KINETICS AND MECHANISM OF OXIDATION OF SUGARS BY CHROMIUM (VI) IN PERCHLORIC ACID MEDIUM

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ABSTRACT

Kinetic data for the oxidation of D-glucose, fructose, maltose and sucrose by chromium (VI) in perchloric acid medium are reported The results of the reactions studied spectrophotometrically over a wide range of experimental conditions show that the rate of the reaction is enhanced by increase in pR ionic strength and concentrations of the sugars.

The reactions are first -order with respect to both the sugars and Cr (VI) while the order with respect to [H⁺] is complex. The order of reactivities of the sugars is fructose > maltose > glucose > sucrose. Formation of free radical intermediate complex was demonstrated and the kinetic results indicate the formation of a 1: 1 intermediate complex between Cr (VI) and the sugars. The activation parameters have been evaluated and lend further support to the proposed mechanism.

INTRODUCTION.

The kinetics of oxidation of sugars have been a subject of extensive research in recent years [1-3]. The biological as well as the economic importance of carbohydrates is responsible for the great interest in the study of their bio-and physicochemical properties. 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 [1-5]. The results of these experiments have revealed that in some cases the mechanism was proposed based on the formation of intermediate complexes while in others the results were analysed on the basis of formation of free radicals. Much work has been done on the oxidation of aldoses and ketoses by Cr (VI) while no data for the disaccharides have been reported. The present study is therefore undertaken to clarify the mechanism of oxidation of D-glucose, fructose, maltose and sucrose by Cr (VI) as a follow-up of previous studies in our laboratory on the oxidation of sugars [6]

EXPERIMENTAL

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

Spectral measurement: The absorption spectra of solutions of different concentrations of the chromium (VI) were measured in the visible region between 300 and 800nm and kinetic data collected at 350nm, 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 excess compared to that of the oxidant. All reactant solutions were placed in a thermostated water bath for one hour to attain a temperature of 30°C. Appropriate quantities of the reagent solutions were mixed in a 250cm³ conical flask already placed in the thermostated bath. The reaction rate was followed by measuring the decrease in absorbance at 350nm, the reaction was completed when the Cr(VI)-sugar solution turned from yellow to green [6]. The rate constants calculated were averages of at least two measurements.

Polymerization test: Aqueous 20% acrylamide was added to the various reaction mixtures, which were then monitored for gel formation. Methanol was then added to see if a precipitate would be formed {6-7]. Blank experiments in which either the substrates or the oxidant was excluded were also carried out.

Stoichiometry of the reactions: The Cr (VI) solution was prepared in large excess compared to the concentration of the sugar solutions. The two solutions were mixed together inside a conical flask in appropriate volumes and left to react at 30°C for three days. The excess Cr(VI) left in the solution after the reaction was then determined iodometrically [6.8]. The consumption ratios, i.e. the number of moles of Cr(VI) consumed per mole of the sugars, were estimated by assuming

that all the sugars were totally consumed under the reaction conditions.

RESULTS AND DISCUSSION

Effect of reactant concentration: The reactions were studied at various initial concentrations of the Cr(VI) but at constant [sugar], [HClO₄], [NaClO₄] and temperature.

The pseudo -first -order rate constants recorded in Table 1 indicates that the reactions are independent of initial concentrations of Cr(VI). This suggests a first-order dependence on Cr(VI). In another set of experiments, the pseudo -first order rate constants were determined at various initial concentrations of the sugars while the [HClO₄], [NaClO₄], [Cr(VI)] and temperature were kept constant. The rates increased as the concentration of the sugars increased (Table 2), 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 sugars [2]. The plots of k_{obs} against the sugar concentration are linear and passed through the origin (Fig 1). This confirms that the reactions are first- order with respect to the sugars [9]. The average values of the second-order rate constants, k_2 at 30°C are 6.48 x 10^{-3}, 4.17 x 10^{-3}, 3.77 x 10^{-3} and 3.27 x 10^{-3} M^{-1} S^{-1} respectively for fructose, maltose, glucose and sucrose. Therefore the order of reactivity of these sugars is fructose > maltose >glucose > sucrose. This result agrees in part with the one obtained by Upadhay and Kambo [10].

Effect of perchloric acid concentration: The effect of acidity on the rate of the reactions was studied by varying the concentration of the perchlroric acid medium in the range 1.0 to 4.0M. The results show that the reaction rate increased with increase in acid concentration. The Zucker-Hammet plot of the data was linear (Fig 2) which indicates that these reactions are acid catalysed [11]. The values of the slopes of these plots are less than unity both at [HClO₄] > 2.0 M and [HClO₄] < 2 M, this indi-

Table I: Variation of rate constant with Cr (Cr(VI)) concentration

[Cr (VI)] x 10^4 M	GLUCOSE k_{obs} x $10^5 s^{-1}$	FRUCTOSE k_{obs} x $10^5 s^{-1}$	MALTOSE k_{obs} x $10^5 s^{-1}$	SUCROSE k_{obs} x $10^5 s^{-1}$
2	40.51	4.56	3.97	2.57
3	40.83	4.96	4.48	2.86
4	43.51	5.40	4.54	3.14
5	44.42	4.96	3.87	2.78
6	49.14	5.44	4.78	2.85
7	50.01	5.91	4.33	2.89

[Sugar] = 1.2 x 10-2 M, [NaClO₄] = 0.2 M, [HClO₄] = 2.4 M. Temperature = 30°C

Table 2: Variation of rate constant with sugar concentration at 30°C

SUGAR x 10^2 M	GLUCOSE k_{obs} x $10^5 s^{-1}$	GLUCOSE k_2 x $M^{-1}s^{-1}$	FRUCTOSE k_{obs} x $10^5 s^{-1}$	FRUCTOSE k_2 x $M^{-1}s^{-1}$	MALTOSE k_{obs} x $10^5 s^{-1}$	MALTOSE k_2 x $M^{-1}s^{-1}$	SUCROSE k_{obs} x 10^5	SUCROSE k_2 x $M^{-1}s^{-1}$
1.00	3.37	0.0034	-	-	4.31	0.0043	2.78	0.0029
1.20	4.17	0.0035	7.94	0.0066	4.63	0.0039	3.92	0.0033
1.40	5.05	0.0036	8.90	0.0064	6.27	0.0045	4.18	0.0030
1.60	6.17	0.0039	9.47	0.0060	6.58	0.0041	5.83	0.0035
1.80	7.29	0.0041	11.94	0.0066	7.41	0.0041	6.25	0.0036
2.00	-	-	13.30	0.0066	8.33	0.0042	-	-
2.20	8.12	0.0037	14.50	0.0066	-	-	7.74	0.0035

[Cr (VI)] = 5 x 10^{-4} M, [NaClO₄] = 0.2 M, [HClO₄] = 2.4 M

Table 3: Activation parameters for the oxidation of the sugars by in perchloric acid medium at 313K

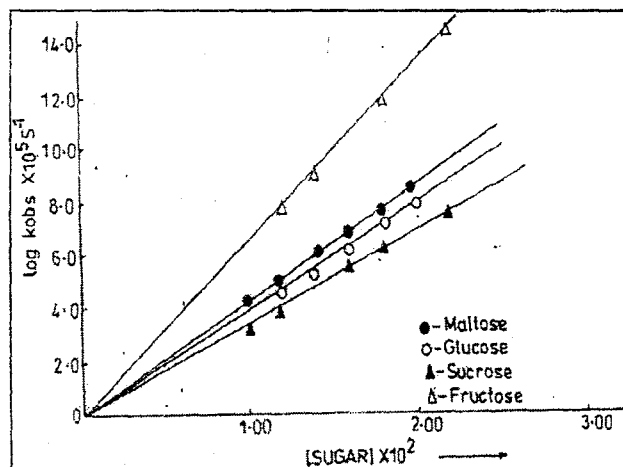| SUGAR	E_a kJ mol^{-1}	A dm^3 $mol^{-1}s^{-1}$	$\Delta H^\#$ kJ mol^{-1}	$\Delta S^\#$ J mol^{-1}	$\Delta G^\#$ kJ mol^{-1}
GLUCOSE	52.65	3.98 x 10^5	50.05	- 138.05	93.26
FRUCTOSE	48.51	6.98 x 10^7	45.90	- 95.16	75.69
MALTOSE	30.23	6.92 x 10^5	27.63	- 117.75	81.39
SUCROSE	55.72	7.59 x 10^4	53.11	- 151.84	100.64

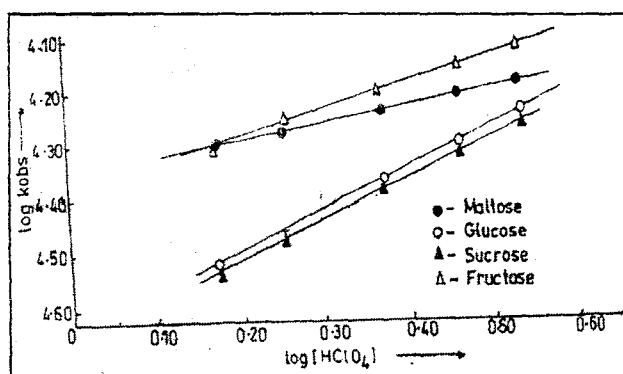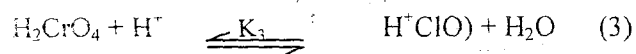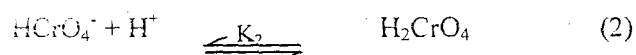Fig. 1: kobz versus [SUGAR] for Cr(VI) oxidation.

Fig.2: Zucker- Hammet plot for Cr(VI) oxidation

sugars are considered to be hard bases, therefore a rapid and reversible transfer of H^+ to the ring oxygen atom of the sugars will occur in strong acidic medium i.e.

$$S + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} \quad SH^- \qquad (1)$$

The fonnation of the protonated chromic acid molecule, $H_3CrO_4^+$ or its anhydride fonn, H^+CrO_3, has been shown to occur in acidic medium according to the equations below [17]

$$HCrO_4^- + H^+ \underset{}{\overset{K_2}{\rightleftharpoons}} \quad H_2CrO_4 \qquad (2)$$

$$H_2CrO_4 + H^+ \underset{}{\overset{K_3}{\rightleftharpoons}} \quad H^+CIO) + H_2O \qquad (3)$$

Thus the protonated chromic ~ule reacts with the protonated sugar molecule, SW, according to the equation below

$$SH^+ + H^+CrO_3 \xrightarrow[slow]{k} Products + H_2CrO_3 \qquad (4)$$
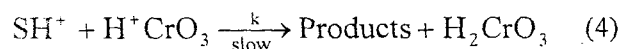
In our experiment, the positive salt effect and the negative values of the entropies of activation, $\Delta S^{\#}$, give further support for the reaction in equation 4. The positive polymerization test provides ample evidence that free radicals were formed during the reactions [6]. According to literature report [18], for all the sugars to be oxidized via free radical mechanism, the Cr(VI) oxidation of the sugars must follow the usual reaction of alcohols, but a two electron C–C cleavage leading to a carbonium ion intermediate will be the rate limiting step. This can be expressed in the following Scheme:

$$S + Cr(VI) \rightarrow R + Cr(V) \qquad (5)$$

$$S + Cr(V) \rightarrow R + Cr(IV) \qquad (6)$$

$$S + Cr(IV) \rightarrow R + Cr(III) \qquad (7)$$
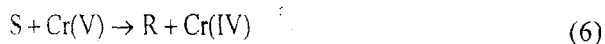
where R is the free radical intermediate which reacts further with another molecule of Cr(VI) or Cr(V) to give products according to the equations below:

$$R + Cr(VI) \rightarrow P + Cr(V) \qquad (8)$$

$$R + Cr(V) \rightarrow P + Cr(IV) \qquad (9)$$

where P is the product of the reaction. The Cr(IV) which is generated in the rate limiting step (equation 4) reacts rapidly with Cr(VI) to give Cr(V):

$$Cr(IV) + Cr(VI) \rightarrow 2Cr(V) \qquad (10)$$
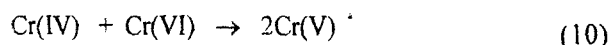
The Cr(V) oxidizes the sugars in a rapid step according to equation 6 above, the Cr(IV) which is generated is being finally reduced to Cr(III) which is the green colour being observed at the end of the reaction [18].

The rate equation: The rate law derived from the above mechanism is

$$\frac{-d[Cr(VI)]}{dt} = \frac{k_1[S]_T[HCrO_4^-][H^+]^3}{\{1 + K_1[H^+]\}[H_2O]} \qquad (11)$$

where k1 = kK]K2K3 and [S]T = the total reducing sugar concentration.

Thus from equation 11,

$$k_{obs} = \frac{k_1[S]_t[H^+]^3}{\{1 + K_1[H^+]\}[H_2O]} \qquad (12)$$

Similar equation was obtained by Gupta & coworkers in their study of the kinetics of oxidation of some aldoses by chromium (VI) [1]. Equation 12 thus confirms the complexity of the order of the reaction with respect to $[H^+]$ and its first -order dependence on the sugars which we have observed experimentally. This is consistent with the reaction formulated in equation 4.

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