



REACTIVITIES OF SOME ALDOSES TOWARDS IODINE IN ALKALINE AQUEOUS MEDIUM

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The kinetics studies of oxidation of some reducing sugars by aqueous alkaline solution of iodine investigated. Results demonstrated that iodine in the presence of alkali converted into hypoiodous acid which was effective oxidizing species. Reaction between iodine and sugars was slowest reaction. The rate of oxidation of sugars was affected by change in pH of the medium and maximum at pH 11.4 where the concentration of hypoiodous acid was maximum which oxidized the sugars into respective acids. The rate of oxidation followed first order kinetics with respect to substrate and obeyed zero order kinetics with that of iodine. Change in ionic strength of the medium showed no effect on the rate of oxidation indicating that reaction occurred between molecular species and there was no ionic species present in the rate determining step. Reaction was affected by the change in temperature and value of energy of activation corresponding to glucose, galactose, D-mannose and L-arabinose were 10.16 kJ/mol, 12.17 kJ/mol, 14.00 kJ/mol and 20.22 kJ/mol respectively.

Keywords: Reducing sugars, Iodine, pH, Reaction mechanism

1. Introduction

Investigations pertaining to the oxidation of reducing sugars with different oxidizing agents have been widely reported [1-5].

Number of researchers worked on oxidation of D-glucose using alkaline potassium ferricyanide [1], peroxydisulphate [2], alkaline iodine with maltose and lactose [3], chromium (VI) and vanadium (V) [4], a bromide catalyzed oxidation of fructose by Ce (IV) in acidic medium at constant ionic strength followed first order dependent on each fructose and Ce(IV) reported by Sah [5]. Besides the oxidation of D-glucose other reducing sugars also got attention of researchers. Singh et al. [6] reported the kinetics of oxidation of D-galactose and D-ribose by N-bromoacetamide in the presence of ruthenium (III) chloride in perchloric acid medium. Singh [7] and Singh et al. [8] described the mechanistic studies of maltose and lactose by Cu (II) and oxidation of L-arabinose. Xylose and galactose by N- bromosuccinimide in acidic medium by using Pd as a catalyst. Neelu et al. [9] worked on the kinetics of ruthenium (III) catalyzed oxidation of reducing sugars by chloramines in alkaline medium. Badel and coworkers [10] studied periodate oxidation of

sucrose derivative. The oxidation of sugars is first order dependence on substrate concentration. The oxidation of melibiose and cellobiose by alkaline aqueous iodine at different pH were investigated by Singh et al. [11]. The maximum oxidation of both sugars was around at pH 11.4 with first order kinetics.

The present work reports the kinetics of the oxidation of reducing sugars (aldoses) by iodine in alkaline medium under the influence of concentration of sugar, iodine, pH, ionic strength and temperature to establish the mechanism of the reaction. The aim of this study is to investigate the oxidation of L-arabinose, D-mannose, galactose and glucose in aqueous alkaline medium to get more information about oxidation of these sugars. The results so obtained will be explained on the basis of configuration of aldoses. A mechanism consistent with above findings is proposed.

2. Experimental

All the reagents like glucose, galactose, D-mannose, L-arabinose, iodine, potassium iodide, sodium hydroxide, sodium carbonate, hydrochloric acid, sodium hydrogen phosphate, used were of A.R grade (Merck & BDH). Stock aqueous

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solutions of reducing sugars and iodine ($1 \times 10^{-2} \text{ mol dm}^{-3}$) in potassium iodide were freshly prepared. Reaction was studied on a thermostat. The kinetics of reaction was followed by removing aliquots (10ml) from the reaction mixture at different time intervals, and the reaction was stopped by adding 3% cold sulphuric acid. The iodine liberated was immediately titrated against standard sodium thiosulphate solution. pH of reaction in the range of 10.3 to 12.2 were adjusted by using phosphate buffer solution and sodium hydroxide. The first order rate constants were calculated from the slope of log concentration vs. time of sugars and oxidant HOI.

3. Results and Discussion

When iodine was mixed with alkali, three oxidizing species IO^- , HOI and I_3^- were formed and preliminary experiment had indicated that oxidizing agent effective in the reaction between aldoses and iodine in basic medium was free hypoiodous acid which is also supported by earlier work [3,11]. This conclusion has been confirmed in case of four aldoses, i.e. L-arabinose, D-mannose, galactose and glucose by comparing the ratio of oxidation using buffer solutions of pH ranging from 10.3 to 12.2. The concentration of free hypoiodous acid, which was measured by determining the change in concentration of iodine consumed during the reaction. Total concentration of iodine is $[\text{I}_2] = \text{IO}^- + \text{HOI} + \text{I}_3^-$

The equilibrium constant for the hydrolysis of iodine at 25°C is $\text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOI} + \text{H}^+ + \text{I}^-$.

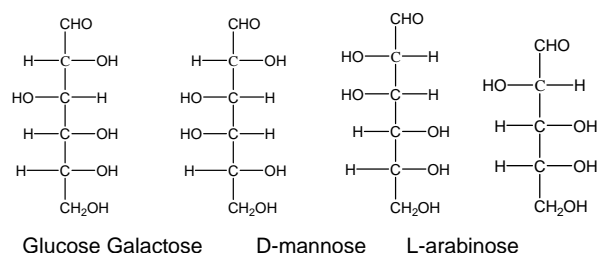
$$K = \frac{[\text{H}^+][\text{I}^-][\text{HIO}]}{[\text{I}_2]} = 3 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_2 = \frac{[\text{I}_2][\text{I}^-]}{[\text{I}_3^-]} = 1.36 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_3 = \frac{[\text{H}^+][\text{OI}^-]}{[\text{HOI}]} = 10^{-11} \text{ mol dm}^{-3}$$

From the values of these three equilibrium constants K , K_2 and K_3 established when iodine mixed with alkali and known concentration of total iodine in any given mixture, it is possible to calculate the concentration of hypoiodous acid. Investigations showed that reactions follows first order reaction rate for each substrate. A plot of log concentration of sugars vs. time is shown in

Figure 1 and results are tabulated in Table 1, slopes determined rate constants. A first order reaction kinetics was observed with respect to sugars. Results showed that glucose and arabinose react with hypoiodous acid at almost the same rate, which may be due to identical in configuration about carbon atoms, 2, 3 and 4.



A comparative study of oxidation of sugars at different pH showed that maximum rate of oxidation of aldoses into aldonic acid takes place at pH 11.4 (Table 2) where maximum concentration of HOI was formed with alkali. The values of rate constant k corresponding to this pH for different aldoses were $11.50 \times 10^{-3} \text{ s}^{-1}$, $5.2 \times 10^{-3} \text{ s}^{-1}$, $5.7 \times 10^{-3} \text{ s}^{-1}$ and $41.0 \times 10^{-3} \text{ s}^{-1}$ for glucose, galactose, D-mannose and L-arabinose, respectively, indicating that rate of oxidation of each aldose was different showing that the configuration of the aldoses chain affected the rate of oxidation at which the sugar oxidized into respective acids (Figure 2). The results are summarized in Table 2.

Results showed that the rate of oxidation of arabinose at pH 11.4 is greater than aldohexoses, which may be due to small chain (5 Carbon) of sugar as compared to other aldohexoses. The plot of rate constant k and pH is shown in Figure 2. The oxidation rate of D-mannose is much smaller than that of glucose. Thus it appears that configuration of the aldoses examined have some bearing on the rates at which they are oxidized by iodine in alkaline medium i.e. hypoiodous acid.

Table 2 shows that the rate of oxidation increases first with the increase of pH and reaches to a maximum value in vicinity of pH 11.40 where the concentration of hypoiodous acid was maximum and then gradually decreased at higher pH range which was probably due to conversion of hypoiodous acid into hypoiodous ion which was slower oxidizing agent as compared to hypoiodous acid.

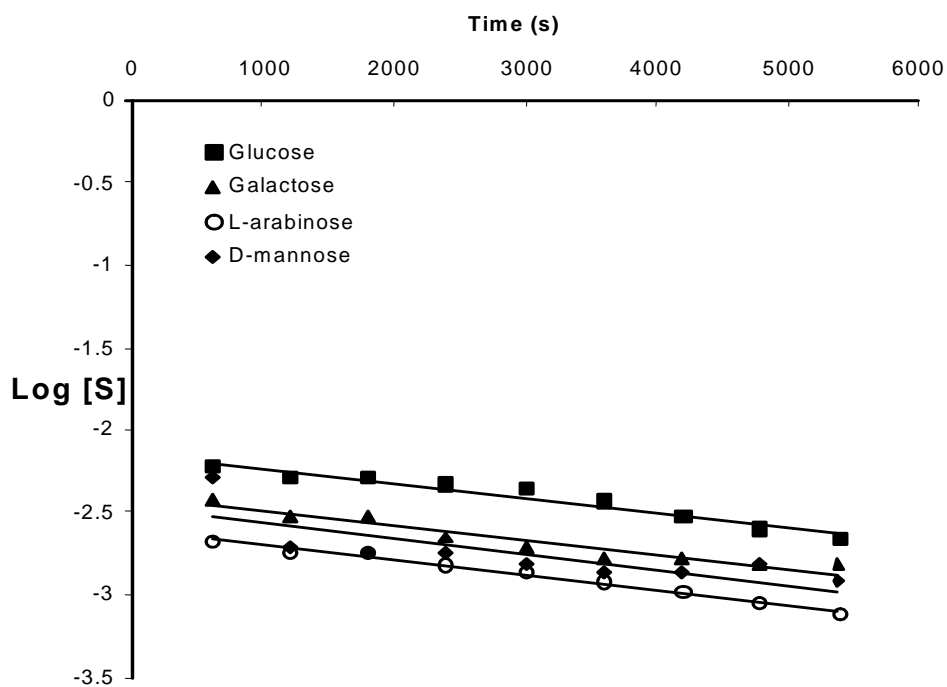


Figure 1. Plot of log of [sugars] vs. time.

Table 1. Effect of concentration of aldoses on the rate of oxidation of sugars.

Temp. = 30°C $[\text{I}_2] = 3 \times 10^{-2} \text{ mol.dm}^{-3}$ pH = 10.1

$[\text{S}] \times 10^2 \text{ mol/dm}^3$	Glucose $k(\text{s}^{-1}) \times 10^2$	Galactose $k(\text{s}^{-1}) \times 10^2$	D-mannose $k(\text{s}^{-1}) \times 10^2$	L-Arabinose $k(\text{s}^{-1}) \times 10^2$
2.0	1.19	4.0	8.12	1.19
2.5	1.19	4.1	8.39	1.20
3.0	1.16	4.5	8.12	1.18
3.5	1.15	4.5	8.22	1.20
4.0	1.15	4.0	8.10	1.20
4.5	1.15	4.1	8.20	1.20
5.0	1.15	4.0	8.20	1.20

where $[\text{S}]$ = sugars concentration.

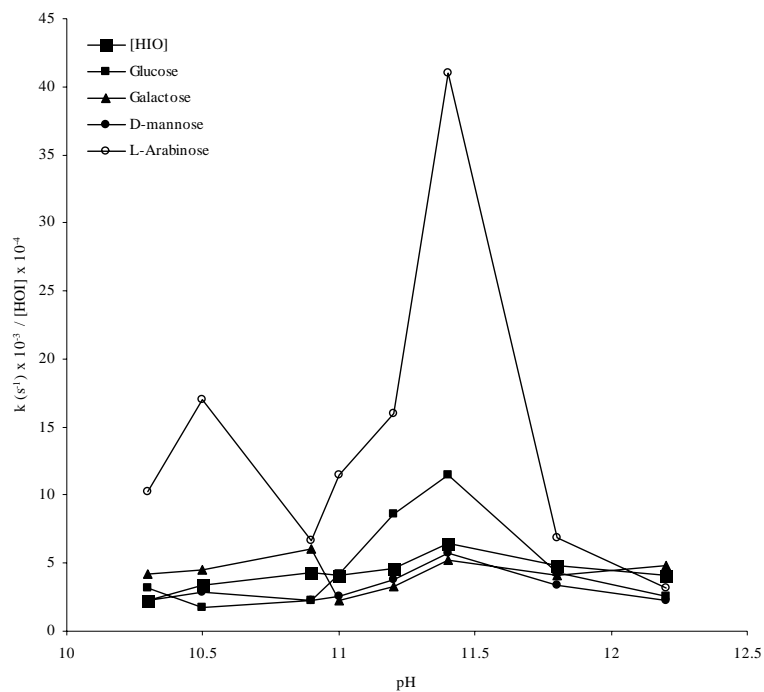


Figure 2. A plot of pH vs $k (s^{-1}) \times 10^3 / [HOI] \times 10^{-4}$.

Table 2. Effect of pH on rate of oxidation of sugars.

$[S] = 3 \times 10^{-3} \text{ mol dm}^{-3}$, $[I_2] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$

$Na_2S_2O_3 \cdot 5H_2O = 3 \times 10^{-3} \text{ mol dm}^{-3}$ Temp. = 30°C.

pH	[HIO] $\times 10^4$	Glucose $k(s^{-1})\times 10^3$	Galactose $k(s^{-1})\times 10^3$	D-Mannose $k(s^{-1})\times 10^3$	L-Arabinose $k(s^{-1})\times 10^3$
10.3	2.21	3.2	4.2	2.3	10.20
10.5	3.4	1.70	4.5	2.9	17.00
10.9	4.3	2.30	4.0	2.3	6.70
11.0	4.1	4.18	2.3	2.6	11.50
11.2	4.6	8.60	3.3	3.8	16.0
11.4	6.5	11.50	5.2	5.7	41.00
11.8	4.8	4.30	4.1	3.4	6.90
12.2	4.1	2.60	4.8	2.3	3.20

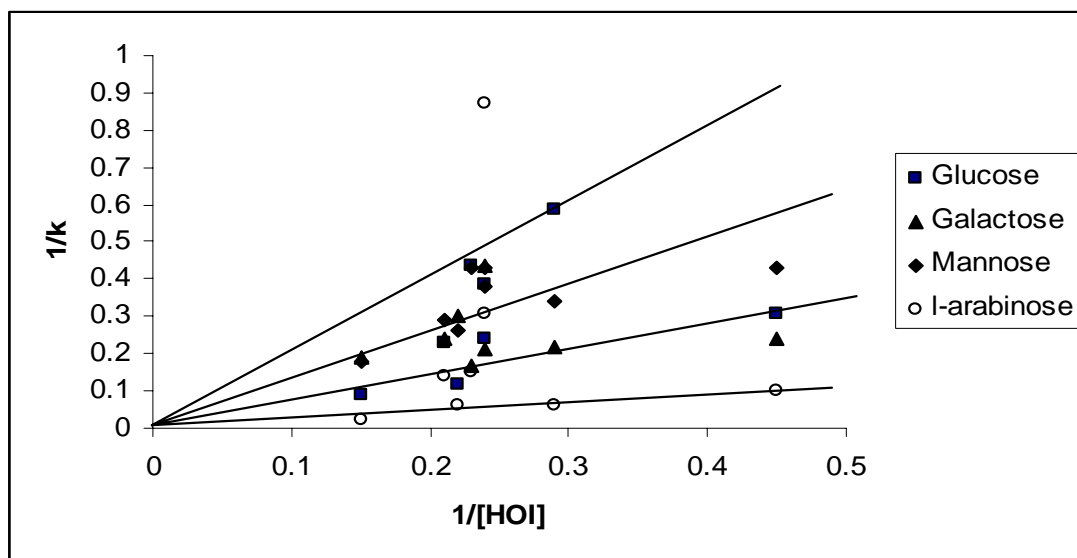


Figure 3: Plot of $1/k_{obs}$ vs. $1/[HIO]$ at $30^{\circ}C$.

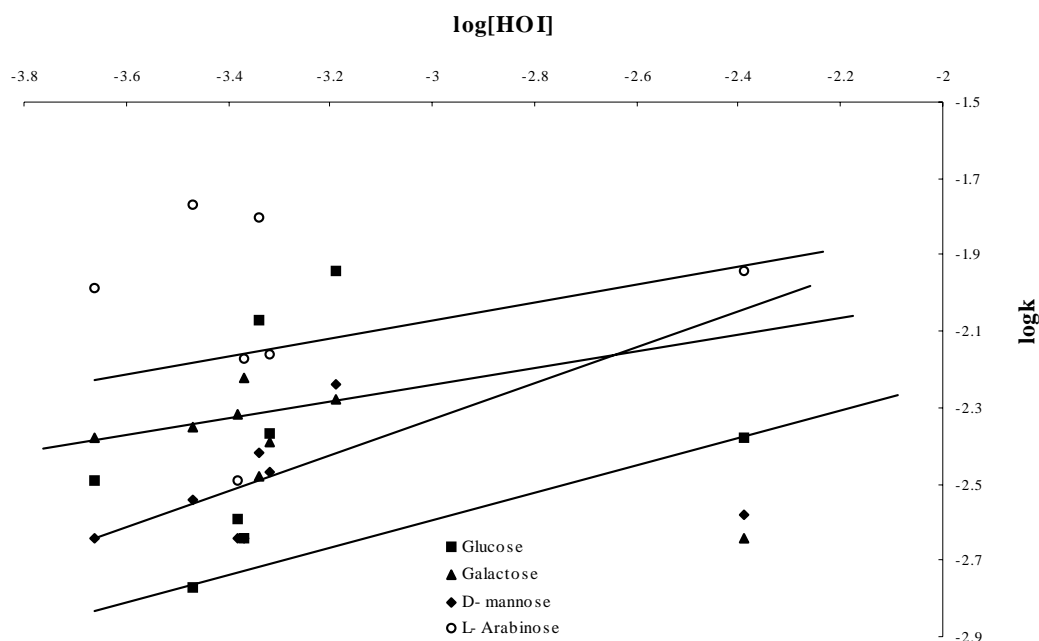


Figure 4: Plot of $\log k_{obs}$ vs. $\log[HIO]$ at $30^{\circ}C$.

The plots for $1/[HIO]$ vs. $1/k_{obs}$ and $\log [HIO]$ vs. $\log k$ are shown in Figures 3 and 4. The linear regression analysis is used for coefficient "R" and found to be 0.5124, 0.482, 0.3766 and 0.8120, galactose, mannose and arabinose respectively.

The plot of $\log k_{obs}$ vs. $\log [HIO]$ is linear for all the three aldohexoses and one aldopentose (Figure 4) in the $[HIO]$ range $2.21 \times 10^{-4} \text{ mol dm}^{-3}$ to $6.5 \times 10^{-4} \text{ mol dm}^{-3}$ with slopes of -0.95 , 0.41 , 0.70 , and 0.33 respectively. Similarly the plot of $1/k_{obs}$ vs.

Table 3. Effect of concentration of iodine on rate of oxidation

Temp = 30° C , pH = 10.1 [s] = 1.92 × 10⁻³ mol dm⁻³

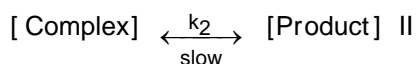
[I ₂] × 10 ³ (Mol/ dm ⁻³)	Glucose k.10 ⁴ mol dm ⁻³ s ⁻¹	Galactose k.10 ⁴ mol dm ⁻³ s ⁻¹	D-mannose k.10 ⁴ mol dm ⁻³ s ⁻¹	L-Arabinose k.10 ⁴ mol dm ⁻³ s ⁻¹
2.0	4.49	3.2	5.35	3.45
3.0	4.49	2.9	5.61	3.33
4.0	4.48	2.8	5.75	3.28
5.0	4.94	2.5	5.74	3.43
6.0	4.31	2.6	5.32	3.41
7.0	4.62	2.6	5.1	3.62
8.0	4.5	2.7	5.1	3.71

1/[HIO] (Figure 3) is also linear with slopes of -0.15, 0.36, 0.17 and 0.21 respectively. These plots showed that oxidation follows first order kinetics with respect to substrate.

The rates of oxidation of sugars at several initial concentrations of iodine were studied and followed zero order kinetics with respect to iodine (Table 3).

4. Reaction Mechanism

On the basis of results the following mechanism is proposed for the oxidation reaction of aldoses with iodine in alkaline medium.



Rate of formation of complex will be given as

$$\frac{d[Complex]}{dt} = k_1[RCHO][HOI] - [k_{-1} - k_2][Complex] \quad (1)$$

At steady state

$$\frac{d[Complex]}{dt} = 0 \quad (2)$$

From equation no (1) and (2) concentration of complex comes out to be:

$$[Complex] = \frac{k_1[RCHO][HOI]}{k_1 + k_2} \quad (3)$$

At steady state, rate of disappearance of HOI may be:

$$-\frac{d[HOI]}{dt} = k_2[Complex] \quad (4)$$

or

$$-\frac{d[HOI]}{dt} = \frac{k_1 k_2 [RCHO][HOI]}{(k_{-1} + k_2)} \quad (5)$$

Now the total [HOI] may be considered as:

$$[HOI]_T = [HOI] + [Complex] \quad (6)$$

Putting the value of complex

$$[HOI]_T = [HOI] + \frac{k_2 [RCHO][HOI]}{(k_{-1} + k_2)} \quad (7)$$

from equation (7) the value of [HOI] comes out

$$[HOI] = \frac{(k_1 + k_2) [HOI]_T}{[k_{-1} + k_2] + k_2[RCHO]} \quad (8)$$

The final rate law from 5 to 8 is

Table 4. Activation parameters.

Sugars	E_a kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J k mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹
Glucose	10.16±0.01	7.68±0.01	-25.50±0.01	6.92±0.01
Galactose	12.17±0.01	9.60±0.02	-25.27±0.01	2.10±0.01
D-mannose	14.02±0.01	11.50±0.01	-24.88±0.02	4.10±0.01
L-arabinose	20.22±0.01	17.00±0.01	-25.56±0.01	10.12±0.01

$$\begin{aligned} -\frac{d[\text{HOI}]}{dt} &= \frac{k_1 k_2 [\text{RCHO}] [k_{-1} + k_2] [\text{HOI}]_T}{\{[k_{-1} + k_2 + k_1] [\text{RCHO}]\} [k_{-1} + k_2]} \\ &= \frac{k_1 k_2 [\text{RCHO}] [\text{HOI}]_T}{[k_{-1} + k_2] + k_1 [\text{RCHO}]} \end{aligned}$$

In present experimental conditions

$$(k_1 + k_2) > k_1 [\text{RCHO}]$$

Hence above equation reduces to

$$\frac{d[\text{HOI}]}{dt} = \frac{k_1 k_2 [\text{RCHO}] [\text{HOI}]_T}{k_{-1} + k_2} = k [\text{RCHO}] [\text{HOI}]_T$$

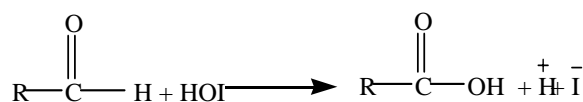
where, $k = k_1 k_2 / k_{-1} + k_2$

The above reaction shows overall second order kinetics with respect to substrate (sugars) and hypiodous acid while first order with respect to sugars.

Further with D-mannose as the aldose in the reaction mixture, the influence of change in ionic strength by adding varying amount of NaCl to reaction mixture reveals that no appreciable electrolyte effect was detected. The absence of effect of salt electrolyte on oxidation indicated that reaction took place in between non-ionic species, which indicated that reactions were taken place between aldoses and free hypiodous acid.

Oxidation reaction mixture was analyzed with glucose as a substrate in the solution by taking TLC (Thin layer chromatography) at the end of reaction to check the oxidation process. Gluconic acid was identified as the main constituent of reaction indicating that probable mechanism of the

oxidation of aldoses by aqueous alkaline solution of iodine follows the equation.



where R is carbohydrate chain.

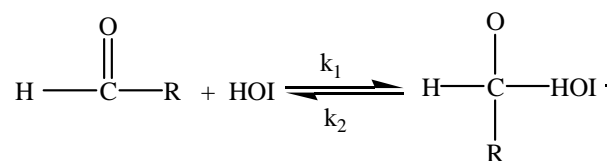
Oxidation of different reducing sugars has been studied at different temperatures. Activation parameters like E_a (energy of activation), ΔH^\ddagger (enthalpy of activation), ΔS^\ddagger (entropy of activation) and ΔG^\ddagger (free energy) were tabulated in Table 4.

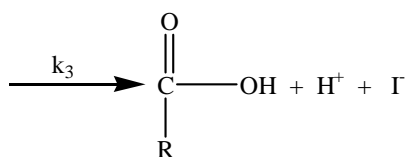
Investigation shows that rate of oxidation is affected by a change in temperature. The energy of activation has been found to be 10.16, 12.17, 14.02 & 20.22 kJmol⁻¹ for glucose, galactose, D-mannose and L-arabinose respectively.

The low values of energy of activation indicate that non-ionic reacting species in rate determining step may be involved. No electrolyte effect also showed that reaction was taking place in between neutral molecules. Therefore above proposed mechanism is verified with the result of activation of energy.

Conclusions

This study showed that reaction between iodine and sugars follows first order kinetics with respects to substrate. Hence the overall reaction products are $\text{I}_2 + \text{NaOH} \rightleftharpoons \text{HOI} + \text{I}^- + \text{Na}^+$.





Reaction between alkaline iodine and aldoses followed slowest kinetics due to non-ionic species in rate determining step. The rate of oxidation at pH 11.4 was higher where concentration of active oxidizing species [HOI] was maximum. At this pH rate of oxidation of l-arabinose was highest which may be attributed with the configuration of aldopentose.

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