

Kinetics and Mechanism of Oxidation of Some Simple Reducing Sugars by Permanganate Ion in Alkaline Medium

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The kinetics of oxidation of glucose, galactose, fructose, maltose and sucrose by alkaline permanganate anion has been studied. The reactions studied spectrophotometrically over a wide range of experimental conditions show that the rate of the reactions is enhanced by increase in pH, ionic strength, and temperature as well as the reactant concentrations. The mechanism has been proposed to proceed *via* the formation of enediol intermediate complexes and the order of reactivities of the sugars is fructose > glucose \approx galactose > maltose > sucrose. The activation parameters were evaluated and lend further support to the proposed mechanism.

Keywords: Kinetics and mechanism, Oxidation, Reducing sugars, Enediol intermediate, Permanganate, Activation parameters

INTRODUCTION

The kinetics of oxidation of sugars have been subject of extensive research in recent years. This is attributed to the economic and biological importance of carbohydrates to living organisms. The oxidations have been carried out in both acidic and alkaline media using such oxidants as transition metal ions, inorganic acids, organometallic complexes and enzymes [1-8]. The results of these experiments have revealed that in some cases the mechanism is proposed based on the formation of intermediate complexes while in others the results are analyzed on the basis of formation of free radicals.

Despite much work already done on the oxidation of sugars, very little attention was given to the use of permanganate anion [2]. The present study is therefore undertaken to clarify the mechanism of oxidation of D-glucose, galactose, fructose, maltose and sucrose by permanganate anion in alkaline medium as a follow up of the previous studies in our laboratory on the oxidation of sugars

with chromium(VI) and iridium(IV) ions [9,10].

EXPERIMENTAL

Chemical Reagents

The reagents were of analytical grade and were used without further purification. Stock solutions of both the oxidant and the substrates were freshly prepared using doubly distilled water.

Spectral Measurement

The absorption spectra of solutions of different concentrations of the permanganate were measured in the visible region between 320 and 800 nm using a Jenway 6405 UV/Vis Spectrophotometer. The kinetic data were collected at 520 nm, the wavelength corresponding to maximum absorbance.

Kinetic Measurements

The kinetic studies were carried out under pseudo-first order conditions with the concentration of the sugars in large

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excess compared to that of the oxidant. All reactant solutions were placed in a thermostated water bath for at least 1 h to attain a temperature of 30 °C. Appropriate quantities of the reagent solutions were mixed in a 250 ml conical flask already placed in the thermostated bath. The reaction was initiated by introducing the oxidant solution into the mixture. The reaction rate was followed by measuring the decrease in absorbance at 520 nm. The reaction was completed when permanganate-sugar solution turned from purple to brown. The rate constants calculated were averages of at least two measurements. The results are generally reproducible within $\pm 2\%$.

Polymerization Test

Aqueous 20% acrylamide was added to various reaction mixtures. Formation of gel was noticed in each case and on further addition of methanol polyacrylamide was precipitated. Blank experiments in which either the oxidant or substrate was excluded were also carried out and no gel formation was noticed. These results indicate that free radicals were formed during the reactions [9,11].

Stoichiometry of the Reactions

The procedure was adapted from that used by Sircar and Saika [12]. An excess of the permanganate solution was added to the sugar solution and allowed to react for several hours. The excess of the permanganate was then determined. Blanks were prepared without addition of sugar solution for each set of the experiment. The volume of the primary standard (Fe^{2+}) consumed by blanks was always found to be greater than the corresponding reacting species and consequently the consumption ratio, *i.e.* the number of moles of the permanganate consumed per mole of the sugars were estimated by assuming that all the sugars were totally consumed under the reaction conditions. The results on the stoichiometry show that one mole of the monosaccharides consumed 6 moles of the permanganate anion while 12 moles were consumed per mole of the disaccharides.

Product Analysis

Chromotropic acid (1,8-dihydronaphthalene-3,6-disulfonic acid) was added to various reaction mixtures of both the substrates and the permanganate anion under the exact kinetic conditions. A violet pink color developed which confirmed the

presence of formic acid in the reaction products [13]. Also formation of a lower sugar has been reported earlier [2]. Thus, the products of these reactions are formic acid and the corresponding lower sugars.

RESULTS AND DISCUSSION

Effect of Reactants Concentration

The pseudo-first order rate constants, k_{obs} , were determined at different initial concentrations of the sugars while maintaining constant the concentration of the permanganate, ionic strength, pH and temperature at 30 °C. The results as presented in Table 1 show that the rate increases as the concentration of the sugars increase. This increase in rate is almost in direct proportion such that when divided by the corresponding reducing sugar concentration, fairly constant values were obtained. This suggests that the reactions are first-order with respect to the reducing sugars [2]. The plots of k_{obs} against the sugar concentrations were linear and passed through the origin (Fig. 1). This confirms that the reactions are first-order with respect to the sugars [4].

The average values of the second-order rate constants, k_2 , at 30 °C are 0.04, 0.042, 0.02, 0.073 and 0.005 $\text{M}^{-1} \text{s}^{-1}$, respectively for glucose, galactose, maltose, fructose and sucrose. Therefore the order of reactivities of these sugars is fructose > glucose \approx galactose > maltose > sucrose. This result agrees with the literature reports [14,15]. In another set of experiments, the reactions were studied at various initial concentrations of the permanganate but at constant sugar concentration, ionic strength, pH and temperature. The pseudo-first order rate constants recorded in Table 2 indicate that the reactions are independent of the initial concentrations of the permanganate.

Effect of Ionic Strength

The effect of ionic strength on the rate of the reaction was investigated by varying the concentration of KNO_3 in the range 0.05 to 0.25 M. The initial rates of the reaction increased with increase in KNO_3 concentration. This suggests that the reactions occur between ions of similar charges [1].

Effect of pH

The effects of pH on the rate of oxidation of the sugars

Table 1. Variation of Rate Constants with Sugar Concentrations at 303 K, pH = 11, $[\text{KMnO}_4] = 5 \times 10^{-4} \text{ M}$, $[\text{KNO}_3] = 0.2 \text{ M}$

[Sugar] $\times 10^2 \text{ M}$	Glucose		Galactose		Fructose		Maltose		Sucrose	
	$k_{\text{obs}} \times 10^4$ (s^{-1})	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{obs}} \times 10^4$ (s^{-1})	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{obs}} \times 10^4$ (s^{-1})	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{obs}} \times 10^4$ (s^{-1})	k_2 ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{obs}} \times 10^4$ (s^{-1})	k_2 ($\text{M}^{-1} \text{s}^{-1}$)
1.0	3.37 \pm 0.02	0.03 \pm 0.01	3.43 \pm 0.06	0.03 \pm 0.02	8.03 \pm 0.03	0.08 \pm 0.02	1.54 \pm 0.01	0.02 \pm 0.01	0.62 \pm 0.01	0.006 \pm 0.07
1.2	5.13 \pm 0.02	0.04 \pm 0.02	4.77 \pm 0.05	0.04 \pm 0.03	9.27 \pm 0.03	0.08 \pm 0.02	1.96 \pm 0.01	0.02 \pm 0.03	0.64 \pm 0.01	0.005 \pm 0.05
1.4	5.42 \pm 0.02	0.04 \pm 0.01	5.65 \pm 0.06	0.04 \pm 0.02	9.45 \pm 0.05	0.07 \pm 0.05	2.15 \pm 0.01	0.02 \pm 0.02	0.70 \pm 0.01	0.005 \pm 0.06
1.6	7.10 \pm 0.02	0.04 \pm 0.01	7.10 \pm 0.03	0.04 \pm 0.02	11.42 \pm 0.03	0.07 \pm 0.02	3.13 \pm 0.02	0.02 \pm 0.01	0.83 \pm 0.01	0.005 \pm 0.05
1.8	8.45 \pm 0.01	0.04 \pm 0.03	8.22 \pm 0.06	0.05 \pm 0.03	12.45 \pm 0.03	0.07 \pm 0.03	3.39 \pm 0.01	0.02 \pm 0.01	0.94 \pm 0.01	0.005 \pm 0.06
2.0	9.58 \pm 0.02	0.05 \pm 0.01	11.38 \pm 0.06	0.05 \pm 0.02	14.43 \pm 0.03	0.07 \pm 0.02	3.55 \pm 0.01	0.02 \pm 0.01	1.08 \pm 0.01	0.005 \pm 0.07

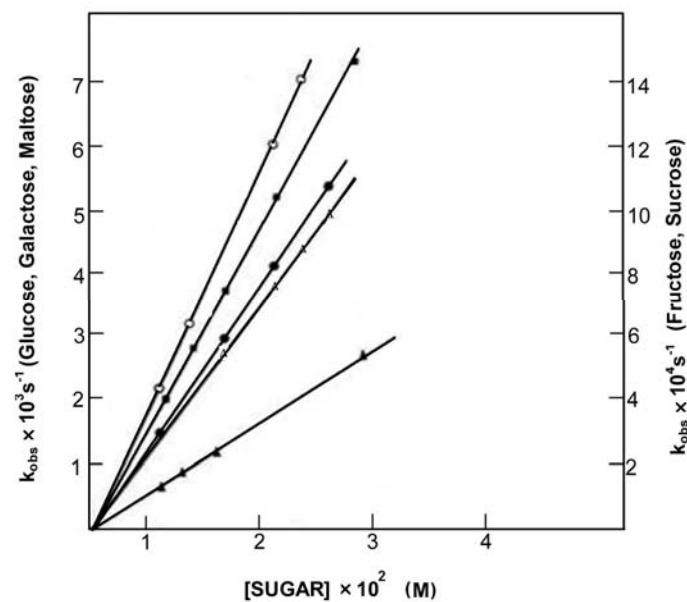
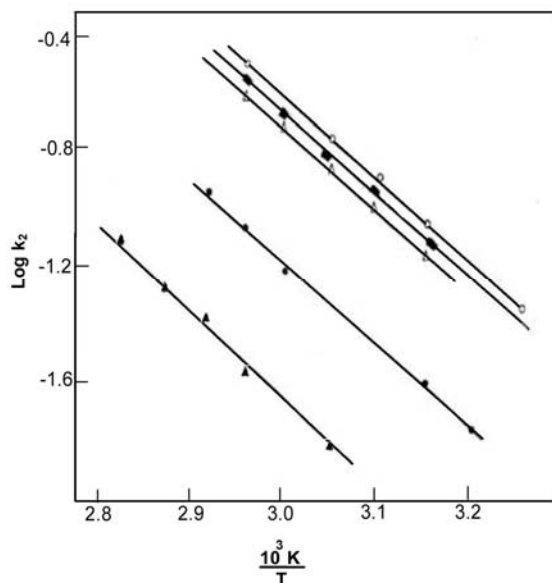
**Fig. 1.** Plots of k_{obs} against the Sugar concentrations at 303 K, $[\text{MnO}_4^-] = 5 \times 10^{-4} \text{ M}$, pH = 11, $[\text{KNO}_3] = 0.2 \text{ M}$: (●) Maltose, (○) Glucose, (▲) Sucrose and (△) Fructose.

Table 2. Variation of Rate Constants, $k_{\text{obs}} \times 10^4 \text{ (s}^{-1}\text{)}$, with KMnO_4 Concentration at 303 K, $[\text{Sugar}] = 0.02 \text{ M}$, $[\text{KNO}_3] = 0.2 \text{ M}$, $\text{pH} = 11$

$[\text{KMnO}_4] \times 10^4 \text{ (M)}$	Glucose	Galactose	Fructose	Maltose	Sucrose
3.0	3.98 ± 0.02	2.77 ± 0.06	7.23 ± 0.01	1.78 ± 0.02	0.16 ± 0.02
4.0	3.08 ± 0.02	2.92 ± 0.07	7.32 ± 0.01	1.08 ± 0.02	0.13 ± 0.02
5.0	3.13 ± 0.03	2.02 ± 0.05	7.85 ± 0.01	2.00 ± 0.02	0.15 ± 0.02
6.0	3.45 ± 0.02	2.05 ± 0.05	7.42 ± 0.03	1.46 ± 0.02	0.12 ± 0.02
7.0	3.85 ± 0.02	2.32 ± 0.05	7.78 ± 0.01	2.50 ± 0.02	0.17 ± 0.03
8.0	3.17 ± 0.02	2.62 ± 0.06	7.58 ± 0.01	1.88 ± 0.02	0.14 ± 0.03

**Fig. 2.** Arrhenius plots for the sugar- MnO_4^- oxidation at $\text{pH} = 11$, $[\text{MnO}_4^-] = 5 \times 10^{-4} \text{ M}$, $[\text{Sugar}] = 0.02 \text{ M}$, $[\text{KNO}_3] = 0.2 \text{ M}$: (Δ) Fructose, (\blacksquare) Galactose, (\circ) Glucose, (\bullet) Maltose and (\blacktriangle) Sucrose.

were studied at 30 °C and 40 °C in the pH range 10.1-11.6. The results show that at both temperatures, the rate of oxidation increased with increase in the pH of the reaction medium. These results indicate that these reactions are base-catalysed [16].

Effect of Temperature

The oxidation of the sugars was carried out at different temperatures from 30 °C to 80 °C. The pseudo-first-order rate constants increased with increase in temperature. The second-order rate constants, k_2 were calculated from the relation $k_2 = k_{\text{obs}}/[\text{SUGAR}]$. The plots of $\log k_2$ against $1/T$ were linear (Fig. 2) and the Arrhenius activation energy, E_a , plus other

thermodynamic activation parameters were evaluated as described in the literature [17]. The results are presented in Table 3. The negative values of entropies of activation (ΔS^\ddagger) are indication that the reactions occur between ions of similar charge [2] and also confirmed an associative mechanism [18].

Mechanism of the Reaction

It has been established that, in strongly alkaline media, the stable reduction product of permanganate is manganate ion, MnO_4^{2-} [19,20]. It was also reported in the literature that in alkaline media carbohydrates will form enediols with the hydroxyl group and that the rate of enolization is the same as the rate of oxidation [21]. However, in the present study, the

Table 3. Arrhenius and Thermodynamic Activation Parameters for the Oxidation of the Sugars by Alkaline KMnO_4 at 313 K

Substrate	E_a (kJ mol^{-1})	A ($\text{l mol}^{-1} \text{s}^{-1}$)	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$)	ΔG^\ddagger^a (kJ mol^{-1})	ΔG^\ddagger^b (kJ mol^{-1})
Glucose	66.8 ± 0.6	$5.0 \pm 0.1 \times 10^9$	64.2 ± 0.8	-59.6 ± 0.4	82.9 ± 0.9	83.8 ± 0.1
Galactose	56.3 ± 0.6	$1.6 \pm 0.1 \times 10^8$	53.7 ± 0.7	-88.3 ± 0.5	81.3 ± 0.9	82.5 ± 0.2
Fructose	42.5 ± 0.6	$7.1 \pm 0.1 \times 10^8$	39.9 ± 0.6	-75.8 ± 0.5	63.6 ± 0.8	68.1 ± 0.3
Maltose	53.0 ± 0.4	$1.0 \pm 0.1 \times 10^7$	50.4 ± 0.8	-112.0 ± 0.5	85.2 ± 0.9	101.7 ± 0.3
Sucrose	80.4 ± 0.6	$7.9 \pm 0.1 \times 10^5$	77.8 ± 0.8	-132.3 ± 0.5	119.2 ± 0.9	137.8 ± 0.2

^a ΔG^\ddagger values are calculated from $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ while ^b ΔG^\ddagger are estimated from the equation $\Delta G^\ddagger = -RT \ln k_2$.

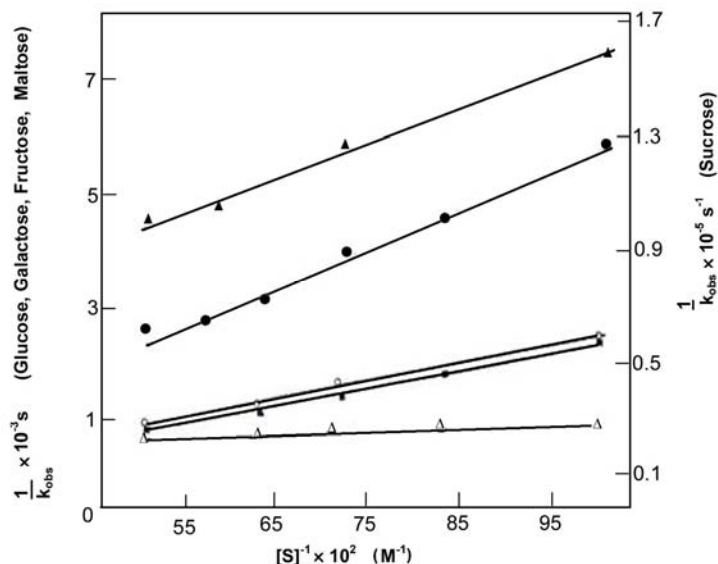
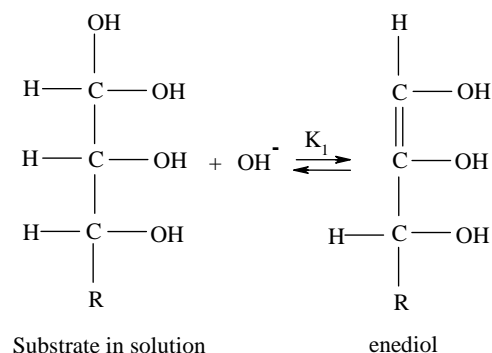


Fig. 3. Plots of $1/k_{\text{obs}}$ against $1/[S]$ at 303 K, pH = 11, $[\text{MnO}_4^-] = 5 \times 10^{-4} \text{ M}$, $[\text{KNO}_3] = 0.2 \text{ M}$: (Δ) Fructose, (\blacksquare) Galactose, (\circ) Glucose, (\bullet) Maltose and (\blacktriangle) Sucrose.

double reciprocal plots of the pseudo-first-order rate constants against the sugar concentrations were linear (Fig. 3). This provides ample evidence for the formation of a 1:1 intermediate complex during the reactions [2]. Therefore the rate of disproportionation of the activated complex is considered to be the rate determining step. If we combine the kinetic data with the positive polymerization test, then the oxidation of the sugars takes place by the reaction between the permanganate and the sugars resulting in electron transfer between them to give an enediol intermediate complex which then disproportionates in a slow step to give a free radical. The free radical then reacts further with the permanganate ion in a fast step to give the products.

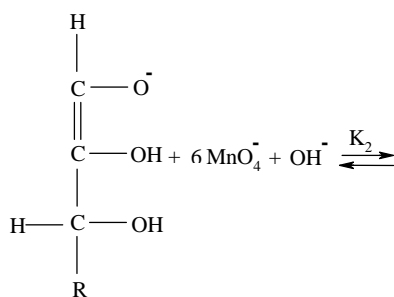
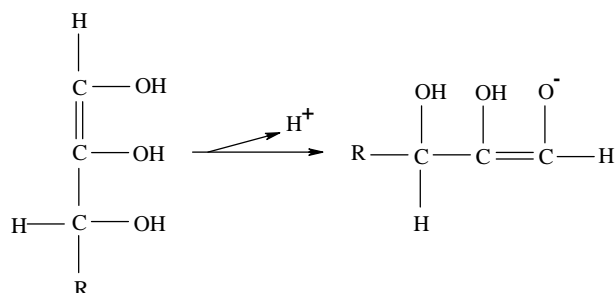
The steps of the reaction are as shown below:



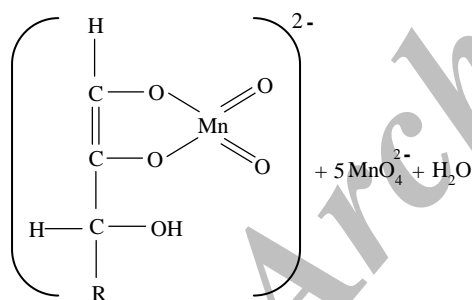
(1)

where $R = \text{CH}_2\text{OH}(\text{CHOH})_2$ for glucose.

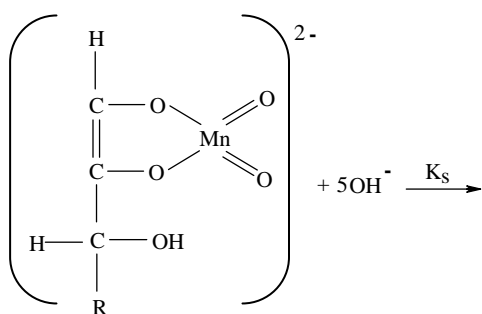
The enediol formed in the scheme above is transient and is readily deprotonated in solution as represented below.



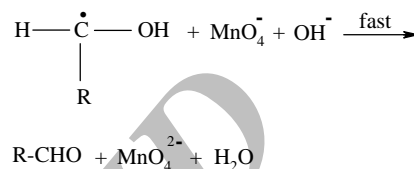
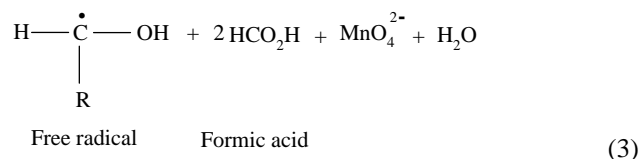
Enediolate ion



Complex C



Complex C



The Rate Equation

The rate law derived from the above mechanism is:

$$-\frac{d[\text{Mn}^{\text{VII}}]}{dt} = \frac{k_s K_1 K_2 [\text{S}][\text{OH}^-][\text{Mn}^{\text{VII}}]_{\text{T}}}{1 + K_1 K_2 [\text{S}][\text{OH}^-]} \quad (4)$$

where $[\text{Mn}^{\text{VII}}]_{\text{T}}$ is the total Mn(VII) concentration.

From Eq. (4)

$$k_{\text{obs}} = \frac{k_s K_1 K_2 [\text{S}][\text{OH}^-]}{1 + K_1 K_2 [\text{S}][\text{OH}^-]} \quad (5)$$

Equation (5) thus confirmed the first-order dependence of reaction rates on the sugars at low concentration of the sugars which is what we observed experimentally.

Rearrangement of Eq. (5) gives:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_s K_1 K_2 [\text{S}][\text{OH}^-]} + \frac{1}{k_s} \quad (6)$$

Equation (6) implies that a plot of $1/k_{\text{obs}}$ against $1/[\text{S}]$ at constant $[\text{OH}^-]$ should give a straight line with slopes equal to $1/k_s K_1 K_2$ and intercept of $1/k_s$ (Fig. 4). From the values of the slopes and intercepts of this plot, k_s and $K_1 K_2$ were calculated and recorded in Table 4. Also from equation (6) a plot of $1/k_{\text{obs}}$ against $1/[\text{OH}^-]$ at constant $[\text{S}]$ is expected to be linear (Fig. 4). The values of k_s and $K_1 K_2$ were calculated from the slopes and intercepts as above and recorded in Table 4. Similarities in the values from both plots confirmed the validity of Eq. (4) and also supported the proposed mechanism.

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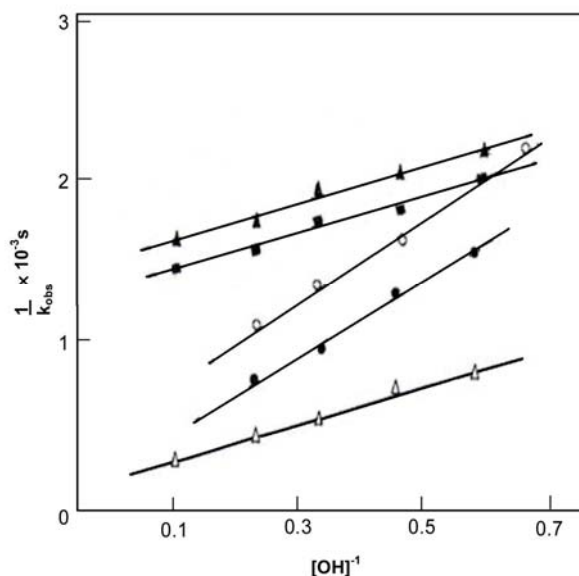


Fig. 4. Plots of $1/k_{\text{obs}}$ against $1/[\text{OH}^-]$ at 303 K, $[\text{Sugar}] = 0.02 \text{ M}$, $[\text{MnO}_4^-] = 5 \times 10^{-4} \text{ M}$, $[\text{KNO}_3] = 0.2 \text{ M}$: (Δ) Fructose, (\blacksquare) Galactose, (\circ) Glucose, (\bullet) Maltose and (\blacktriangle) Sucrose.

Table 4. Values of K_1K_2 and k_s Obtained from the Plots of $1/k_{\text{obs}}$ vs. $1/[\text{S}]$ and $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$ at 313 K

Sugar	$K_1K_2 (\text{M}^{-2})$	$K_1K_2 (\text{M}^{-2})$	$k_s (\text{s}^{-1})$	$k_s (\text{s}^{-1})$
	From $1/k_{\text{obs}}$ vs. $1/[\text{S}]$	From $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$	From $1/k_{\text{obs}}$ vs. $1/[\text{S}]$	From $1/k_{\text{obs}}$ vs. $1/[\text{OH}^-]$
Galactose	20.5	20.8	1.54×10^{-3}	1.61×10^{-3}
Fructose	45.0	46.5	2.22×10^{-3}	2.46×10^{-3}
Glucose	20.8	21.4	1.25×10^{-3}	1.28×10^{-3}
Maltose	27.2	27.4	4.76×10^{-4}	4.65×10^{-4}
Sucrose	60.0	60.8	1.19×10^{-5}	1.16×10^{-5}

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