

Chemistry

KINETICS AND MECHANISM OF OXIDATION OF D-MANNOSE BY
Cu(II) IN THE PRESENCE OF AMMONIUM HYDROXIDE

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The oxidation of D-mannose by Cu(II) in the presence of ammonium hydroxide shows that the reaction rate is independent of [Cu(II)] and first order both with respect to $[\bar{\text{O}}\text{H}]$ & [D-mannose]. The reaction proceeds after a slight induction period. A general mechanism involving the intermediate enediol anion has been proposed. It is found that the rate of enolization is the rate of oxidation. Formic acid and arabonic acid have been identified as the oxidation products.

INTRODUCTION

SINGH *et al.* (1955, 1956, 1958) studied the oxidation of reducing sugars by Cu(II) in the alkaline medium in the presence of complexing agents and reported that the reaction is zero-order with respect to [Cu(II)] and first order with respect to $[\bar{\text{O}}\text{H}]$ and [reducing-sugar]. They also observed that the reaction has an induction period and shows autocatalysis due to Cu_2O produced in the system. These results were confirmed by Marshall & Waters (1960, 1961) and Singh *et al.* (1970), Wiberg and Nigh (1965) have studied the oxidation of α -hydroxy acetophenone by Cu(II) in aqueous pyridine and they have supported the explanation of Singh *et al.* (1955, 1956, 1958, 1970) at lower concentrations of Cu(II). The essential kinetic features of oxidation of D-mannose by ammoniacal Cu(II) have been studied for the first time. The system remains homogeneous due to formation of soluble Cu(I)-ammonia complex (James & William, 1961) $\text{Cu}(\text{NH}_3)_2^+$. Our main aim and interest was to find out whether the role of ammoniacal Cu(II) in the oxidation of D-mannose is similar to the role of ammonical Ag(I) or role of Cu(II) in the presence of complexing agents like tartrate, citrate, picolinate & pyridine. In order to confirm the above facts, the present study comes about dealing with the kinetics of oxidation of D-mannose by Cu(II) complexed with ammonia.

EXPERIMENTAL

All the reagents except D-mannose used were of AR (B.D.H.) grade samples. The standard solution of D-mannose (NRC Pfanstich Laboratories, Inc.) was always prepared daily. The rate of reaction was determined by estimating the amount of Cu(I) produced at different intervals of time against standard solution of $\text{K}_2\text{Cr}_2\text{O}_7$, using N-phenyl anthranilic acid as redox indicator.

RESULTS AND DISCUSSION

The rate law and mechanism for the oxidation of D-mannose by ammoniacal Cu(II), have been derived by studying the effect of varying [reactants] on the reaction rate.

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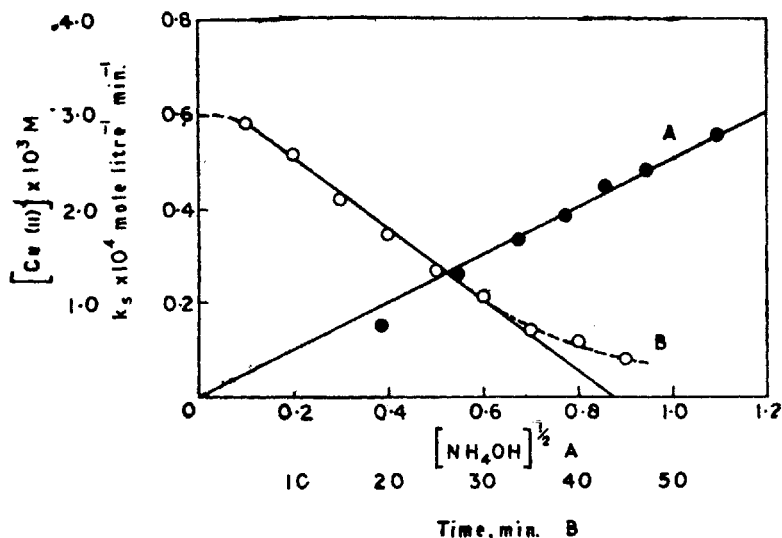


FIG. 1 (A) A plot of k_s values versus $[\text{NH}_4\text{OH}]^{1/2}$ at 40°

[D-mannose]	$= 6.00 \times 10^{-2} \text{ M}$;
$[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$	$= 3.00 \times 10^{-2} \text{ M}$;
[KCl]	$= 4.88 \times 10^{-1} \text{ M}$; $\mu = 0.50 \text{ M}$.

(B) A plot of $[\text{Cu(II)}]$ against time at 40°

[D-mannose]	$= 8.00 \times 10^{-2} \text{ M}$;
$[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$	$= 3.00 \times 10^{-2} \text{ M}$;
$[\text{NH}_4\text{OH}]$	$= 10.00 \times 10^{-1} \text{ N}$;
[KCl]	$= 4.88 \times 10^{-1} \text{ M}$;
μ	$= 0.50 \text{ M}$

The oxidation proceeds after a slight induction period (Fig. 1, curve B). There is some fall in zero-order rate constants in the later part of the reaction when $[\text{Cu(II)}]$ is very high or $[\text{NH}_4\text{OH}]$ is very low. Table I shows the effect of variation of $[\text{Cu(II)}]$ on the reaction rate. There is a gradual decrease in k_s values with increasing $[\text{Cu(II)}]$, probably due to decrease in pH of the system. This is further confirmed by performing the same study in a buffer of NH_4Cl and NH_4OH . In buffer k_s values are practically uniform (Table I (B)) indicating the zero-order kinetics with respect to $[\text{Cu(II)}]$.

Table II shows that k_s values are directly proportional to [reducing sugar]. The ratio $k_s/[\text{sugar}]$ is fairly constant in the third column of above table, confirming the first order kinetics with respect to [reducing sugar].

The plot of k_s vs. $[\text{NH}_4\text{OH}]^{1/2}$ at constant concentrations of other reactants (Fig. 1, curve A) is linear passing through the origin. This clearly explains that the order with respect to $[\text{OH}^-]$ is unity because $[\text{OH}^-] = \sqrt{k_b [\text{NH}_4\text{OH}]}$. As k_b is constant hence in order to calculate $[\text{OH}^-]$ only $[\text{NH}_4\text{OH}]^{1/2}$ has been taken into consideration.

In view of the above experimental results, the probable reaction mechanism for

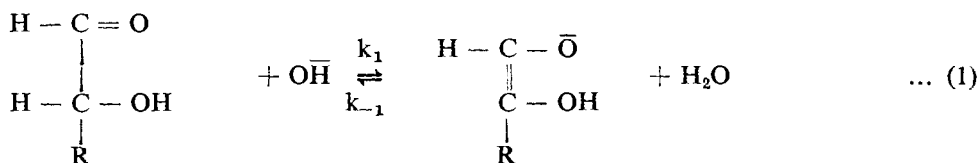
TABLE I

Effect of varying [Cu(II)] on the reaction rate at 40°

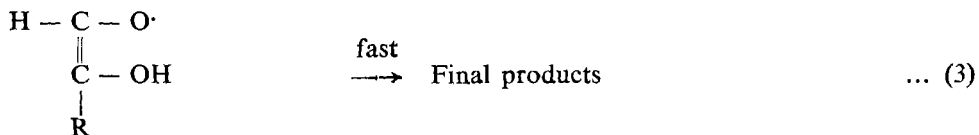
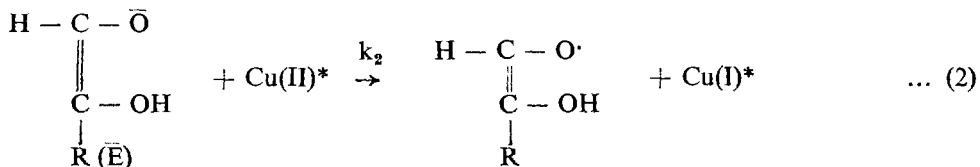
(A)		(B)	
[D-mannose]	= $8.00 \times 10^{-2}M$	[D-mannose]	= $1.60 \times 10^{-1}M$
[NH ₄ OH]	= $10.00 \times 10^{-1}N$	[NH ₄ OH]	= $10.00 \times 10^{-1}N$
μ	= 0.50 M	[NH ₄ Cl]	= $5.0 \times 10^{-2}M$
		μ	= 0.50 M

CuSO ₄ ·5H ₂ O × 10 ³ M	(A) $k_s \times 10^5$ mole lit. ⁻¹ min ⁻¹	(B) $k_s \times 10^5$ mole lit. ⁻¹ min ⁻¹
3.00	7.90	3.40
4.00	7.30	3.20
5.00	6.90	3.30
6.00	6.20	3.50
8.00	5.75	3.40
10.00	5.15	3.20

the oxidation of D-mannose by ammoniacal Cu(II) might be formulated as shown in the following scheme 1.



enediol anion ($\bar{\text{E}}$)



where $\text{Cu(II)}^* = \text{Cu(NH}_3)_4^{2+}$ and $\text{Cu(I)}^* = \text{Cu(NH}_3)_2^+$

Scheme 1

TABLE II

Effect of varying [D-mannose] on the reaction rate at 40°

$$\begin{aligned}
 [\text{NH}_4\text{OH}] &= 15.00 \times 10^{-2}\text{N} \\
 [\text{CuSO}_4 \cdot 5\text{H}_2\text{O}] &= 3.00 \times 10^{-3}\text{M} \\
 \mu &= 0.50 \text{ M}
 \end{aligned}$$

[D-mannose] $\times 10^3\text{M}$	$k_s \times 10^5$ mole litre ⁻¹ min ⁻¹	$k_s \times 10^3$ [D-mannose] min ⁻¹
2.00	2.60	1.30
3.00	3.80	1.27
4.00	4.90	1.23
5.00	6.00	1.20
6.00	7.20	1.20
7.00	8.60	1.23
10.00	11.80	1.18

The rate law in terms of disappearance of Cu(II) would be given by Eqn. (5).

$$-\frac{d[\text{Cu(II)}^*]}{dt} = k_2 [\bar{\text{E}}] [\text{Cu(II)}^*] \quad \dots (5)$$

By applying the steady state condition, eqn. (5) reduces to eqn. (6):

$$-\frac{d[\text{Cu(II)}^*]}{dt} = \frac{k_1 k_2 [\text{S}] [\text{OH}^-] [\text{Cu(II)}^*]}{k_{-1} [\text{H}_2\text{O}] + k_2 [\text{Cu(II)}^*]} \quad \dots (6)$$

Further, it can safely be taken that the enediol anion is rapidly oxidised by Cu(II)* so it is quite probable that $k_2 > k_{-1}$. The inequality $k_2 [\text{Cu(II)}^*] \gg k_{-1} [\text{H}_2\text{O}]$ might be valid and the rate law then reduces to eqn. (7)

$$-\frac{d[\text{Cu(II)}^*]}{dt} = k_1 [\text{S}] [\text{OH}^-] \quad \dots (7)$$

The rate law (7) clearly confirms the observed first order kinetics with respect to both $[\text{OH}^-]$ & [reducing sugar] and zero order kinetics with respect to $[\text{Cu(II)}^*]$. The above rate law is also in complete agreement with the observations of Marshall and Waters (1960, 1961) and Singh *et al.* (1955, 1956, 1958, 1970). The formation of hypothetical enediol anion as an intermediate in the interconversion of reducing sugars was suggested by Anet (1964), Speck (1958) and Isbell *et al.* (1971).

The rate law (7) indicates that the rate of enolization is actually the rate of oxidation. The induction period observed is due to oxidation of Cu(I) produced initially by dissolve oxygen (Singh *et al.*, 1970). The calculated thermodynamic parameters at 40 °C are given below.

Specific Rate Constant

$(k_r) \times 10^3$ mole lit ⁻¹ min ⁻¹	ΔE^\ddagger kcal/mole	ΔS^\ddagger e.u.	ΔF^\ddagger kcal/mole	A mole ⁻¹ lite sec ⁻¹ .
4.00	34.78	39.52	22.41	7.67×10^{21}

In the present study of oxidation of D-mannose by ammoniacal Cu(II) the activated state will be less polar caused by the reactants $\text{Cu}(\text{NH}_3)_2^{2+}$ and the enolate anion. The increase in entropy is due to desolvation of the activated state than the reactant. Formic acid and arabonic acid are confirmed as the main oxidation products.

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