



COMPARATIVE STUDY ON OXIDATION OF MALTOSE AND SUCROSE BY [Cu(BIP)₂]₂²⁺ IN ALKALINE MEDIUM

Chemistry

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ABSTRACT

The kinetic study of Maltose and Sucrose by [Cu(Bip)₂]₂²⁺ in alkaline medium has been investigated spectrophotometrically at λ max 380 & 430 nm under pseudo first order condition. The above said investigation of Maltose and Sucrose shows a first order dependence on reducing sugars and hydroxyl ions at their low conc. but tends towards zero order at their higher concentration and follow zero order kinetics w.r.t Cu (II). The rate determining step involves the reaction between hydroxyl ions and reducing sugars leading to intermediate diol active products. A mechanism that involves the formation of an intermediate enediol anion has been proposed for the oxidation of substrate. In the present condition, these substrates are also oxidised with [Cu(Bip)₂]₂²⁺ itself. The empirical rate law, in terms of disappearance of [Cu(Bip)₂]₂²⁺ might be proposed.

$$-\frac{d[\text{Cu}]}{dt} = k_1[\text{S}][\text{OH}]$$

Where k₁ is observed first order rate constant in [Cu(Bip)₂]₂²⁺ depending upon the conc. of substrate and hydroxyl ions.

Reducing sugars including (Maltose and Sucrose) are multifunctionality naturally occurring materials, the oxidation products of which play a key role as intermediates for the synthesis of more complex molecules and also display biological activities.

KEYWORDS

spectrophotometry, kinetics, mechanism, oxidation, [Cu(Bip)₂]₂²⁺

Introduction:

Carbohydrates are the most abundant class of organic compounds found in living organisms and the oxidation of sugars¹⁻² is therefore immense importance. Kinetics and Mechanism of oxidation of oxidation of monosaccharides and disaccharides have been studied in both acidic³⁻⁵ and alkaline media⁶⁻⁹, employing different transition metals¹⁰ ions, inorganic acids, complex ions¹¹⁻¹² and hydrogen peroxide as oxidants. Maltose is disaccharide of two molecules of glucose and obtained by careful acid hydrolysis of starch. It is found in germinating grains and is important in the production of alcohol by fermentation. Sucrose consists of glucose & fructose found in the brush border of the small intestine. Therefore the intestinal brush border enzyme that hydrolysed sucrose is sometimes called invertase. Various oxidation products of the redox reactions¹³ having reducing sugars as reductant are reported to have industrial and biological significance.

Oxidation of maltose and lactose by Cu (II) in the presence of ammonium hydroxide has been reported by Singh¹⁴⁻¹⁵. The reactions are zero order in Cu (II) and first order in substrate and hydroxide ion concentration. It was suggested that the rate determining step involves the reaction between hydroxyl ion and reducing sugar, leading to an intermediate active product which is rapidly oxidized by Cu (II) complex through an electron transfer process. Cu (II) oxidation of D-xylose, Larabinose, D-glucose, D-fructose, D-mannose, D-galactose, L-sorbose, lactose, maltose, cellobiose and melibiose in alkaline medium was studied by Singh and co-workers¹⁶⁻¹⁷. The reaction showed a first order dependence with reducing sugar and alkalis concentration and the oxidation process was independent of Cu (II) concentration for all the reducing sugars.

Most of studies carried out in alkaline medium¹⁸⁻²⁰ reported that the reaction was base catalysed. Compared to studies on the oxidation of sugars has received little attention. This paper describes the kinetics and mechanism of oxidation of maltose and Sucrose by Cu(Bip)₂]₂²⁺ in alkaline medium. The system remains homogenous due to formation of Cu(II) and Cu (I) Bipyridyl complex. In present study we have compared the reactivities of sugars, their rate of oxidation and to establish the reaction pathways for the oxidation reaction.

Materials and Methods:

All stock solutions for kinetic investigations were prepared in double distilled water. The standard solution of Maltose and Sucrose (E merck) were always prepared fresh. The other reagents employed were cupric sulphate, 2,2'' Bipyridyl in 25% ethyl alcohol, potassium chloride AR (BDH) quality. Cu(Bip)₂]₂²⁺. The kinetic runs were performed on Shimadzu 1800 UV Visible Spectrophotometer. The initiation of the reaction was carried out by mixing the requisite volume of the sugars solution to the reaction mixture and zero time was

noted. Then this reaction mixture was taken in a cell and was kept in the sample compartment. An increasing trend of absorbance was recorded by the automatic recorder and was noted down simultaneously. The increasing trend of absorbance clearly indicates the change of [Cu(Bip)₂]₂²⁺ to [Cu(Bip)₂]₂⁺.

Initially for measuring maximum absorbance of products the spectra was scanned over the range of 700 nm to 350 nm. Thus we obtain wavelength 380 nm and 430 nm at which the products [Cu(Bip)₂]₂²⁺ absorbs maximum and reactant [Cu(Bip)₂]₂²⁺ absorbs minimum radiation. The reaction mixture was prepared by mixing the requisite volume of Cu(II), 2,2'' Bipyridyl and alkali solution of sodium carbonate.

Result and Discussion:

The rate law and mechanism for oxidation of sugars by [Cu(Bip)₂]₂²⁺ in alkaline medium have been derived by studying the effect of varying concentration of reactants on the reaction rate.

Kinetics of oxidation of Maltose and Sucrose by Cu(Bip)₂]₂²⁺ in alkaline medium have been studied at constant temperature 40°C. Order of reaction w.r.t each reactant was determined by varying the concentrations of reducing sugars and Cu(Bip)₂]₂²⁺. Under these condition the reaction rate will mainly be determined by the change in concentration of Cu(II) ion. Table I shows the effect of variation of Cu(II) concentration on the reaction rate. There is approximately no change in ΔA/ΔT values, which is proportional to zero order rate constant (k₀), with increasing [Cu(II)]. This indicates that reaction rate is independent of [Cu(II)].

Experiments were performed to determine the order of reaction w.r.t [maltose] and [sucrose]. ΔA/ΔT values proportional to zero order rate constant are increasing in direct proportion with the increase in concentration of maltose and sucrose, which is evident from the summarised table 1. It indicates that the reaction is first order with respect to [Maltose] and [Sucrose].

Table I

CuSO ₄ X10 ³ M	[Maltos e]X10 ² M	ΔA/ΔT X10 ³ Sec ⁻¹	(ΔA/ ΔT) [Mal] Mol ⁻¹ lit ⁻¹ Sec ⁻¹	CuSO ₄ X10 ³ M	[Sucros e] X10 ² M	ΔA/ΔT X10 ³ Sec ⁻¹	(ΔA/ ΔT) [Sucr] Mol ⁻¹ lit ⁻¹ Sec ⁻¹
0.5	10.0	4.8	-	0.2	10.0	1.20	-
1.0	10.0	5.0	-	0.3	10.0	3.00	-
1.5	10.0	5.2	-	0.4	10.0	3.50	-
2.0	10.0	4.9	-	0.5	10.0	3.60	-
2.5	10.0	4.7	-	0.6	10.0	3.70	-

3.0	10.0	5.0	-	0.7	10.0	3.80	-
1.25	3.0	2.20	7.34	1.25	4.0	1.3	3.25
1.25	5.0	3.80	7.60	1.25	8.0	2.8	3.5
1.25	7.0	5.20	7.42	1.25	12.0	3.9	3.25
1.25	10.0	7.70	7.70	1.25	16.0	5.3	3.31
1.25	13.0	9.50	7.30	1.25	20.0	6.8	3.40
1.25	15.0	11.6	7.74	1.25	24.0	9.0	3.75

Effect of variation of sodium bicarbonate on the reaction rate showed by table II (A&B). There is a gradual decrease in $\Delta A/\Delta T$ values at increasing concentration of sodium bicarbonate. This decrease in $\Delta A/\Delta T$ values is due to the fact that the dissociation of sodium bicarbonate is gradually suppressed with the increase in sodium bicarbonate concentration. The concentration of free OH⁻ has been calculated by the equation $pH + pOH = 14$ in each run. From column 3rd and 4th of table II (A&B), it is quite evident that $\Delta A/\Delta T$ values are increasing in the same proportion in which concentration of OH⁻ ion is increased. When $\Delta A/\Delta T$ values are divided by OH⁻ concentration, more or less constant values are obtained. On the basis of above results and fig 1 (A&B) it can be concluded that order of reaction w.r.t OH⁻ is unity.

Effect of variation of dielectric constant on the rate of reaction has also been studied. Results are presented in table II (A&B) which indicates that there is small increase in mean zero order rate constant values with the decrease in dielectric constant of the medium. This demonstrates that reaction is occurring between a positive ion and a dipolar molecule. This is further confirmed by the plot of $\log \Delta A/\Delta T$ vs. $1/D$ which gave a straight line, having a positive intercept on y-axis.

There is approximately no change in reaction rate by varying ionic strength of the medium. The values of $\Delta A/\Delta T$ has been collected at two different temperature and with the help of these values energy of activation has been calculated, which are 49.96 KJmol⁻¹ for Maltose and 85.70 KJmol⁻¹ for sucrose.

It is also observed that initially there is some induction period and then $\Delta A/\Delta T$ assumed uniform values throughout the course of reaction. The decrease $\Delta A/\Delta T$ values in the later of the reaction are due to interference of reaction products (Table IV).

From the above result it, can be concluded that the reacting species is $[Cu(Bip)_2]^{2+}$ instead of free Cu(II). A careful study of the oxidation of Maltose and sucrose shows that in absence of autocatalysis, the rate expression is of the form

$$-\frac{d[Cu(II)]}{dt} = k[OH][S]$$

Where $[S] = [Maltose]$ or $[Sucrose]$
 $[Cu(II)] = [Cu(Bip)_2]^{2+}$

For any given concentration of alkali if the concentration of substrate is very large as compared to $[Cu(II)]$ the rate expression will become,

$$-\frac{d[Cu(II)]}{dt} = k_0$$

Where $k_0 = k[OH][S]$ known as mean zero order rate constant.

This k_0 which is meant zero order rates constant is approximately the same as $\Delta A/\Delta T$.

Table II: Effect of varying $[NaHCO_3]$ on rate constant of oxidation of Maltose and Sucrose

(A) For Maltose oxidation

$[CuSO_4] = 1.25 \times 10^{-3} M$, $[Maltose] = 10.0 \times 10^{-2} M$, $[free Bip] = 4.0 \times 10^{-3} M$, $Temp = 40^\circ C$

$NaHCO_3 \times 10^3 M$	pH	$[OH^-] \times 10^4 M$	$(\Delta A/\Delta T) \times 10^3 Sec^{-1}$	$(\Delta A/\Delta T) / [OH^-] Mol^{-1} lit^{-1} Sec^{-1}$
3.0	11.0	5.0	3.8	7.6
5.0	10.7	4.5	3.5	7.8
7.0	10.6	4.0	3.0	7.5
10.0	10.5	3.5	2.6	7.4
13.0	10.4	3.2	2.4	7.5
18.0	10.3	2.8	2.1	7.5

(B) For Sucrose oxidation

$[CuSO_4] = 1.25 \times 10^{-3} M$, $[Sucrose] = 5.0 \times 10^{-2} M$, $[Free Bip] = 4.0 \times 10^{-3} M$, $Temp = 40^\circ C$

$NaHCO_3 \times 10^3 M$	pH	$[OH^-] \times 10^4 M$	$(\Delta A/\Delta T) \times 10^3 Sec^{-1}$	$(\Delta A/\Delta T) / [OH^-] Mol^{-1} lit^{-1} Sec^{-1}$
2.0	11.2	8.0	5.5	6.8
4.0	11.0	7.0	4.5	6.4
6.0	10.8	6.0	4.0	6.7
10.0	10.5	5.0	3.2	6.4
14.0	10.3	4.0	2.6	6.5
18.0	10.2	3.0	2.0	6.7

Table III: Effect of varying dielectric constant (D) on rate constant of oxidation of Maltose and Sucrose

(A) For Maltose oxidation

$[CuSO_4] = 1.25 \times 10^{-3} M$, $[Maltose] = 10.0 \times 10^{-2} M$, $[free Bip] = 2.5 \times 10^{-3} M$, $Temp = 40^\circ C$

Percentage of Ethanol by vol.	D	$[1/D] \times 10^3 M$	$(\Delta A/\Delta T) \times 10^3 Sec^{-1}$	$3 + \log(\Delta A/\Delta T) Sec^{-1}$
4.0	76.0	16.8	5.0	0.69
8.0	73.6	15.6	5.2	0.71
12.0	70.8	14.5	5.6	0.74
16.0	69.0	13.3	6.0	0.77
20.0	66.4	12.0	6.3	0.79

(B) For Sucrose oxidation

$[CuSO_4] = 1.25 \times 10^{-3} M$, $[Sucrose] = 5.0 \times 10^{-2} M$, $[Free Bip] = 2.5 \times 10^{-3} M$, $Temp = 40^\circ C$

Percentage of Ethanol by vol.	D	$[1/D] \times 10^3 M$	$(\Delta A/\Delta T) \times 10^3 Sec^{-1}$	$3 + \log(\Delta A/\Delta T) Sec^{-1}$
4.0	75.0	15.8	4.2	0.62
8.0	74.4	15.0	5.0	0.69
12.0	73.5	14.0	6.2	0.79
16.0	72.3	13.2	7.0	0.84
20.0	71.0	13.0	7.5	0.87

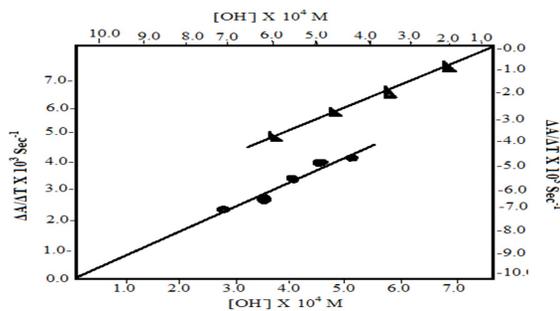


Fig: 1 Effect of varying $[OH^-]$ on the rate of reaction

- A. $[Maltose] = 10.0 \times 10^{-2} M$, $[CuSO_4] = 1.25 \times 10^{-3} M$, $[Bipyridyl] = 6.0 \times 10^{-3} M$, $[Na_2CO_3] = 0.5 \times 10^{-3} M$, $Temp = 35^\circ C$
- B. $[Sucrose] = 8.0 \times 10^{-2} M$, $[CuSO_4] = 1.25 \times 10^{-3} M$, $[Bipyridyl] = 8.0 \times 10^{-3} M$, $[Na_2CO_3] = 0.2 \times 10^{-3} M$, $Temp = 35^\circ C$

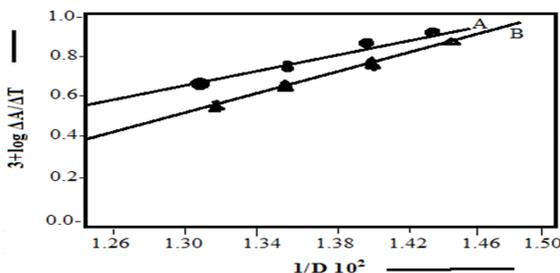


Fig: 2 Effect of varying Dielectric constant on the rate of reaction

- A. $[Maltose] = 10.0 \times 10^{-2} M$, $[CuSO_4] = 1.25 \times 10^{-3} M$, $[Bipyridyl] = 6.0 \times 10^{-3} M$, $[Na_2CO_3] = 0.5 \times 10^{-3} M$, $Temp = 35^\circ C$
- B. $[Sucrose] = 8.0 \times 10^{-2} M$, $[CuSO_4] = 1.25 \times 10^{-3} M$, $[Bipyridyl] = 8.0 \times 10^{-3} M$, $[Na_2CO_3] = 0.2 \times 10^{-3} M$, $Temp = 35^\circ C$

Table IV

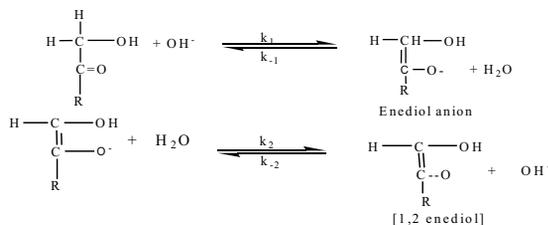
[Maltose] = 10.0×10^{-2} M, [CuSO₄] = 1.25×10^{-3} M, [free Bip] = 2.5×10^{-3} M, Temp. = 35°C

Time (min)	Absorbance	($\Delta A/\Delta T$) Min ⁻¹
2.0	0.080	
5.0	0.085	0.000
8.0	0.100	0.008
10.0	0.120	0.023
11.0	0.200	0.120
12.0	0.225	0.200
13.0	0.400	0.210
15.0	0.620	0.208
18.0	0.840	0.215
20.0	1.260	0.220
23.0	1.530	0.250
25.0	1.010	0.268
28.0	4.000	0.250

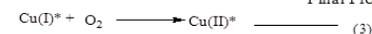
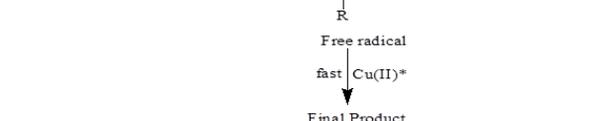
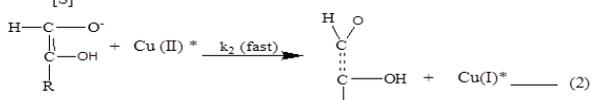
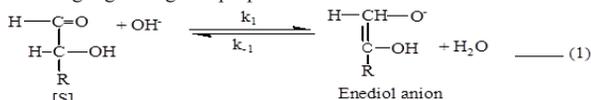
It is well known that, in the presence of alkali, reducing sugars undergo a tautomeric change through the formation of an intermediate enediol.

The base catalysed formation of enediol might be written as:

Keto Sugars



Oxidation of reducing sugars will take place through enediol ion with respect to OH⁻ ion. In our experimental study, since reaction rate is directly proportional to the hydroxyl ion concentration. Hence it is the enediol anion which is being fast oxidized by [Cu(Bip)₂]²⁺, resulting in a free radical species and [Cu(Bip)₂]²⁺. This free radical species is further oxidised by other [Cu(Bip)₂]²⁺ giving the final products. This induction period observed initially is due to the oxidation of Cu(I)* to Cu(II)* by the dissolved oxygen. The reaction rate for the oxidation of reducing sugars might be proposed as follows:



where S = maltose / Sucrose
 Cu(II)* = [Cu(Bip)₂]²⁺

Cu(I)* = [Cu(Bip)₂]⁺

Since [Cu(Bip)₂]²⁺ complex is soluble, hence system remains homogenous in experiment. Considering these steps an applying steady state approximation to the concentration of enediol anions, the rate law in terms of decrease in Cu(II) concentration might be written as.

$$-\frac{d[\text{Cu(II)*}]}{dt} = \frac{k_1 k_2 [\text{S}] [\text{OH}^-] [\text{Cu(II)*}]}{k_1 [\text{H}_2\text{O}] + k_2 [\text{Cu(II)*}]} \quad (4)$$

Since enediol anion in step (2) is rapidly oxidised by Cu(II)* complex, so it is proper to assume that $k_2 \gg k_1$. Thus inequality $k_2 [\text{Cu(II)*}] \gg k_1 [\text{H}_2\text{O}]$, might be assumed valid, hence the rate law becomes.

$$-\frac{d[\text{Cu(II)*}]}{dt} = k_1 [\text{S}] [\text{OH}^-] \quad (5)$$

Keto Sugars confirms the complexity of the order of the reaction with respect to [OH⁻] and its first order dependence on the sugars and hydroxyl ion, which we have observed experimentally. This is consistent with the reaction formulated (5).

Conclusion:

The present paper shows that in oxidation of Maltose and Sucrose by [Cu(Bip)₂]²⁺ in alkaline medium, Cu(II) appears to be reactive species of [Cu(Bip)₂]²⁺ in alkaline medium. The formation of reactive complex, between reactive species of Cu(II) and reducing sugars in alkaline medium is well supported by observed and spectral data. The rate determining step of the proposed reaction involves the interaction between complexes. On the basis of rate of reaction oxidation of Maltose was found to be faster as compared to Sucrose in alkaline medium. Therefore [Cu(Bip)₂]²⁺ is a good oxidising agent in sugar conversion.

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