

## Study of the Non-Catalyzed Molecular Reaction of Reducing Sugars

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**Abstract.** *The study of the non-catalyzed molecular reaction of reducing sugars by a spectrophotometry technique, at different concentrations of sugar, iodine and temperature has been undertaken for the first time. The absence of a salt effect indicates that a reaction does not take place between ionic substances and that at least one of the reactants must be non-ionic. This adds further confirmation to the hypothesis that the reaction takes place directly between sugars and hypoiodous acid. The results indicate that the reaction is first order kinetics with respect to sugars and hypoiodous acid, but it is zero order kinetic, with respect to iodine concentration. The low value of energy of activation confirmed the presence of neutral molecules in the rate determining step. The negative value of entropy shows that the process is not spontaneous, but the reverse process is spontaneous at all temperatures. Thermodynamic parameters have been evaluated by studying kinetics at various temperatures. A suitable mechanism has been proposed in consistency with the kinetic results.*

**Keywords:** *Non-catalyzed; Molecular reaction; Reducing sugar; Spectrophotometry technique; Hypoiodous acid; Kinetics.*

### INTRODUCTION

The study of carbohydrates is one of the most exciting fields of organic chemistry. Carbohydrates serve as the chief fuel of biological systems, supplying living cells with usable energy. They are the body's primary source of energy. 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. The oxidation of aldoses by chlorine and bromine have been reported in alkaline media [1,2]. Aldonic acids, as primary products of the

oxidation of aldoses by bromine, have been extensively studied by Isbell and co-workers [3-7] who pointed out that  $\beta$ -aldoses (C-1 equatorial) are oxidized much faster than  $\alpha$ -aldoses (C-1 axial). The catalyzed and non-catalyzed oxidation of sugars has been studied in detail using organic oxidants such as N-halo compounds [8-16]. Inorganic oxidants such as Cu (II), ammonical Ag (I) and Nessler's reagent have been used in the non-catalyzed oxidation of sugars in an aqueous alkaline medium [17-19]. The mechanism for the oxidation of some aldoses by Cr(VI), V(V) and Ce(IV) are investigated in acidic media [20]. The use of periodate in the non-catalyzed oxidation of carbohydrates and Ru (III) and the ruthenate ion-catalyzed oxidation of reducing sugars in an alkaline medium are available [21-23]. In the present paper, the primary aim is to ascertain the non-catalyzed molecular reaction of reducing sugars by the spectrophotometric method. In view of the biological importance of reducing sugars and iodine, the reaction rate is found to be first order with respect to sugars and zero order with respect to iodine. Iodine is an essential component of the human diet and, in fact, appears to be the heaviest required element in a diet. Iodine compounds are useful in medicine and

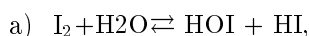
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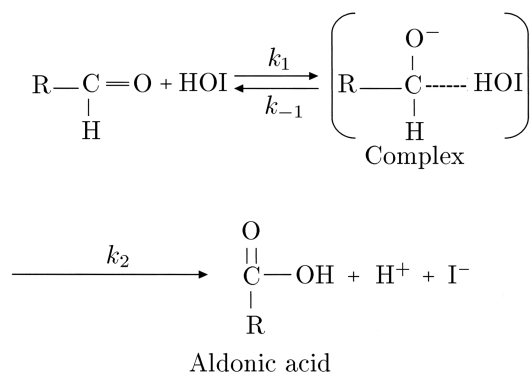
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lack of iodine in the diet is a cause of goiter. Iodine is absolutely necessary for a healthy thyroid as well as ovaries, breasts and prostate. These are just a few of the reasons to become interested in iodine. In an age of increasing toxic exposure, we all need more and not less iodine, because it has very specific protective effects against several common poisons like fluoride and bromide and, to a lesser extent, helps eliminate lead and mercury from the body. In recent years, partly due to the development of new electronic techniques, a good deal of effort has been devoted to the study of reactions that are difficult to study by conventional methods. The purpose of this paper is to ascertain the reaction mechanism put forward to account for kinetics and other experimental data for oxidation in an alkaline medium. It is not expected for a single mechanism to satisfy every reaction; the nature of the substrate and the medium profoundly affect the course of the reaction. It is reported [24-26] that, in the presence of an alkali, reducing sugars undergo a tautomeric change, resulting in the formation of an enolate anion and enediol. The formation of enediol in the presence of alkali is also supported by the work of Isbell et al. [27]. The molecular reaction involves hypoiodous acid, a reactive oxidizing specie and a sugar complex in the rate determining step.



b)



R= Carbohydrate chain

The presence of corresponding aldonic acids as the product were determined chromatographically [28] and spot test method [29,30]; this was also confirmed by statistical regression analysis data. The various activated parameters were computed and recorded.

## EXPERIMENTAL

Experiments were carried out for measurement with various ionic strengths, different concentrations of sugar and iodine solutions and also at different temperatures. All chemicals used in this study were of an

analytical grade supplied by E. Merck; deionized water was used in the preparation of stock solutions. An iodine solution, buffer solution and sugar were prepared and used. For selecting the wavelength, the absorption spectrum of the iodine solution in a 200-700 nm range was recorded. The spectrum shows the peak at 352 nm.

## KINETIC MEASUREMENTS

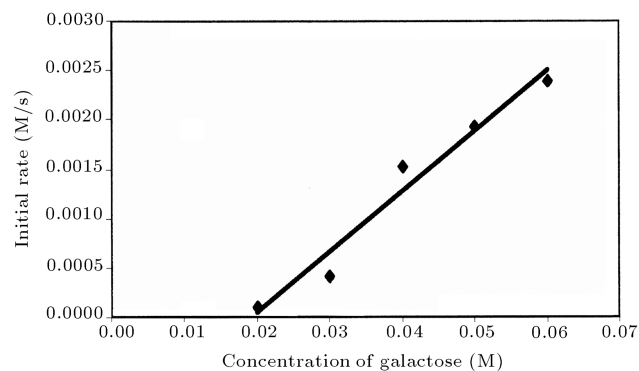
The mixed solutions were immediately transferred to a 1 cm thick rectangular quartz cell, to a total volume of 3 ml, in a temperature regulated cell holder. The optical density was monitored spectrophotometrically, as a function of time of each set of the reaction mixture at a wavelength of 352 nm. The initial rate was calculated from the slope by taking the tangent on the absorbance-time graph in the kinetic mode of the spectrophotometer. The pseudo first order plot of  $\ln(A_\infty - A_t)$  versus time was also plotted to confirm the initial rate method. Where  $A_t$  is the absorbance at any time and  $A_\infty$  is the absorbance at infinite time.

## INSTRUMENTATION

Kinetic measurements were carried out using a Shimadzu UV - Visible Niolet Evolution 100 spectrophotometer with a Thermospectronic PCB 150 water peltier system thermostat. pH measurements were made on a HANN - HI - 8314 pH meter.

## RESULTS AND DISCUSSION

The redox reaction was carried out under conditions having a non-catalyzed aqueous alkaline iodine solution with varying concentrations of galactose and fructose sugar at pH 12.80, by adding 0.1 M NaOH at 40°C. Using the initial rate method and by plotting the initial rate of the reaction versus the initial concentration of sugars (Table 1, Figures 1a and 1b) at a constant iodine concentration, it is found to be a straight line,



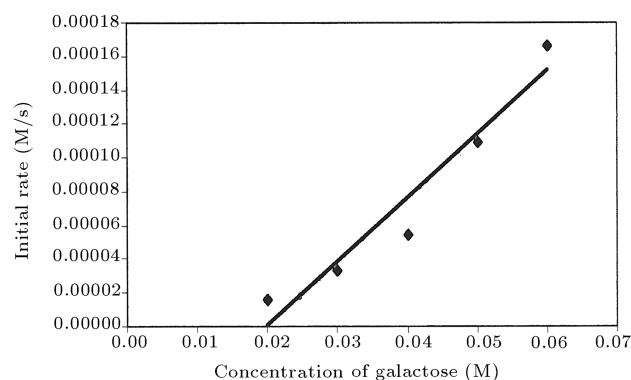
**Figure 1a.** Plot of initial rate versus initial concentration of galactose.

**Table 1.** Kinetic rate data for initial rate method. NaOH=0.1 M, pH=12.80, temperature=313 K,  $\lambda_{\max} = 352$  nm,  $[I_2] = 1.6 \times 10^{-3}$  M.

Reducing Sugars (mol/dm <sup>3</sup> )	0.02	0.03	0.04	0.05	0.06
Galactose k (Ms <sup>-1</sup> )	0.000117	0.000416	0.00153	0.00194	0.0024
Fructose k (Ms <sup>-1</sup> )	0.0000166	0.000033	0.000055	0.00011	0.000167

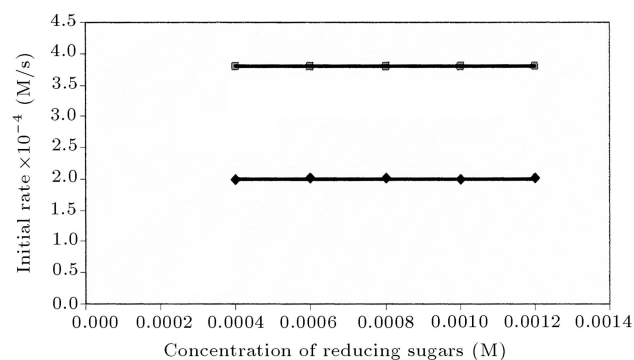
**Table 2.** Effect of concentration of iodine on rate of reaction. Galactose =  $2 \times 10^{-2}$  M, fructose =  $2 \times 10^{-2}$  M, NaOH = 0.1 M, pH = 12.80, temperature = 313 K,  $\lambda_{\max} = 352$  nm.

Iodine (mol/dm <sup>3</sup> )	0.0004	0.0006	0.0008	0.001	0.0012
galactose k $\times 10^4$ (Ms <sup>-1</sup> )	2.00	2.01	2.01	2.00	2.01
Fructose k $\times 10^4$ (Ms <sup>-1</sup> )	3.81	3.81	3.80	3.81	3.81

**Figure 1b.** Plot of initial rate versus initial concentration of fructose.

indicating that the rate is directly proportional to the concentration of sugars, also indicating a first order in each sugar. The rate constants calculated from the slopes of the above plots are low due to the breaking of the compound into small fragments. At constant concentrations of sugar and varying concentrations of iodine (range  $4 \times 10^{-4} - 1.2 \times 10^{-3}$  M), a different set of experiments were performed and a graph of the initial rate of reaction versus the initial concentration

of the iodine solution was plotted (Table 2, Figure 2). This shows a zero order reaction for iodine, due to its isolation [31] and the rate of reactions are independent of the concentration of the iodine solution. The effect of ionic strength on the rate constant is also investigated by adding varying concentrations of  $KNO_3$  to the medium, keeping all other conditions constant. The results obtained are summarized in Table 3. The plot of  $\log k$  versus  $(I)^{1/2}$  (Figure 3),

**Figure 2.** Plot of initial rates versus initial concentration of iodine solution.**Table 3.** Dependence of  $k$  on ionic strength. Galactose =  $2 \times 10^{-2}$  M, fructose =  $2 \times 10^{-2}$  M, pH = 12.80,  $[I_2] = 1.6 \times 10^{-3}$  M, NaOH = 0.1 M, temperature = 313 K.

I( $KNO_3$ )	$(I)^{1/2}$	Galactose k	Galactose log k	Fructose k	Fructose log k
0.001	0.0316	0.0014	2.85387	0.0021	2.67778
0.003	0.0547	0.0014	2.85387	0.0020	2.69897
0.005	0.0707	0.0013	2.88606	0.0020	2.69897
0.025	0.1581	0.0014	2.85387	0.0020	2.69897
0.075	0.2738	0.0014	2.85387	0.0021	2.67778

confirmed the independence of the velocity constant on the concentration of  $\text{KNO}_3$ . According to the Debye-Huckel limiting law, if one of the reactants is a neutral molecule,  $Z_A Z_B$  become zero, then, the rate constant,  $k$ , is expected to be independent of the ionic strength and the associated product has a definite chemical structure.

The reactions at different temperatures in the range of 313-333 K were studied and plotted as  $\ln k$  versus  $1/T$ , using an Arrhenius equation (Figure 4). The graph is linear and, from the slope, the value of  $E_a$  is calculated. The values of activated parameters such as energy of activation ( $E_a$ ), entropy of activation, enthalpy of activation and Gibbs free energy of activation at 318 K are given in Table 4. The values of activation parameters indicate that the slowest reaction is between the reducing sugars and hypiodous acid.

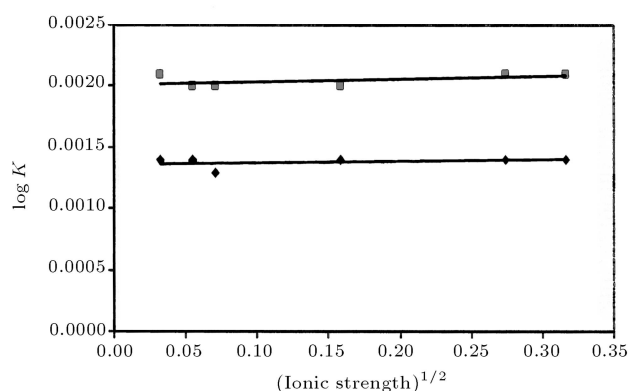


Figure 3. Plot of  $\log k$  versus  $(\text{ionic strength})^{1/2}$ .

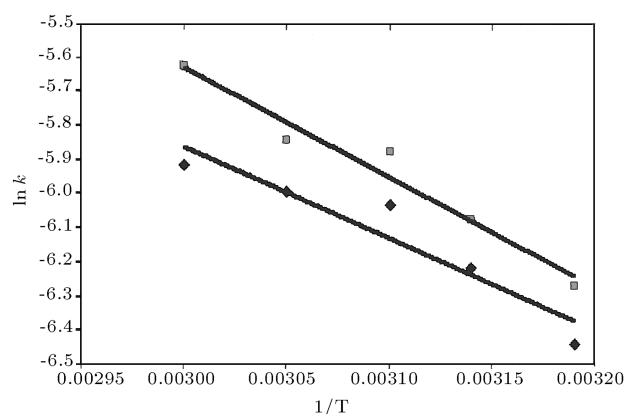


Figure 4. Plot of  $\ln k$  versus  $1/T$ .

Table 4. Activated parameters of molecular reaction of reducing sugars. Galactose =  $2 \times 10^{-2}$  M, fructose =  $2 \times 10^{-2}$  M, pH = 12.80,  $[\text{I}_2] = 1.6 \times 10^{-3}$  M, NaOH = 0.1 M, temperature = 318 K.

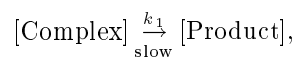
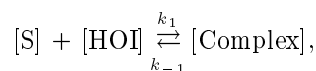
Reducing Sugars	$\Delta E_a$ $\text{kJ mol}^{-1}$	$\Delta H^\ddagger$ $\text{kJ mol}^{-1}$	$\Delta S^\ddagger$ $\text{JK}^{-1} \text{mol}^{-1}$	$\Delta G^\ddagger$ $\text{KJ mol}^{-1}$
Galactose	26.270	23.892	-297.332	118.443
Fructose	21.938	19.561	-298.775	114.571

The low value of energy of activation confirmed the presence of a neutral molecule in the rate-determining step. Entropy of activation is negative and enthalpy of activation is positive, which shows that rate largely depends upon the association of sugar and hypiodous acid. The concentration of the intermediate depends upon  $k_{-1}$  and  $k_2$  (rate of disappearance of intermediate) and  $k_1$  and the association followed by dissociation. A suitable mechanism has been proposed in consistency with the kinetic results.

These reducing sugars contribute to a number of pharmaceutical, food processing and chemical industries. Galactose, needed by the human body for the synthesis of lactose (in the mammary glands), is found in dairy products, sugar beet and other gum and mucilage. Fructose is used in beverages, soft moist cookies, frozen juice concentrates and energy products.

## REACTIN MECHANISM

On the basis of the results, the following mechanism may be proposed in order to explain the mechanistic path of the molecular reaction of sugar and iodine in alkaline medium:



where  $[\text{S}]$  is the concentration of reducing sugars, and  $[\text{HOI}]$  is the concentration of hypiodous acid. The rate-determining step is the action of hypiodous acid on the organic substrate which probably forms a complex and which further gives products. The following probable rate law might be proposed:

$$-d[\text{HOI}]/dt = k[\text{S}][\text{HOI}].$$

Before coming to the actual mechanism, it would be more appropriate to discuss the reacting species of iodine in the alkaline solution. A detailed survey of literature reveals that iodine dissolved in an alkaline medium gives hypiodous acid along with hypiodite and triiodite ions. It has been reported [32-34] earlier by several researchers that  $\text{I}_2$  dissolved in alkaline produces hypiodous acid  $[\text{HOI}]$ , a hypiodate ion  $[\text{IO}^-]$  and a triiodate ion  $[\text{I}_3^-]$ . The disproportionation of

hypoiodite into iodate is not considered because of the fact that iodate has no action on aldose sugars. Kinetic studies suggest that the oxidizing agent can be either [HOI] or  $\text{IO}^-$  in an alkaline medium [35].  $[\text{IO}^-]$ ,  $[\text{I}_2]$  and [HOI] are oxidizing species, but the most effective oxidizing specie is hypoiodous acid [HOI], which reacts with an aldehydic group of reducing sugar and oxidizes it into aldonic acid [36]. The concentration of an oxidizing species that is probably responsible for the oxidation of sugars was calculated by using the following equilibrium constants:

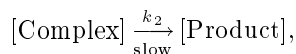
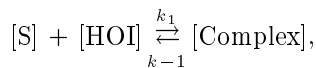
$$K_1 = \frac{[\text{H}^+][\text{I}^-][\text{HOI}]}{[\text{I}_2]} = 3 \times 10^{-13},$$

$$K_2 = \frac{[\text{H}^+][\text{IO}^-]}{[\text{HOI}]} = 1 \times 10^{-11},$$

$$K_3 = \frac{[\text{I}_2][\text{I}^-]}{[\text{I}_3]} = 1.36 \times 10^{-3}.$$

Thus, the formation of the ions mentioned above, i.e.  $[\text{I}_2] + [\text{HOI}] + [\text{IO}^-] + [\text{I}_3^-]$  is equal to the total concentration of the  $\text{I}_2$ .

The active oxidizing species in each case is the unionized hypoiodous acid. This was further supported by a study of the oxidation of aldoses with bromine [37] in an alkaline medium in which it has been suggested that hypobromous acid is the predominant oxidizing specie in alkaline pH. In the light of kinetic observations, sugar and HOI are assumed to be the main reactive species for the present investigation. The above findings clearly suggest a single mechanism for the oxidation of galactose and fructose:



where  $k_1$  and  $k_{-1}$  are the rate constant in the forward and reverse direction and  $k_2$  is the rate of formation of the product. The rate of formation of the complex will be given as:

$$\begin{aligned} \frac{d[\text{Complex}]}{dt} &= k_1[\text{S}][\text{HOI}] - k_{-1}[\text{Complex}] \\ &\quad - k_2[\text{Complex}], \end{aligned} \quad (1)$$

at steady state:

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

Therefore, the concentration of the complex becomes:

$$[\text{Complex}] = \frac{k_1[\text{S}][\text{HOI}]}{k_{-1} + k_2}. \quad (3)$$

At a steady state condition, the rate of disappearance of [HOI] may be given as:

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

or:

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

Now, the total [HOI] may be considered as:

$$[\text{HOI}]_T = [\text{HOI}] + [\text{Complex}]. \quad (6)$$

Putting the value of the complex:

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

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

The value of  $[\text{HOI}]_T$  comes out to be:

$$[\text{HOI}] = \frac{(k_{-1} + k_2)[\text{HOI}]_T}{(k_{-1} + k_2) + k_1[\text{S}]}. \quad (9)$$

From Equations 5 and 9, the final rate law comes out to be:

$$-\frac{d[\text{HOI}]}{dt} = \frac{k_1 k_2 [\text{S}][\text{HOI}]_T}{(k_{-1} + k_2) + k_1[\text{S}]}. \quad (10)$$

Under the present experimental condition, one might assume the following equality:

$$k_{-1} + k_2 > k_1[\text{S}]. \quad (11)$$

And, hence, Equation 10 reduces to:

$$-\frac{d[\text{HOI}]}{dt} = \frac{k_1 k_2 [\text{S}][\text{HOI}]_T}{(k_{-1} + k_2)}, \quad (12)$$

$$-\frac{d[\text{HOI}]}{dt} = k[\text{S}][\text{HOI}]_T, \quad (13)$$

where:

$$k = \frac{k_1 k_2}{k_{-1} + k_2}, \quad (14)$$

$$-\frac{d[\text{HOI}]}{dt} = k[\text{S}][\text{HOI}]. \quad (15)$$

## CONCLUSION

Reducing sugars have been studied spectrophotometrically in a basic medium at different temperatures. It appears that configuration of the carbohydrate chain affects the rate at which the sugars are oxidized. Equation 15 clearly indicates first order kinetics with respect to reducing sugars, and hypiodous acid concentration and zero order kinetics with respect to the iodine solution. One of the advantages of carbohydrates is that they enter into the body, undergo an oxidation process much more quickly and provide energy more rapidly. The rate of galactose is found to be greater than fructose. The absence of a salt effect indicates the presence of a neutral molecule in the rate determining step, which is further confirmed by the low values of energy of activation ( $E_a$ ). The high and negative value of entropy of activation  $\Delta S^\ddagger$  shows that the rate largely depends upon the association of reducing sugar and HOI. The first order rate of the reaction also proves its dependence upon the formation of the intermediate complex. Therefore, the proposed reaction mechanism is in agreement with the results of the above reaction.

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