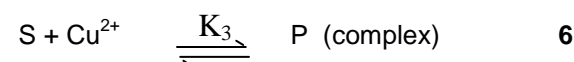
$$\frac{1}{k_{obs}} = \frac{k_{-1}}{k_2 k_1 [\text{S}] [\text{OH}^-] [\text{Fe}(\text{CN})_6^{3-}]} + \frac{1}{k_1 [\text{S}] [\text{OH}^-]} \quad 4$$

Equation 4 predicts that the plots of the reciprocal of rate constant versus reciprocal of [Sugar] at fixed [OH⁻] and [Fe(CN)₆³⁻] or of [Fe(CN)₆³⁻] at fixed [OH⁻] and [Sugar] or of [OH⁻] at fixed [Sugar] and [Fe(CN)₆³⁻] should be a straight line with a positive intercept at Y axis; such plots were actually observed. The values of k₁ were calculated to be 0.0233 Ms⁻¹ and 0.0185 Ms⁻¹ while the values of k₁/k₂ were calculated to be 9.4 X 10⁻⁶ and 9.2 X 10⁻⁶ for maltose and xylose, respectively.

Since step 2 is very fast (k₂ >> k₁), hence k₁ can be neglected. Then Equation 6 becomes:

$$\frac{d [\text{Fe(CN)}_6^{3-}]}{dt} = k_1 [\text{S}] [\text{OH}^-] \quad 5$$

From the experimental data (Tables 1 and 4) and Ardon plot (Figure 1b), it has been shown that there is formation of a complex between copper and sugar.



The total concentration of the sugar [S]_T at any time will be:

$$[\text{S}]_T = [\text{S}] + [\text{P}] + [\text{R}] \quad 8$$

From equations 6 and 7:

$$[\text{P}] = K_3 [\text{S}] [\text{Cu}^{2+}] \quad 9$$

$$[\text{R}] = K_4 [\text{S}]^2 [\text{Cu}^{2+}] \quad 10$$

Substituting Equation 9 and 10 into Equation 8:

$$[\text{S}] = \frac{[\text{S}]_T}{1 + K_3 [\text{Cu}^{2+}] + K_4 K_3 [\text{S}] [\text{Cu}^{2+}]} \quad 11$$

Substitute Equation 11 into Equation 5:

$$\frac{d [\text{Fe(CN)}_6^{3-}]}{dt} = \frac{k_1 [\text{S}]_T [\text{OH}^-]}{1 + K_3 [\text{Cu}^{2+}] + K_4 K_3 [\text{S}] [\text{Cu}^{2+}]} \quad 12$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_1 [\text{S}]_T [\text{OH}^-]} + \frac{K_3 [\text{Cu}^{2+}]}{k_1 [\text{S}]_T [\text{OH}^-]} + \frac{K_4 K_3 [\text{S}] [\text{Cu}^{2+}]}{k_1 [\text{S}]_T [\text{OH}^-]} \quad 13$$

Equation 13 predicts that the plots of the reciprocal of rate constant versus reciprocal of [Sugar] at fixed [OH⁻] and [Cu²⁺] or of [OH⁻] at fixed [Sugar] and [Cu²⁺] and a plot of reciprocal of rate constant versus [Cu²⁺] at fixed [Sugar] and [OH⁻] should be a straight line with a positive intercept at Y axis. Such plots were actually observed (figure 4). The value of K₃ and K₄ were calculated to be 0.293 and 35.92 for maltose; and 0.462 and 65.55 for xylose, respectively.

Equation 12 agrees with the experimental results; zero order with respect to oxidant concentration, inhibiting effect of copper (II) and the decrease in order of reaction in sugar at higher concentration (Figure 1a).

However, at low sugar concentrations K₄=0 and therefore, the rate law (12) may be written as:

$$\frac{d [\text{Fe(CN)}_6^{3-}]}{dt} = \frac{k_1 [\text{S}]_T [\text{OH}^-]}{1 + K_3 [\text{Cu}^{2+}]} \quad 14$$

Thus, Equation 14 also suggests a first order dependence of rate with respect to sugar at low sugar concentration and the decrease in rate with increase in copper (II) ion concentration.

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