

Mechanism of Hg(II) Oxidation of D-Galactose in Alkaline Medium

M. P. Singh, A. K. Singh, and Mandhir Kumar

Chemical Laboratories, University of Allahabad, Allahabad-211002, India

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D-Galactose, Nessler's Reagent

The present paper deals with the kinetics of oxidation of D-galactose by Nessler's reagent in alkaline medium. The reaction is zero order with respect to Hg(II) and first order with respect to reducing sugar. The direct proportionality of the reaction rate at low hydroxide ion concentrations shows retarding trend at higher concentrations. The reaction rate is inversely proportional to iodide ion concentration. A mechanism has been proposed taking HgI_3^- as the reacting species.

Introduction

In this laboratory, Singh *et al.* studied the kinetics and mechanism of oxidation of reducing sugars by potassium ferricyanide [1], Cu(II) [2] and Ag(I) [3] in alkaline medium. They have shown the rate of enolization is the rate of oxidation. Goswami *et al.* [4] 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. In the present communication, we are reporting the kinetics and mechanism of oxidation of D-galactose by Nessler's reagent in the presence of sodium hydroxide.

Experimental

All the chemicals used were of AnalaR (BDH) grade. A freshly prepared standard solution of potassium iodide was used so that the solution may be free from iodine. The standard solution of sugar was freshly prepared in distilled water. The stock solution of potassium thiocyanate was prepared in distilled water and standardised according to Volhards' method [5].

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 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 Hg^{2+} with the help of standard solution of potassium thiocyanate (Volhards' method) using ferric alum as an indicator.

Results and Discussion

The oxidation of D-galactose by Nessler's reagent in aqueous alkaline medium was investigated at different initial concentrations of the reactants ($u = 0.50$). Table I shows that $(-dc/dt)$ values are practically independent of Hg(II) concentrations.

Table I. Effect of varying Hg(II) concentration on the reaction rate at 30°C .

$[\text{KI}] = 1.0 \times 10^{-1} \text{ M}$, $[\text{NaOH}] = 4.0 \times 10^{-2} \text{ M}$, $[\text{D-galactose}] = 4.0 \times 10^{-2} \text{ M}$, $[\text{HgCl}_2] \times 10^3 \text{ M} = 1.0, 2.0, 3.0, 5.0, 7.5, 10.0$ $(-dc/dt) \times 10^5 \text{ M min}^{-1} =$
3.60, 3.65, 3.75, 4.00, 4.76, 5.00

The typical kinetic run is shown in Fig. 1 (A), in which the remaining Hg(II) is plotted against time. The straight line obtained demonstrates the zero order kinetics whereas the slight deviation from the straight line is attributed to the retarding effect of iodide ion. The pseudo first order kinetics with respect to reducing sugar is quite explicit from Fig. 1 (B). The exact dependence of the reaction rate on hydroxide ion concentration is shown graphically in Fig. 2 (A), which shows that at low hydroxide ion concentration levels, the reaction rate follows first order dependence and becomes independent at higher concentrations. A plot of k_s against inverse of iodide ion concentration gives a straight line with an intercept on Y-axis (Fig. 2 (B)). This indicates that reaction rate is inversely proportional to iodide ion concentration.

Requests for reprints should be sent to Dr. M. Kumar, 51, International House, Allahabad University, Allahabad, India.

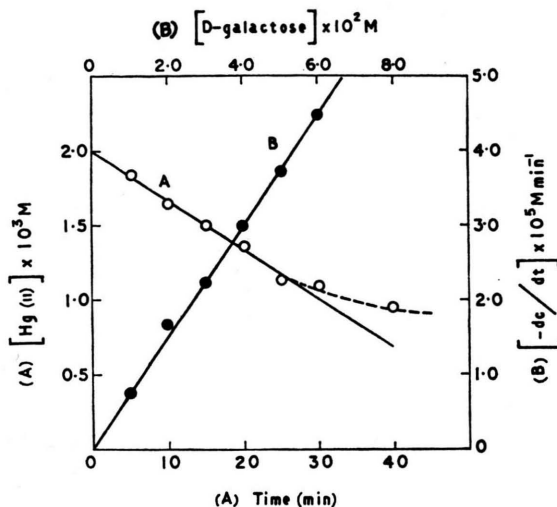


Fig. 1. (A) Reaction feature with respect to Hg(II) at 30 °C. [HgCl₂] = 2.0 × 10⁻³ M, [KI] = 1.0 × 10⁻¹ M, [NaOH] = 4.0 × 10⁻² M, [D-galactose] = 4.0 × 10⁻² M. (B) Effect of Varying D-galactose concentration on the reaction rate at 30 °C. [KI] = 1.0 × 10⁻¹ M, [HgCl₂] = 4.0 × 10⁻³ M, [NaOH] = 4.0 × 10⁻² M.

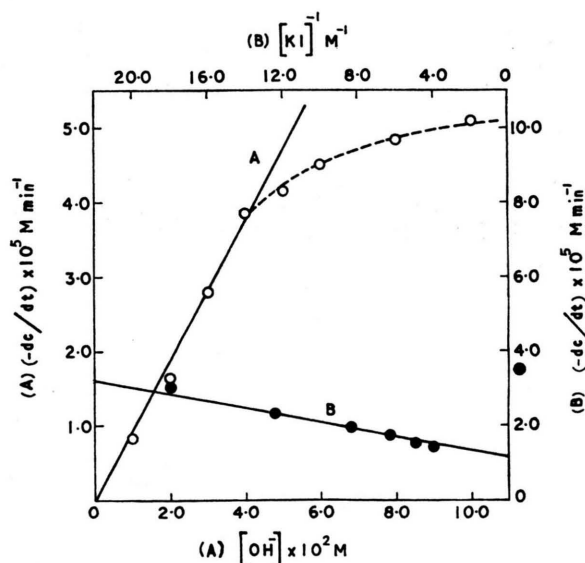
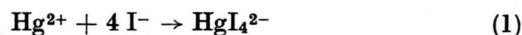


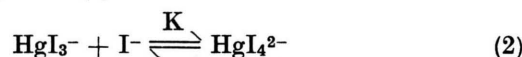
Fig. 2. Effect of varying hydroxide ion and iodide ion concentration on the reaction rate at 30 °C.

(A) [KI] = 1.0 × 10⁻¹ M, [HgCl₂] = 4.0 × 10⁻³ M, [D-galactose] = 4.0 × 10⁻² M.
(B) [NaOH] = 3.0 × 10⁻² M, [HgCl₂] = 4.0 × 10⁻³ M, [D-galactose] = 4.0 × 10⁻² M.

Before going to actual mechanism, it is worthwhile to discuss the chemistry of Nessler's reagent. The reaction between iodide ion and Hg(II) might be mentioned as follows.



Since iodide ion concentration was always kept greater than four times the Hg(II) concentration, the main existing species would be HgI₄²⁻. However, existence of species HgI₃⁻ has also been reported. According to Moeller [6] there cannot be the formation of halo complexes other than HgI₃⁻ and HgI₄²⁻ in the presence of excess of iodide ions. 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 (2).



Due to the 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 (2), total [Hg(II)]_T at any time would be

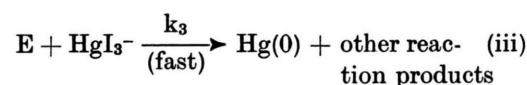
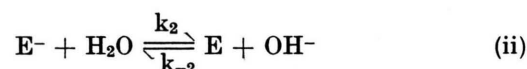
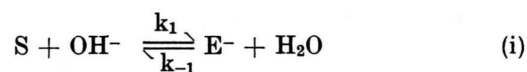
$$[\text{Hg(II)}]_T = [\text{HgI}_3^-] + [\text{HgI}_4^{2-}] \quad (3)$$

provided there are no free Hg²⁺ ions.

Substituting the value of [HgI₄²⁻] from eq. (2), the value of [HgI₃⁻] becomes

$$[\text{HgI}_3^-] = \frac{[\text{Hg(II)}]_T}{1 + K[\text{I}^-]} \quad (4)$$

In the light of these facts, a probable scheme of oxidation might be formulated as follows:



Where S, E⁻ and E represent the reducing sugar, intermediate enediol anion and enediol respectively.

In the above scheme, it has been assumed that enediol instead of enediol anion is being attacked by HgI₃⁻ in the fast process of the oxidation step. Considering this to be plausible scheme of oxidation, the final rate law, in terms of the total Hg(II) concentration, would be

$$-\frac{d[\text{Hg(II)}]}{dt} = \frac{a[\text{S}][\text{OH}^-][\text{Hg(II)}]_{\text{T}}}{b[\text{OH}^-] + bK[\text{OH}^-][\text{I}^-] + c[\text{Hg(II)}]_{\text{T}}} \quad (5)$$

where $a = k_1 k_2 k_3$, $b = k_{-1} k_{-2}$ and $c = k_3 (k_{-1} + k_2)$.

Equation (5) clearly represents the rate equation of the oxidation of D-galactose by Hg(II) in alkaline medium and completely justifies the experimental results. It depicts direct proportionality of the reducing sugar and also first order kinetics at lower hydroxide ion concentration leading to lesser order at higher concentrations. At higher Hg(II) concentration, inequality $b[\text{OH}^-][1 + K[\text{I}^-]] \ll c[\text{Hg(II)}]_{\text{T}}$ will hold good and reaction rate becomes independent of Hg(II) concentration. Further, in a particular run, as the Hg(II) concentration is decreasing with time, the factor $b[\text{OH}^-][1 + K[\text{I}^-]]$ is increasing due to gradual liberation of iodide ions. The above

inequality will not hold good and hence zero order kinetics will not be observed in later part of the reaction (Fig. 1 A).

Evidence of an enediol from the sugars in alkaline solution is afforded by the ability of alkaline sugar solutions to take up large quantities of iodine [7] by observation that sugars are oxidised with cleavage between C₁ and C₂ in alkaline solutions [8] and by the studies of the ultraviolet absorption spectra [9] (which shows a maximum characteristic of dicarbonyl compounds attributed to an enediol). Further, evidence for the formation of an enediol is furnished by the observed ability of alkaline solutions of carbohydrates to decolourize the solution of 2,6-dichlorophenolindophenol [10].

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- [1] M. P. Singh and N. Nath, *J. Phys. Chem.* **69**, 2038 (1965).
 [2] S. V. Singh, O. C. Saxena, and M. P. Singh, *J. Am. Chem. Soc.* **92**, 537 (1970).
 [3] M. P. Singh, H. S. Singh, S. C. Tiwari, K. C. Gupta, A. K. Singh, V. P. Singh, and R. K. Singh, *Indian J. Chem.* **13**, 819 (1975).
 [4] (a) M. Goswami, H. N. Das-Gupta, and K. L. Ray, *J. Indian Chem. Soc.* **12**, 714 (1935);
 (b) M. Goswami and B. C. Das-Purkayastha, *ibid.*, **13**, 73 (1936);
 (c) M. Goswami and A. Shaha, *ibid.* **14**, 208 (1937).
 [5] I. Vogel, *A text book of quantitative inorganic analysis*, Longman's Green & Co. Ltd., 265 and 275 (1962).
 [6] T. Moeller, *Inorganic chemistry, an advanced text book*, Asia Publishing, 865 (1963).
 [7] (a) M. L. Wolfson and M. L. Lewis, *J. Am. Chem. Soc.* **50**, 837 (1928);
 (b) J. H. Simons and H. C. Struck, *ibid.* **56**, 1947 (1934).
 [8] O. Spengler and A. Pfanneustel, *Z. Zuckerind.* **85**, 546 (1933).
 [9] F. Petuely and M. Meixner, *Ber.* **86**, 1255 (1953).
 [10] A. Kusin, *ibid.* **69**, 1041 (1936).