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KINETICS OF THE OXIDATION OF DULCITOL BY IODINE IN ACIDIC MEDIUM

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ABSTRACT

Kinetics of the oxidation of D-dulcitol by molecular iodine was carried out in acidic medium at λmax 460nm. The reactions were found to be first order in the case of iodine, inverse fractional order with respect to D-dulcitol concentration and first order to [H^+] and independent of ionic strength. Stoichiometric study showed a 1:1 consumption of dulcitol by iodine. Arrhenius parameters obtained were Ea 8.79 kJ mol^{-1}, $\Delta H^{\#}$ 13.27 kJ mol^{-1}, -$\Delta S^{\#}$ 0.24 kJ $mol^{-1}K^{-1}$ and $\Delta G^{\#}$ 84.79 kJ mol^{-1}. A plausible mechanism was proposed based on the fact that the oxidizing specie is the triiodide ion.

Key words: D-dulcitol, Iodine, Kinetics, Mechanism, Tetraoxosulphate (VI) acid.

INTRODUCTION

Iodine is a versatile reagent in organic synthesis as catalyst. It acts as an oxidizing agent and occurs in many oxidation states including iodide (I^-), iodate (IO_3^-) and periodate ions [1]. Iodine has been used to oxidize several substrates among which are alcohols [2-4], divalent sulphur [5], arsenious acid [6], hydrogen peroxide [7].

Dulcitol, otherwise known as galactitol, is a sugar alcohol with slightly sweet taste which can be reduced to galactose by aldose reductase. Excess of dulcitol can cause cataracts [8]. Dulcitol accumulation in the body can also cause hepatosplenomegaly and cognitive dysfunction [9].

Dulcitol can be produced by yeast growth on galactose sugar [10]. It is used for shaping medicine in order to improve the appearance and stability of the tablets. Furthermore, it is used for curing rheumatoid and it is anti-leukemic.

Literature survey showed no report on the kinetics of the oxidation of dulcitol. Hence, as an appraisal to researches on the oxidation of sugar alcohols, this research was to ascertain the kinetics, thermodynamics and mechanism of dulcitol oxidation by iodine in acidic medium.

MATERIALS AND METHODS

All chemicals utilized were of analytical grade and doubly distilled water was used. Stock solutions of iodine, H_2SO_4 and KNO_3 were prepared and placed in a water bath for 30 minutes before any kinetic run. H_2SO_4 (BDH, UK) and KNO_3 (MERCK, UK) were used to study the effect of acidity and ionic strength respectively.

Kinetic measurements were done using UV-1800 Schmadzu (UK) spectrophotometer attached to a cryocool cc-60T compressor, GallenKamp thermostating unit and a Techne circulator C-100 which pumps water from water bath at the required temperature around the cell compartment. For product analysis, FTIR (Agilent Technologies, UK) was utilized.

Kinetic measurement

All kinetic measurements were undertaken via pseudo-first order condition, where the concentration of D-dulcitol was far in excess of iodine concentration at constant temperature, 298K. The measurements of kinetic data were established by monitoring a decrease in absorbance of iodine at λmax 460 nm as a function of time. The reaction components were calculated and mixed in 1cm^3 (3 ml) quartz cell in the following sequence: distilled water, dulcitol, H_2SO_4 and I_2. The kinetic reactions were monitored more than 90% completion. The pseudo first order rate constants (k_1) were obtained from the plot of logarithm of A versus time.

Stoichiometry

Stoichiometry of the reaction was determined by spectrophotometric titration under the conditions used for the kinetic study. Plot of absorbance versus [dulcitol] curve indicated 1:1 consumption of iodine by dulcitol.

RESULTS AND DISCUSSION

Effect of concentration of iodine

The concentration of iodine was varied from $1x10^{-4}$ to $7x10^{-4}$ M and fixing the concentration of dulcitol, H^+ at $3x10^{-2}$ and $3x10^{-3}$M respectively. Ionic strength was fixed at 0.05 M at 298 K. The observed pseudo first order rate constant (k_1) increased with increase in $[I_2]$ (Fig.1). Plot of log k_1 versus log $[I_2]$ showed a first order dependence with respect to $[I_2]$.

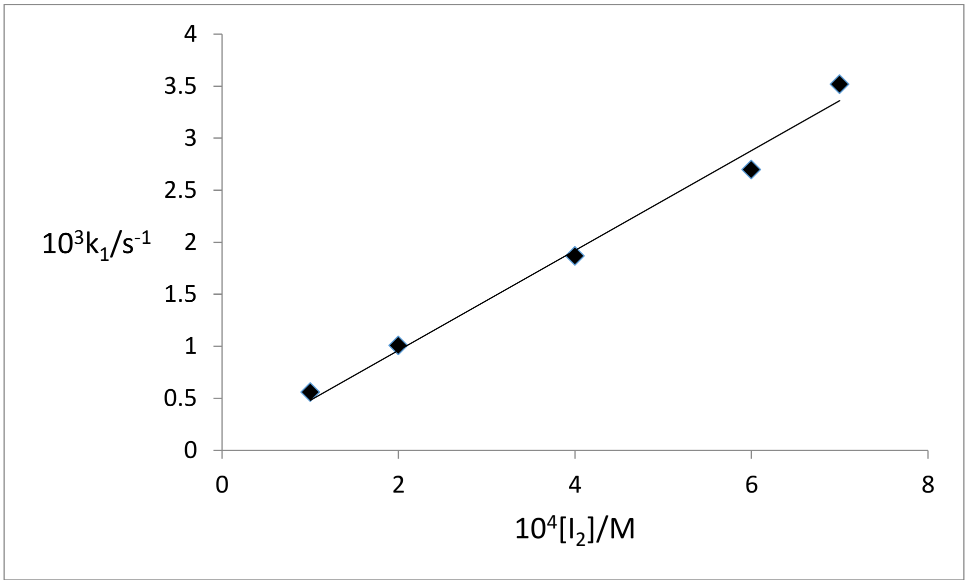


Fig.1: Plot pseudo first order rate constant (k_1) versus $[I_2]$

Effect of concentration of Ducitol

The effect of concentration of dulcitol on the rate of oxidation was studied in the range of $8x10^{-3}$ to $7x10^{-2}$ M and fixing the concentrations of I_2, H^+ at $8x10^{-4}$ and $3x10^{-3}$ M respectively while maintaining ionic strength at 0.05 M at 298 K. The rate of reaction decreased with increase in [dulcitol] (Table1). Fractional inverse order dependence with respect to dulcitol was obtained.

Table 1: Effect of [D-dulcitol]

10^2[Dulcitol]/M	$10^3k_{obs}/s^{-1}$
	D-dulcitol
0.80	5.22
1.00	5.11
2.00	4.23
3.00	3.51
5.00	2.62
7.00	1.68

Effect of concentration of Acid

The dependence of acidity on the rate of reaction was investigated in the concentration range $1x10^{-3}$ – $1x10^{-2}$ and fixing the concentrations of I_2 and dulcitol at $8x10^{-4}$ and $3x10^{-2}$ M respectively and ionic strength, 0.05M at 298K. The reaction was found to be dependent on $[H^+]$ as there was increase in the observed rate constant with increase in $[H^+]$.

Effect of ionic strength

The effect of ionic strength was investigated by varying ionic strength of the reaction mixture from $1x10^{-2}$ to $8x10^{-2}$ M and keeping constant the concentrations of I_2, dulcitol and H^+ at $8x10^{-4}$, $3x10^{-2}$ and $3x10^{-3}$ respectively at 298 K. No appreciable change in the observed pseudo first order rate constant (k_1) with increase in ionic strength was observed [12]. Zero effect of ionic strength on the reaction was observed.

Effect of Temperature

Activation parameters were obtained by studying the effect of temperature on the reaction (Table 2). Concentrations of I_2, dulcitol and H^+ were kept constant at $8x10^{-4}$, $3x10^{-2}$ and $3x10^{-3}$ M respectively, and ionic strength was 0.05 M, while varying the temperature in the range 298 K-328 K.

Table 2: Activation parameters

Sugar alcohol	Ea(kJ mol^{-1})	$\Delta H^{\#}$(kJ mol^{-1})	$-\Delta S^{\#}$ (kJ mol^{-1}K^{-1})	$\Delta G^{\#}$(kJ mol^{-1})
D-dulcitol	8.79	13.27	0.24	84.79

Test for free radicals

2 ml of acrylonitrile was added to 10 ml of reaction mixture and kept in an inert atmosphere for 10 hours and diluted with methanol. No precipitate was formed, indicating absence of free radicals.

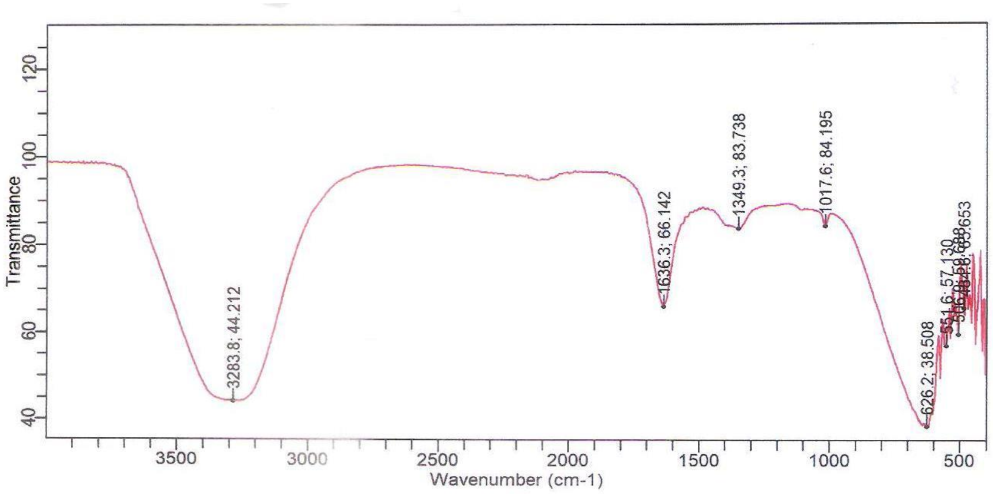


Fig. 2: FTIR Spectrum of the Product

Product Analysis

FTIR analysis of the product showed a very broad band –OH stretching of carboxylic acid at 3400-2400 cm^{-1} and a medium intensity due to C-O stretching attributed to carboxylic acid at 1320-1210 cm^{-1}. Furthermore, the spectrum showed a C=O stretching due to carboxylic acid at 1725-1700 cm^{-1}(Fig.2).

Rate Law

In acidic medium, iodine undergoes hydrolysis to give iodide ions which in turn reacts with free iodine to form triiodide ion. Hence, the oxidizing specie is the triiodide ion. Therefore, the triodide ion complexes with dulcitol which in turn disproportionate to give the products.

$$\text{Dulcitol} + I_3^- \underset{}{\overset{K_1}{\rightleftharpoons}} \text{Complex} \xrightarrow{k_2} \text{Products}$$

$$[I_3^-]_T = [I_3^-] + [\text{Complex}]$$

$$K_1 = \frac{[\text{Complex}]}{[\text{Dulcitol}][I_3^-]}$$

$$[\text{Complex}] = K_1[\text{Dulcitol}][I_3^-]$$

$$[I_3^-]_T = [I_3^-] + K_1[\text{Dulcitol}][I_3^-]$$

$$[I_3^-]_T = [I_3^-](1 + K_1[\text{Dulcitol}])$$

$$\text{Complex} = \frac{K_1[\text{Dulcitol}][I_3^-]_T}{1 + K_1[\text{Dulcitol}]}$$

$$\text{Rate} = k_2[\text{Complex}]$$

$$Rate = \frac{\mathrm{k_2K_1[Dulcitol][I_3^-]_T}}{1 + \mathrm{K_1[Dulcitol]}}$$

$$\text{Where } 1 \ll \mathrm{K_1[Dulcitol]}$$

$$\text{Rate} = k_2\mathrm{[I_3^-]_T}$$

The absorption spectrum of a freshly prepared iodine solution in aqueous medium is usually characterized by λmax at 460 nm, 288 nm and 352 nm. However, if the aqueous solvent is adjusted to pH 2 with an acid, the only observable λ_{max} is at 460nm as observed in this experiment. This could be attributed to hydrolysis of aqueous iodine according to the equations below [11]:

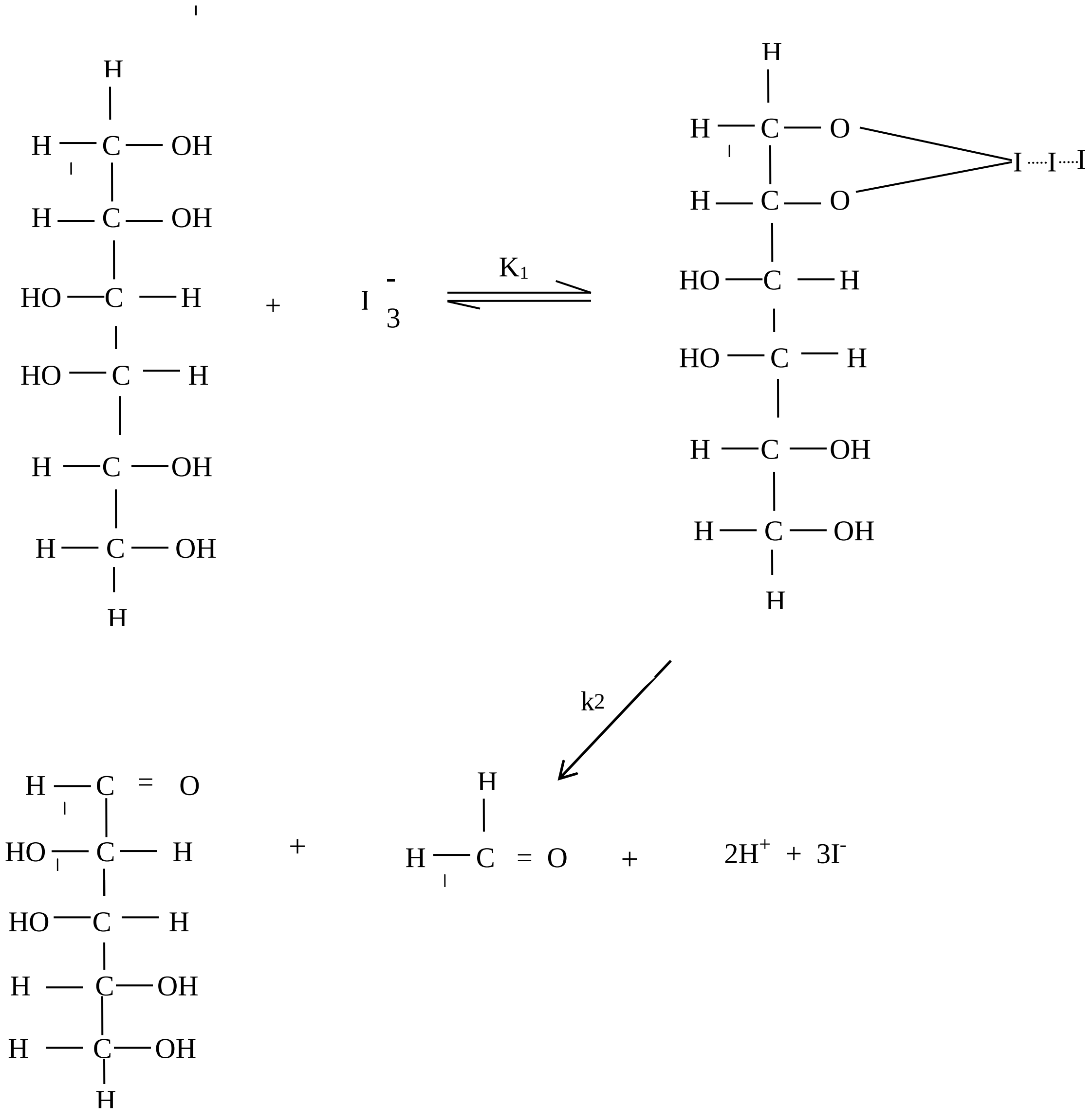
$$I_2(aq) + H_2O \rightleftharpoons H_2IO^+ + I^- \qquad K = 1.20 \times 10^{-11}$$
$$I_2(aq) + H_2O \rightleftharpoons HIO^+ \; I^- + H^+ \qquad K = 5.40 \times 10^{-13}$$
$$3I_2(aq) + 3H_2O \rightleftharpoons IO_3^- + 5I^- + 6H^+ \qquad K = 7.10 \times 10^{-48}$$

In acid medium the specie H_2IO^+ has been suggested as one products of the hydrolysis of iodine, but vague evidence has been reported for its existence [12]. The iodide ion produced in the hydrolysis reacts with aqueous iodine which gave rise to additional λmax in the ultraviolet absorption spectrum of aqueous iodine. The primary reaction between I_2 and I^- in aqueous results in the formation of the triiodide ion I_3^-. An equilibrium is rapidly established as follows:

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \qquad K = 7.45 \times 10^2$$

The oxidizing specie is the triiodide ion I_3^-. Oxidation of dulcitol in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. This indicates that one electron oxidation leading to free radicals is not likely to occur in this reaction and hydrogen abstraction mechanism leading to the formation of free radicals is ruled out. Hydride-ion transfer involves a higher enthalpy of activation compared to the concerted process. The low value of entropy of activation is in favour of concerted process and low value of entropy of activation is indicative of the possibility of the involvement of two hydroxyl groups in the rate determining step[13] . Moreover, the observed negative entropy of activation suggests that as charge separation takes place in the transition state of the rate-determining step, the charge ends become highly solvated which leads to immobilization of a large number of solvent molecules [14]. Relatively low value of $\Delta H^\#$

suggests absence of free radicals in the course of reaction. The overall mechanism is proposed to involve the formation of a complex in a fast pre-equilibrium step which disproportionates in a subsequent step via a cyclic concerted transition state into product.



Scheme 1

CONCLUSION

The oxidation reaction showed an inverse fractional order with respect to dulcitol due to the formation of a stable complex formation which is resistant to oxidation.. The reaction showed a

1:1 consumption of the dulcitol by iodine. Negative entropy of activation revealed an associative mechanism and rigid transition state surrounded by immobilized water molecules.

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