

KINETICS AND MECHANISM OF OXIDATION OF D-FRUCTOSE BY NESSLER'S REAGENT

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A study is reported of the Hg(II) oxidation of D-fructose in aqueous alkaline medium. The reaction showed a first order dependence with [reducing sugar] and $[\text{OH}^-]$ and is independent of $[\text{Hg(II)}]$. The reaction rate is inversely proportional to $[\text{I}^-]$. A mechanism has been proposed taking HgI_3^- as the reacting species.

Keywords : Kinetics; Mechanism; Oxidation; D-Fructose; Nessler's Reagent

INTRODUCTION

GOSWAMI *et al.* (1935, 1936, 1937) have studied, from an analytical point of view, the oxidation of a number of organic compounds by Nessler's reagent (HgI_4^{2-}) in aqueous alkaline medium. Singh *et al.* (1977) were the first to examine the kinetic features of oxidation of formaldehyde by Nessler's reagent. Recently, Singh *et al.* (1978) have also studied the kinetic features of oxidation of D-galactose with Nessler's reagent in aqueous alkaline medium. In the present study, the authors have carried out the oxidation of D-fructose by Nessler's reagent in aqueous alkaline medium. The details of the results are presented and accordingly a reaction mechanism has been suggested.

EXPERIMENTAL

All the chemicals used were of analar (BDH) grade. A fresh standard solution of potassium iodide was used so that the solution may be free from iodine. The standard solution of sugar was prepared in distilled water. The stock solution of potassium thiocyanate was prepared in distilled water and standardised according to Volhard's method (Vogel, 1962).

The experimental procedure consisted of preparing the complex (K_2HgI_4) by mixing the solutions of known volume of potassium iodide and mercuric chloride. The standard solution of potassium chloride was used to keep the ionic strength constant. The reactants were equilibrated with an accuracy of $\pm 0.1^\circ$. 10 ml portions of the reaction mixture were taken in different conical flasks and after adding 10 ml

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of reducing sugar solution to each flask at an interval of one minute, which was also counted while recording the time, the progress of the reaction was followed by estimating the amount of Hg(O) produced after definite time intervals. The mercury produced was filtered and washed carefully to make free from all other contents. This mercury was dissolved with the help of nitric acid. The solution was boiled to drive off nitrous fumes. Then the conical flask containing mercuric nitrate solution was cooled below 10 °C. The titration was carried out to estimate the Hg²⁺ with the help of standard solution of potassium thiocyanate (Volhard's method) using ferric alum as an indicator.

RESULTS AND DISCUSSION

Details of the kinetic data for the rate of oxidation of D-fructose are presented in Tables I-V. The ionic strength of the medium was kept constant ($\mu = 0.50$) with potassium chloride.

TABLE I
Reaction feature with respect to Hg(II) at 30 °C

$[\text{HgCl}_2] = 2.0 \times 10^{-3}\text{M}$, $[\text{KI}] = 1.0 \times 10^{-3}\text{M}$, $[\text{NaOH}] = 2.0 \times 10^{-2}\text{M}$, $[\text{D-fructose}] = 4.0 \times 10^{-2}\text{M}$, $[\text{KCNS}] = 1.0 \times 10^{-2}\text{M}$.									
Time (min)	2	4	6	8	10	15	20	30	60
KCNS (ml)	0.48	0.96	1.42	1.86	2.32	3.48	4.68	6.72	6.96
$k_0 \times 10$	2.40	2.40	2.30	2.20	2.30	2.32	2.40	0.20	0.08

TABLE II
Effect of varying [Hg(II)] on the reaction rate at 30 °C.

$[\text{KI}] = 1.0 \times 10^{-3}\text{M}$, $[\text{NaOH}] = 2.0 \times 10^{-2}\text{M}$, $[\text{D-fructose}] = 4.0 \times 10^{-2}\text{M}$						
$[\text{HgCl}_2] \times 10^3 \text{ M} = 1.0$		2.0	4.0	6.0	8.0	10.0
$k_8 \times 10^5 \text{ M min}^{-1} = 5.0$		6.0	7.5	8.30	8.30	8.50

TABLE III
Effect of hydroxide ion concentration on the reaction rate at 30 °C

$[\text{KI}] = 1.0 \times 10^{-3}\text{M}$, $[\text{HgCl}_2] = 4.0 \times 10^{-3}\text{M}$, $[\text{D-fructose}] = 4.0 \times 10^{-2}$							
$[\text{NaOH}] \times 10^{-2}\text{M} =$	0.5	0.7	1.0	1.5	2.0	2.5	3.0
$k_8 \times 10^5 \text{ M min}^{-1} =$	1.5	1.7	3.4	5.1	7.5	8.8	10.7
$\frac{k_8 \times 10^3}{[\text{NaOH}]} \text{ min}^{-1} =$	3.0	2.43	3.40	3.40	3.75	3.52	3.57

TABLE IV
Effect of variation of substrate on the reaction rate at 30 °C

$[\text{KI}] = 1.0 \times 10^{-3}\text{M}$, $[\text{HgCl}_2] = 4.0 \times 10^{-3}\text{M}$, $[\text{NaOH}] = 2.0 \times 10^{-2}\text{M}$					
$[\text{D-fructose}] \times 10^2 \text{ M} = 1.0$		1.5	2.0	2.5	3.0
$k_8 \times 10^5 \text{ M min}^{-1} = 1.8$		2.8	3.5	4.7	5.4
$\frac{k_8 \times 10^3}{[\text{D-fructose}]} \text{ min}^{-1} = 1.80$		1.86	1.75	1.88	1.80

TABLE V
Effect of iodide ion concentration on the reaction rate at 30°C

[HgCl ₂] = 4.0 × 10 ⁻³ M, [NaOH] = 2.0 × 10 ⁻² M, [D-fructose] = 4.0 × 10 ⁻³ M						
[KI] × 10 ³ M	=	1.0	1.50	2.0	2.5	3.0
k _s × 10 ⁶ M min ⁻¹	=	7.5	6.80	6.50	6.17	5.30

In order to avoid the possible intervention of the products, the initial reaction velocity ($-dc/dt$) was calculated from a linear plot of [Hg(II)] (in terms of KCNS) against time. The initial ($-dc/dt$) values at different initial [Hg(II)] are listed in Table II and show the reaction rate to be practically independent of [Hg II].

Table III shows that the values of k_s in the case of hydroxide ion increase in direct proportion with the increase in [OH⁻] and as such, when divided by the corresponding [OH⁻], a fairly constant value is obtained. In other words, the reaction is of the first order with respect to the alkali. Table III confirms the above findings.

Table IV indicates that on dividing the values of k_s by [reducing sugar], practically constant values are obtained. This leads to the conclusion that the reaction follows the first order kinetics with respect to [reducing sugar].

The oxidation kinetics have been found to depend on the [I⁻]. Table V shows that the k_s values decrease with its increasing concentration i.e., it suggests an approximate inverse proportionality of the reaction rate on [I⁻]. A gradual decrease in the zero order rate constant has also been observed with progress in the reaction in a particular run (Table I) and has been attributed to the retarding effect of iodide ion.

Before presenting the probable oxidation scheme, it is necessary to know the probable species of Nessler's reagent. According to Moeller (1963) there cannot be the formation of halo complexes other than HgI₃⁻ and HgI₄²⁻ in the presence of excess of iodide ions (iodide ion concentration was always kept greater than four times the [Hg(II)]). Thus, it is quite possible that the total Hg(II) in alkaline solution containing excess of iodide ions exists as HgI₃⁻ and HgI₄²⁻. Kinetically, it appears that there should be equilibrium of the type shown in equation (1):



Due to greater stability of species HgI₃⁻ and HgI₄²⁻, it appears that free mercuric ions are negligible.

The retarding effect of iodide ion indicates that the main oxidising species is HgI₃⁻ and that HgI₄²⁻ is resistant to reduction.

From equation (1), total [Hg(II)]_T at any time would be :

$$[\text{Hg(II)}]_T = [\text{HgI}_3^-] + [\text{HgI}_4^{2-}] \quad \dots(2)$$

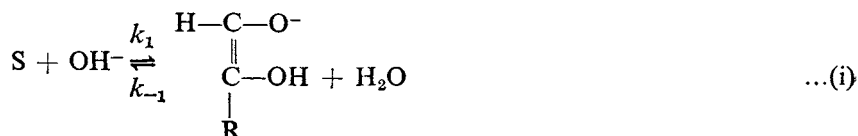
provided there are no free Hg²⁺ ions.

Substituting the value of $[\text{HgI}_4^{2-}]$ from equation (1), the value of $[\text{HgI}_3^-]$ becomes :

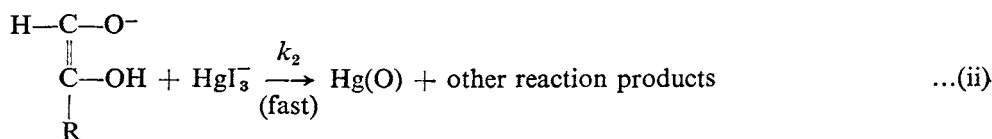
$$[\text{HgI}_3^-] = \frac{[\text{Hg(II)}]_T}{1 + K[\text{I}^-]} \quad \dots(3)$$

Thus, on the basis of the above experimental findings, the probable reaction mechanism shown in Scheme 1 may be proposed.

Scheme 1 :



1, 2 enediol anion (E^-)

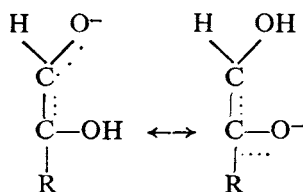


In the above scheme, it has been assumed that enediol anion instead of enediol being attacked by HgI_3^- in the fast process of the oxidation step. Now considering the steady state conditions for the concentration of (E^-), the final rate law in terms of total $[\text{Hg(II)}]$ would be :

$$-\frac{d[\text{Hg(II)}]}{dt} = \frac{k_1[s][\text{OH}^-][\text{Hg(II)}]_T}{k_{-1}/k_2[\text{H}_2\text{O}]\{1 + K[\text{I}^-]\} + [\text{Hg(II)}]_T} \quad \dots(4)$$

The derived rate law (4) is in complete agreement with the observed kinetics. It explains first order kinetics with respect to reducing sugar and hydroxide ion and retarding effect of iodide ion. At higher $[\text{Hg(II)}]$ inequality $k_{-1}/k_2[\text{H}_2\text{O}]\{1 + K[\text{I}^-]\} \ll [\text{Hg(II)}]_T$ will exist and hence the reaction rate becomes independent of $[\text{Hg(II)}]$. Further in a particular run, as $[\text{Hg(II)}]$ is decreasing with time, the factor $k_{-1}/k_2[\text{H}_2\text{O}]\{1 + K[\text{I}^-]\}$ is increasing due to gradual liberation of iodide ions. The above inequality will not exist and hence zero order kinetics will not be observed in the later part of the reaction (Table I).

The formation of hypothetical enediol as an intermediate in the interconversion of reducing sugar was first suggested by Wohl and Neuberger (1900), Nef (1941), Evans (1929), and Lewis (1928). However, Bamford and Collins (1950) have reported two types of enolate anions in the tautomeric equilibrium of reducing sugars in strongly alkaline solutions, as shown below :



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