

Kinetic and Thermodynamic Study of Oxidation of Reducing Sugar in Alkaline Medium by Titrimetric Method

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Abstract: The study of oxidation of lyxose by titrimetric technique at different concentration of lyxose, iodine, temperature and pH has been done. The active oxidizing species is hypoiodous acid. The reaction shows that the reaction is of first order kinetics with respect to lyxose and hypoiodous acid but it is zero order kinetics with respect to iodine. The rate of reaction is directly proportional to both hypo iodous acid and lyxose. This study also reveals that iodine in presence of alkalis can serve the purpose of mild oxidant. Thermodynamic parameters have revealed by studying kinetics at different temperatures. The kinetic results propose a suitable mechanism.

Index Terms: Buffer, Hypoiodous acid, Kinetics, Reducing sugar, Thermodynamic Study

Abbreviations: HOI= Hypoiodous acid; I_2 ; K_s = Standard zero order rate constant; K =Specific rate constant; $t_{0.25}$ = Quarter life, T = Temperature

I. INTRODUCTION

The study of carbohydrates is one of the most exciting fields of organic chemistry. Carbohydrates are known to be the energy stores, fuels, and metabolic intermediate in biosynthesis. They also involve in the transport of energy and their derivatives include many important biomolecules that play key roles in the immune system, fertilization, pathogenesis, blood clotting, and development [1]. Energy is stored in the complex molecular structure of the carbohydrates. When we metabolize complex compounds, the atoms arrange themselves back into simple compounds and, in the process, release their stored energy for our use.

Carbohydrates must be burned or oxidized if energy is to be released. A vast amount of literature is available on the kinetics of oxidation of carbohydrates by various organic and inorganic oxidants. Aldonic acids, as primary products of the oxidation of aldoses by bromine, have been extensively studied by Isbell and co-workers. [2],[3],[4],[5],[6]. The kinetics of oxidation of sugars has been subject of extensive research in recent years. This is due to the increasing economic and biological importance of carbohydrate to living organisms. The oxidation of reducing sugar have been carried out in acidic and alkaline medium using such oxidants as transition metals ions, inorganic acids, organometallic complexes and enzymes [7]. Oxidation occurs under different conditions of pH, temperature and ionic strength giving products that depend on the reaction conditions used [8]. The Kinetics and thermodynamics of glucose oxidase catalyzed oxidation reaction of glucose was studied over different reaction conditions [9]. Kinetics and mechanism of Mn (II) catalyzed oxidation of D-Arabinose and D-xylose by chromium(vi) ions in perchloric acid medium was also reported [10]. Oxidation of reducing sugars (Aldo and Keto hexoses) by alkaline potassium ferricyanide was carried out to study kinetics and transformation [11].

The present work shows the kinetics of oxidation of lyxose with an oxidant iodine in alkaline buffer medium with different conditions substrate concentration, oxidant concentration, pH and temperature.

II. EXPERIMENTAL METHOD

A. Materials Used The reagents lyxose, iodine, sodium thiosulphate, potassium chloride, potassium iodide, sulphuric acid, starch indicator were of AR grade and were used without further purification. The stock solution of both oxidant and substrate were freshly prepared using double deionised water.

B. Kinetic Measurements: The requisite volume of buffer solutions of desired pH and its substrate were taken in 100 ml conical flask kept in a thermostat maintained at the desired temperature. To this was added required volume of iodine solution which was maintained at the same temperature of the reaction. The progress of the reaction was determined by withdrawing an aliquot of 5 ml of the reaction mixture at different intervals of time. This was added to solution of 3% H_2SO_4 to check the progress of the reaction. The amount of iodine was estimated with the standard solution of sodium thiosulphate solution and the values obtained were used for the determination of the order of the reaction with respect to oxidant, substrate and pH of alkaline buffer solutions.

III. RESULTS AND DISCUSSION:

A. Effect of substrate concentration: The reaction rate was studied at different concentration of lyxose keeping the concentration of other reactants constant. The result obtained are shown in Table I. A graph was plotted between volume of hypo versus time and recorded as shown in Fig 1. The rates increased as the concentration of the sugar increases (Table I), the increase is almost in direct proportion such that when divided by the corresponding reducing sugar concentration, a fairly constant value was obtained. This indicates that the reactions are first order with respect to the reducing sugar. The plots of k_{obs} against the sugar concentration are linear and passed through the origin (Fig I). This confirms that the reactions are first-order with respect to the sugar.

B. Effect of oxidant concentration: The effect of Iodine concentration was studied in the presence of alkaline solution keeping the concentration of reactant, pH and temperature constant. The results so obtained were recorded in the given Table II & Figure II.

K_s values do not change with rise of the concentration of Iodine appreciably and rate

constant are also not same. This shows that it is a zero order reaction with respect to Iodine.(12)

C. Effect of temperature on oxidation rate: Increase of temperature generally increases the velocity of a chemical reaction. For a homogeneous reaction, the specific rate is approximately double or thrice for each 10^0 rise in temperature. The experiment were carried out at temperatures 288K, 293K, 298K and 303K and the result were given in Table III & Figure III.

D. Effect of pH : The effect of pH on the rate of oxidation of lyxose in different alkaline buffer solutions between pH 9.70 to 12.40 was studied. The pH of buffer solution was measured before each experiment at constant temperature 297^0K and the concentrations of iodine and lyxose are kept constant. The results are recorded in Table IV & Figure IV.

IV. CONCLUSION:

In all the reactions studied, zero order kinetics with respect to iodine has observed. However the reaction velocity is gradually decreasing in the later part of the reaction and the plot of moles of iodine in terms of volume of hypo solution doesn't give a straight line. In the beginning, rate of reaction was fast and found to be directly proportional to the substrate concentration. The maximum oxidation takes place in the vicinity of pH 11. 2. The reaction kinetics has been found in well agreement with thermodynamic activation parameters. The salt effect is nil. Kinetic studies also provide evidence for complex formation between oxidizing species and substrate species. The rate of reaction is retarded by highly alkaline buffer solution after pH 11. 2. HOI from the oxidant species actively participate in the formation of intermediate with substrate at transition state. It has been concluded that the rate of reaction is directly proportional to both hypoiodous acid and Lyxose. This reveals that iodine in presence of alkalis serve as mild oxidant.

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