Kinetics & Mechanism of Oxidation of Maltose & Cellobiose by Alkaline Mercuric Iodide (Nessler's Reagent)

M.P. SINGH, R.K. SINGH, A.K. SINGH & AMITA SRIVASTAVA
Department of Chemistry, Allahabad University, Allahabad 211002

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The kinetics of oxidation of maltose and cellobiose by Nessler's reagent in alkaline medium, has been investigated. The reaction rate is completely independent of initial [Hg(II)] and is first order with respect to reducing [sugar]. The reaction rate following first order kinetics at low [OH-], tends to be zero order at higher [OH-]. The reaction rate is appreciably retarded with increasing iodide ion concentrations. In the case of each reducing sugar the reaction proceeds after a slight induction period. A general mechanism involving intermediate enediol has been proposed taking HgI₂ as the reacting species.

EARLIER, Singh et al. studied the kinetics of oxidation of some reducing sugars by potassium hexacyanoferrate(III), Cu(II) and Ag(I) in alkaline medium. Goswami et al. studied, from an analytical point of view, the oxidation of various organic compounds by Nessler's reagent (HgI₂) in aqueous alkaline media. Littler and Halpern studied the oxidation of cyclohexanone and carbon monoxide using mercuric ion as an oxidant in acidic media and postulated a two-electron transfer process. Hg(0) produced was converted into Hg²⁺ by Hg⁺ rendering the system homogeneous. The present study has been undertaken to delineate the mechanism of oxidation of maltose and cellobiose by Nessler's reagent and to find out the heterogeniety of the Hg(0) produced in the system. The results have been further analysed in detail in order to find out the similarities between this system and the silver ammonia complex system.

Materials and Methods
Maltose (Riedel), cellobiose (A R, BDH), mercuric chloride (A R, BDH), potassium thiocyanate (A R, BDH), NaOH (E. Merck) and KI (E. Merck) were used as such. Sugar solutions and potassium iodide solution were always prepared fresh. The stock solution of potassium thiocyanate prepared in distilled water was standardised according to Volhard's method.

The complex (K₂HgI₄) was first prepared by mixing the solutions of potassium iodide and mercuric chloride in stoichiometric ratio followed by the addition of the requisite amount of sodium hydroxide and potassium chloride solutions. Aliquots (10 ml each) of the above reaction mixture were taken separately and thermostated. The reaction was initiated by adding the requisite volume of reducing sugar solution to the above aliquots at one-minute intervals. The progress of the reaction was followed by estimating the amount of Hg(0) produced after definite intervals of time. The mercury produced was filtered, washed carefully to remove all the other impurities, dissolved in nitric acid and this solution boiled to drive off nitrous fumes produced during the formation of mercuric nitrate. The conical flask containing mercuric nitrate solution was cooled below 10°C and Hg²⁺ estimated volumetrically by titrating against standard potassium thiocyanate solution (Volhard's method) using ferric alum as an indicator.

Results and Discussion
The oxidation of these reducing sugars by Nessler's reagent in an aqueous alkaline medium started after a slight induction period but became independent of [oxidant] for a while followed by a gradual decrease in the later part of the reaction.

The results on the effect of varying [Hg(II)] on the reaction rate (Table 1) show that the initial velocity (−dc/dt) is constant at a particular temperature for various initial [Hg(II)], except at very low [Hg(II)], indicating zero order with respect to [Hg(II)]. The initial velocity has been calculated at a definite time for different kinetic runs by plotting the concentration of remaining Hg(0) produced in the system. The results have been further analysed in detail in order to find out the similarities between this system and the silver ammonia complex system.

First order kinetics in the case of each reducing sugar is quite evident from Table 2 where −dc/dt values are increasing in direct proportion with the increase in [sugar]. The constancy of −(dc/dt)/[sugar] provides additional support for the first order kinetics with respect to maltose and cellobiose. The dependence of the reaction rate on [OH⁻], shown graphically in Fig. 1, shows that at low [OH⁻], the reaction rate follows first order kinetics and becomes almost independent at higher [OH⁻].
TABLE 1 — EFFECT OF VARYING [Hg(II)] ON THE REACTION RATE AT 30°

<table>
<thead>
<tr>
<th>[HgCl₄] x 10⁻⁴ (M)</th>
<th>dc / dt x 10⁻⁶ (mol lit⁻¹ min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>4.73</td>
</tr>
<tr>
<td>1.00</td>
<td>4.00</td>
</tr>
<tr>
<td>0.80</td>
<td>5.00</td>
</tr>
<tr>
<td>0.60</td>
<td>4.81</td>
</tr>
<tr>
<td>0.50</td>
<td>4.32</td>
</tr>
<tr>
<td>0.40</td>
<td>4.12</td>
</tr>
<tr>
<td>0.25</td>
<td>3.54</td>
</tr>
</tbody>
</table>

TABLE 2 — EFFECT OF VARYING [SUGAR] ON THE REACTION RATE AT 30°

<table>
<thead>
<tr>
<th>Maltose x 10⁻² M⁻¹</th>
<th>dc / dt x 10⁻⁶ (mol lit⁻¹ min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>2.22</td>
</tr>
<tr>
<td>1.00</td>
<td>4.66</td>
</tr>
<tr>
<td>1.50</td>
<td>8.11</td>
</tr>
<tr>
<td>2.00</td>
<td>11.76</td>
</tr>
<tr>
<td>2.50</td>
<td>16.66</td>
</tr>
<tr>
<td>3.00</td>
<td>20.51</td>
</tr>
<tr>
<td>4.00</td>
<td>24.44</td>
</tr>
</tbody>
</table>

Also observed that the velocity goes on decreasing with increasing [I⁻] (Fig. 2).

Before proceeding to a mechanism for the reaction, it is essential to go into the details of the formation of the Nessler's reagent. The reaction between the iodide ion and the Hg(II) may proceed by reaction (1).

\[
\text{Hg}^{2+} + 4 \text{I}^- \rightarrow \text{HgI}_4^{2-} \quad \ldots (1)
\]

Since, [I⁻] has always been kept four-times greater than [Hg(II)], the main species existing would be HgI₄²⁻. However, existence of HgI₃ has also been reported. According to Moeller, in the presence of excess I⁻ the formation of halo complexes other than HgI₃ and HgI₂⁻ can be ruled out. Thus, it is quite plausible and justifiable to assume that the total Hg(II) in alkaline solution containing excess iodide ions exists as HgI₃⁻ and HgI₂⁻. Kinetically it appears that there should be an equilibrium of the type shown in Eq. (2).

\[
\text{HgI}_3^- + \text{I}^- \rightleftharpoons \text{HgI}_2^- \quad \ldots (2)
\]

![Fig. 1](image1.png) — Plots of \( \frac{dc}{dt} \) against [NaOH] at 30°C. (A) [HgCl₄] = 1.0 x 10⁻⁴ M, [NaOH] = 5.0 x 10⁻⁴ M, [Maltose] = 1.0 x 10⁻⁴ M; [KI] = 10.0 x 10⁻⁴ M, [Maltose] = 1.0 x 10⁻⁴ M, [KI] = 0.2 M, (B) [HgCl₄] = 0.5 x 10⁻⁴ M, [NaOH] = 5.0 x 10⁻⁴ M, [Maltose] = 1.0 x 10⁻⁴ M, [Cellobiose] = 1.0 x 10⁻⁴ M, [KF] = 0.2 M.

![Fig. 2](image2.png) — Plots of \( k_a \) against [KI] at 30°. (A) [HgCl₄] = 1.0 x 10⁻⁴ M, [NaOH] = 5.0 x 10⁻⁴ M, [Maltose] = 1.0 x 10⁻⁴ M, [KI] = 10.0 x 10⁻⁴ M, [Maltose] = 1.0 x 10⁻⁴ M, [NaOH] = 5.0 x 10⁻⁴ M, [Cellobiose] = 1.0 x 10⁻⁴ M, [KF] = 0.2 M.

Due to greater stabilities of HgI₃⁻ and HgI₂⁻, it appears that free mercuric ions are negligible.

The retarding effect of the I⁻ indicates that it is Hgl⁻ which is actually acting as an oxidising agent and that HgI₂⁻ is stable towards reduction.

From Eq. (2), the total mercury(II) at any time would be given by Eq. (3).

\[
[Hg(II)] = \frac{[Hg(I)]}{1 + K [I^-]} \quad \ldots (3)
\]

Substituting the value of [HgI₂⁻] from Eq. (2) the value of [HgI₃] becomes,

\[
[HgI_3] = \frac{[Hg(II)]}{1 + K [I^-]} \quad \ldots (4)
\]

In the light of these facts a probable scheme of oxidation might be formulated as comprising steps (I—III).

\[
\text{S} + \text{OH}^- \xrightarrow{k_1} \text{E}^- + \text{H}_2\text{O} \quad \ldots (I)
\]

\[
\text{E}^- + \text{H}_2\text{O} \xrightarrow{k_2} \text{E} + \text{OH}^- \quad \ldots (II)
\]
\[
E + HgL^- \xrightarrow{k_3} \text{Hg(II)} + \text{other reaction products (III)}
\]

In steps (I-III), S, E\(^{-}\) and E represent the reducing sugar, enediol anion and the enediol respectively. In this scheme of oxidation it has been assumed that it is the enediol which is being attacked by HgL\(^{-}\) in a fast reaction. Considering this to be a plausible scheme of oxidation, the final rate law in terms of the total Hg(II) is given by Eq. (5).

\[
\frac{d[Hg(II)]}{dt} = \frac{a[S][OH^-][Hg(II)]}{b[OH^-] + bk[OH^-][I^-] + c[Hg(II)]}\quad \ldots (5)
\]

where \(a = k_1k_2k_3\); \(b = k_1k_{2-}\) and \(c = (k_{-1} + k_2)k_3\).

Equation (5) apparently explains the observed kinetics. Initially if the inequality,

\[c[Hg(II)] \geq b[OH^-] (1 + k[I^-])\]

holds good, then Eq. (5) reduces to,

\[
\frac{d[Hg(II)]}{dt} = \frac{k_1k_2}{(k_{-1} + k_2)} [S][OH^-]\quad \ldots (6)
\]

Equation (6) clearly shows a zero order kinetics with respect to [Hg(II)] in the initial part of the reaction. However, as the [Hg(II)] decreases with time in a particular run the term \(c[Hg(II)]\) also decreases in the denominator with simultaneous increase in the term \(b[OH^-] (1 + k[I^-])\) due to increasing [I\(^{-}\)] available to the loss of HgL\(^{-}\) in the reaction. Under such conditions the above inequality will not hold good and hence reaction would not follow zero order kinetics with respect to [Hg(II)] in the later part of the reaction.

Similarly at higher [OH\(^{-}\)] the presumed inequality \(c[Hg(II)] \geq b[OH^-] (1 + k[I^-])\) does not appear to be valid one and hence the [OH\(^{-}\)] would retard the reaction velocity which is actually the case.

Induction period is due to some time lag in reaching the steady state conditions for the concentration of the enediol through which oxidation of disaccharides is taking place.

In alkaline medium it has been established that the reducing sugars give enediol and enediol-anions\(^{5,10}\). The catalysis of [OH\(^{-}\)] in the oxidation of these sugars indicates that the oxidation of these sugars is taking place in their enediol form.

Acknowledgement

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References

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