

A Comparative Study of Kinetics and Mechanism of Oxidation of Maltose and Lactose by Copper (II) Ion and Hexacyanoferrate (III) Ion in Alkaline Solution.

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ABSTRACT

The comparative kinetics and mechanism of oxidation of maltose and lactose by copper (II) and hexacyanoferrate (III) ion has been studied in alkaline medium. The rate of reaction was monitored spectrophotometrically under a wide range of experimental conditions. For both oxidants, the reaction was found to be zero and first order in oxidant and sugar concentration respectively. The rate of reaction shows no significant dependence on the ionic strength of the medium. The values of ΔG^\ddagger revealed that both oxidants follow the same mechanistic pathway. The mechanism involves the formation of enediol intermediate. From rate equation, the rate of reaction was found to be proportional to $k[\text{sugar}][\text{OH}^-]$, where k is the rate constants for the reaction. Arrhenius activation energy and other thermodynamic parameters were also evaluated and reported.

(Keywords: kinetics, oxidation of sugars, mechanism, rate equation, activation energy, thermodynamics)

INTRODUCTION

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 acid and alkaline media [1-2]. The results show that the mechanism may depend on the nature of the oxidant and the substrate. In some cases, the mechanism may involve the formation of an intermediate complex [3]; in others the formation of free radicals [4]; while still in others the formation of a transition state [5-6].

The kinetics and mechanism of oxidation of reducing sugars by Cu (II) ion have been studied by different worker [7]. The rate of oxidation was found to be independent on the Cu (II) ion concentration. Also, a study of entropy activation in the oxidation of some sugars by Cu (II) in the presence of ammonium hydroxide has carried out by Singh. He observed that the rate of oxidation is zero order in Cu (II) ion and first order in substrate and hydroxide ion concentration [8]. In the vein, the kinetics and mechanism of oxidation some reducing sugar by hexacyanoferrate (III) ion have been studied and reported [9-10]. But the comparative study of kinetics and mechanism of oxidation of reducing sugars by both hexacyanoferrate (III) ion and copper (II) ion has not been reported.

EXPERIMENTAL

Chemical Reagents

The reagents were of analytical grade and were used without any further purification. The sample of maltose and lactose used were E. Merck grade. The sample of sodium nitrate, copper sulphate, potassium hexacyanoferrate (III) and sodium hydroxide were of AR (B.D.H) grade. Stock solutions of both the oxidant and the substrate were freshly prepared using doubly distilled water.

Spectral Measurements

The absorption spectra of solutions of different concentrations of hexacyanoferrate (III) ion and copper (II) ion were recorded in the visible region: 340-460 nm, and 620-730 nm, respectively. The wavelengths corresponding to the maximum absorbance were 420 nm and 690nm for

hexacyanoferrate (III) ion and copper (II) ion, respectively.

Kinetic Measurements

All reactant solutions were placed in a thermostated water bath for about one hour to attain the temperature of 40°C. The reaction mixture was prepared by mixing the requisite volume of the reactants in a 250cm³ conical flask. The reaction rate was followed by measuring the decrease in absorbance at 420 nm and 690nm for hexacyanoferrate (III) ion and copper (II) ion respectively. The reaction was completed when the hexacyanoferrate (III) ion – sugar solution changed from yellow to colorless and copper (II) ion-sugar solution changed from blue to colorless.

Bromine Water Test and Iodine Solution Test

The addition of bromine water to alkaline sugar solution resulted into decolorization of bromine water after some time. This indicates the presence of enediol intermediate [7, 11]. Also the addition of iodine solution to alkaline sugar solution resulted into absorption of large quantity of iodine. This also indicates the presence of enediol intermediate formation [7, 11].

RESULTS AND DISCUSSION

Effect of Reactant Concentration

The reactions were studied at various initial concentration of Fe(CN)₆³⁻ or Cu²⁺ but at constant sugar concentration, constant pH, ionic strength, and temperature. The disappearance of hexacyanoferrate (III) ion or copper (II) ion with time uniformly followed zero order kinetics in each run. The values of the k_{obs} were presented Table 2. Looking at the results, it is very clear that the observed rate constants are independent of the initial concentration of hexacyanoferrate (III) ion and copper (II) ion respectively. Also, the plots of k_{obs} versus initial concentration of hexacyanoferrate (III) ion or copper (II) ion are linear, parallel to the x-axis (Figure 2). This further shows that the rate of oxidation of the sugars is zero order with respect to the initial concentration of the hexacyanoferrate (III) ion and copper (II) ion. These results agree with the literature reports [8-13].

In another set of experiments, the observed rate constants k_{obs} were evaluated at different initial concentrations of the sugars but at constant [Fe(CN)₆³⁻] or [Cu²⁺], [NaNO₃], pH and temperature. The rate of reaction increases as the concentration of sugars is increased. A plot of k_{obs} versus the concentration of sugar was linear and passed through the origin for each sugar with hexacyanoferrate (III) ion and copper (II) ion respectively (figure 1). This suggests a first order dependence of rate upon the sugar concentration. The relative reactivity of the sugars is lactose > maltose. This result is in agreement with published data [14-17].

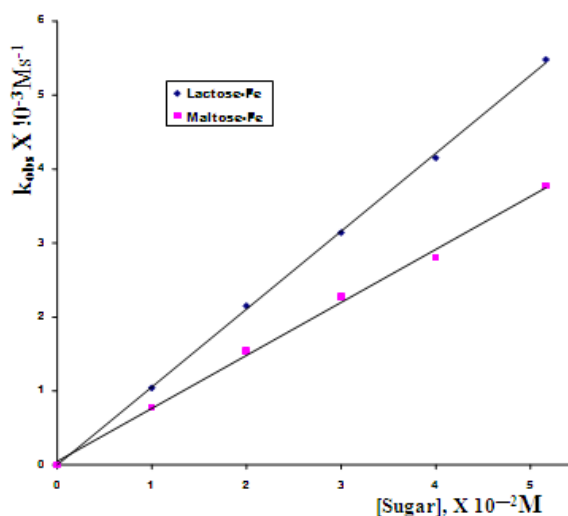


Figure 1: K_{obs} versus Sugar Concentration.

Table 1: Variation of Rate Constant with Hexacyanoferrate (III) and Copper (II) Ion Concentration.

For Fe(CN) ₆ ³⁻ 10 ⁻² [Oxidant] M	Lactose 10 ⁻² k _{obs} , Ms ⁻¹	Maltose 10 ⁻² k _{obs} , Ms ⁻¹
1	2.14	2.16
2	2.13	2.28
3	2.22	2.24
4	2.09	2.07
5	2.14	2.24
For Cu ²⁺ 10 ⁻² [Oxidant] M	Lactose 10 ⁻² k _{obs} , Ms ⁻¹	Maltose 10 ⁻² k _{obs} , Ms ⁻¹
1	2.85	2.27
2	2.97	2.24
3	2.91	2.24
4	2.97	2.23
5	2.67	2.24

T=40° C, [sugar]= 2X10² M, pH = 10,3, [NaNO₃]=0.1M

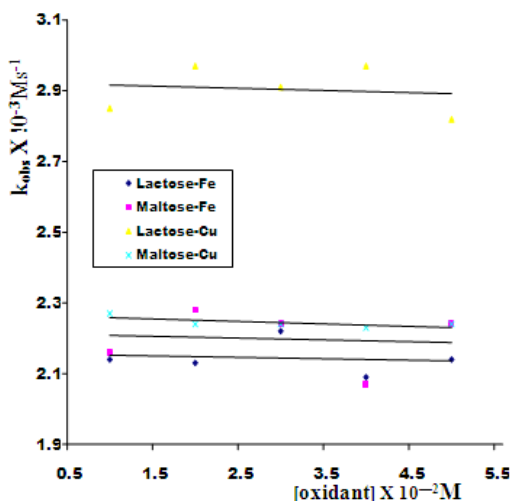


Figure 2: k_{obs} versus Oxidant Concentration.

Table 2: Variation of Rate Constant with Ionic Strength.

For $\text{Fe}(\text{CN})_6^{3-}$	Lactose	Maltose
$10^{-2}[\text{NaNO}_3] \text{ M}$	$10^{-2}k_{obs}, \text{ Ms}^{-1}$	$10^{-2}k_{obs}, \text{ Ms}^{-1}$
1	2.81	2.74
2	2.82	2.83
3	2.83	2.88
4	2.81	2.74
5	2.82	2.74
For Cu^{2+}	Lactose	Maltose
$10^{-2}[\text{NaNO}_3] \text{ M}$	$10^{-3}k_{obs}, \text{ Ms}^{-1}$	$10^{-3}k_{obs}, \text{ Ms}^{-1}$
1	2.22	2.11
2	2.22	2.11
3	2.23	2.01
4	2.22	2.12
5	2.25	2.12

$T=40^\circ\text{C}$, $[\text{Cu}^{2+}]$ or $[\text{Fe}(\text{CN})_6^{3-}] = 2 \times 10^{-4} \text{ M}$,
 $\text{pH} = 10.3$ [Sugar] = $2 \times 10^{-2} \text{ M}$

Effect of Ionic Strength

The reactions were studied at several initial concentrations of sodium nitrate but at constant concentration of sugar, hexacyanoferrate (III) ion, and at constant temperature of 40°C and $\text{pH} 10.3$. 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 does not depend on the ionic strength of the medium. This result is further confirmed by the plot of $\log k_{obs}$ versus \sqrt{I} (Figure 3). 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 [18]. This result shows that oxidation of maltose and xylose involves reaction between an ion and a neutral molecule at the rate-determining step [19].

Table 3: Variation of Rate Constant with Temperature.

For $\text{Fe}(\text{CN})_6^{3-}$	Lactose	Maltose
$T^\circ\text{C}$	$10^{-2}k_{obs}, \text{ Ms}^{-1}$	$10^{-2}k_{obs}, \text{ Ms}^{-1}$
40	0.255	0.101
45	0.486	0.120
50	0.871	0.278
55	1.467	0.493
60	2.420	0.934
For Cu^{2+}	Lactose	Maltose
$T^\circ\text{C}$	$10^{-3}k_{obs}, \text{ Ms}^{-1}$	$10^{-3}k_{obs}, \text{ Ms}^{-1}$
40	1.88	1.05
45	3.86	2.09
50	4.97	2.13
55	8.19	3.13
60	12.42	6.58

$[\text{Cu}^{2+}]$ or $[\text{Fe}(\text{CN})_6^{3-}] = 2 \times 10^{-4} \text{ M}$, $\text{pH} = 10.3$,
 $[\text{sugar}] = 1 \times 10^{-2} \text{ M}$, $[\text{NaNO}_3] = 0.1 \text{ M}$

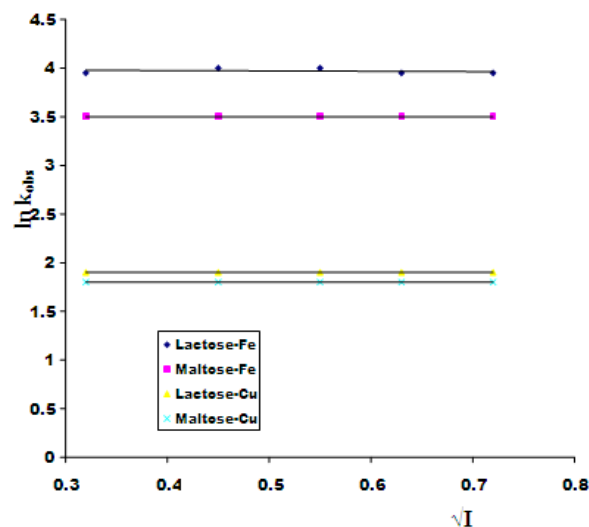


Figure 3: $\ln k_{obs}$ versus Square Root of Ionic Strength.

Effect of Temperature

The oxidation reactions were studied at different temperatures in the range 40 to 65°C while the concentrations of hexacyanoferrate (III) ion and sugar were kept constant. The pH as well as ionic

strength of medium was also kept constant. The observed rate constant increased with increase in temperature as the data in Table 3 show. The Arrhenius parameters were calculated from the logarithmic plot of the observed rate constant against the reciprocal of the temperature in Kelvin (Figure 3).

The values of the Arrhenius activation energy E_a , for the oxidation of maltose and lactose by hexacyanoferrate (III) ion and copper (II) ion were obtained from the slope of the linear plot. Other thermodynamic activation parameters were also evaluated and summarized in Table 4.

The entropy of activation in each case was found to be negative, suggesting the compactness of the transition state as compared to the ground state. Also, similar value of free energy of activation suggests a common mechanism for the oxidation of these reducing sugars [3, 20-23]. The values of the activation energy suggest that hexacyanoferrate (III) ion is a powerful oxidizing agent than copper (II) ion. Also the rate of oxidation of lactose is higher than that of maltose.

Table 4: Activation Energy and their Thermodynamic Activation Parameters.

Parameter	$\text{Fe}(\text{CN})_6^{3-}$		Cu^{2+}	
	Lactose	Maltose	Lactose	Maltose
E_a kJmol ⁻¹	78.39	85.79	97.17	122.96
ΔH^\ddagger kJmol ⁻¹	83.19	75.79	94.57	120.36
ΔS^\ddagger JK ⁻¹ mol ⁻¹	-431.85	-430.6	-430.20	-428.79
ΔG^\ddagger kJmol ⁻¹	210.81	218.52	229.22	254.54

REACTION MECHANISM AND RATE EQUATION

In the oxidation of reducing sugars by copper (II) and iodine ion [11, 24], it has been shown that the reactions occur via the formation of an enediol intermediate. The values of free energy change (ΔG^\ddagger) obtained look similar and this shows that the oxidation of the sugars proceeds via the same mechanism [8, 9, 20]. The independence of rate of oxidation on the ionic strength of the medium supports this fact [Figure 3].

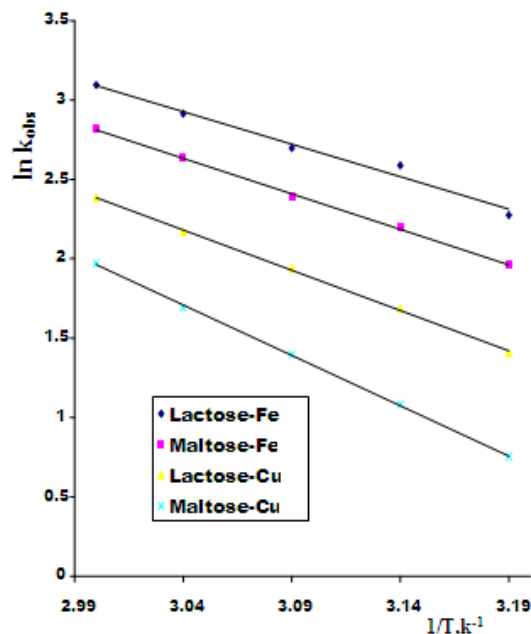
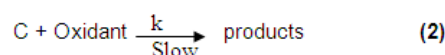
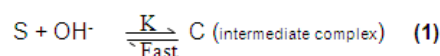


Figure 4: Arrhenius plot K_{obs} versus $1/T$.

Based on the above facts, the mechanism for the comparative oxidation of maltose and lactose by hexacyanoferrate (III) ion and copper (II) may be proposed as follows:



Writing equilibrium expression for Equation 1

$$K = \frac{[\text{C}]}{[\text{S}][\text{OH}^-]} \quad (3)$$

$$[\text{C}] = K[\text{S}][\text{OH}^-] \quad (4)$$

Equation 2 being the rate determining step, the rate of reaction can be written as

$$\frac{d[\text{Oxidant}]}{dt} = k[\text{C}][\text{Oxidant}] \quad (5)$$

Substituting Equation 4 into Equation 5:

$$\frac{d[\text{Oxidant}]}{dt} = Kk[\text{S}][\text{OH}^-][\text{Oxidant}] \quad (6)$$

$$\frac{d[\text{Oxidant}]}{dt} = k'[\text{S}][\text{OH}^-][\text{Oxidant}] \quad (7)$$

where $k' = Kk$

Rate law (7) is in agreement with the experimental results (i.e., first order and zero order dependence of rate with respect to sugars and oxidant, respectively) (Figures 1 and 2). This shows that the rate of reaction is proportional to $\{[S][OH]\}$. From the plot of k_{obs} against $[sugar]$, the values of k have been evaluated and summarized in Table 5 for maltose and lactose.

Table 5: Values of k for the Oxidation of Lactose and Maltose.

	LACTOSE	MALTOSE
$Fe(CN)_6^{3-}$	1.0883	1.0609
Cu^{2+}	0.7334	0.7120

These values show that the rate of oxidation of lactose is greater than that of maltose for both hexacyanoferrate (III) ion and copper (II) ion.

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