The kinetics of catalytic oxidation of D-glucose and D-galactose by potassium heptaoxodichromate (VI) in alkaline medium in the presence of Fe (III)

***Okeola O. Fatai, Odebunmi E. O. and Okoye A. Grace**

Chemistry Department, University of Ilorin, Ilorin, Nigeria.

The kinetics of catalytic oxidation of D-glucose and D-galactose by potassium heptaoxodichromate (VI) in alkaline buffer and in the presence of Fe (III) was investigated spectrophotometrically under pseudo-first order condition, temperature of 308K – 328K and pH of 9.6–11.0. The reaction was first order with respect to oxidant and sugar concentration. The kinetics data show that the rate of oxidation increased with increase in substrate and oxidant concentration, temperature, ionic strength and pH of the reaction medium. The Arrhenius activation energy and other thermodynamic activation parameters are evaluated. Ea for the unanalyzed reaction of glucose and galactose was 139.8kJmol^{-1} and 110.0kJmol^{-1} respectively and 68.8kJmol^{-1} and 58.5kJmol^{-1} respectively for catalysed reaction. The activation energy Ea of the reaction with glucose is higher in both catalysed and uncatalysed reaction. The second order rate constant k_2 for the catalysed reaction for glucose and galactose is 0.023M^{-1}s^{-1} an 0.022 M^{-1}s^{-1} respectively whereas, for the uncatalysed reaction, it was found to be 0.019 M^{-1}s^{-1} and 0.015 M^{-1}s^{-1} for glucose and galactose respectively. The positive effect of the catalyst was observed in the oxidation of both sugars.

Keywords: kinetics, potassium heptaoxodichromate (VI), oxidation; catalyst, glucose, galactose, iron(III), Thermodynamics parameters.

INTRODUCTION

Oxidation of organic compounds for a long time has been used for many useful ends. (Lichtenthaler and Mondel, 1997), Carbohydrates are organic compounds and one of the important natural products. They are important substances in industries and in the living organisms. (Pigman and Horton,1972). Oxidation of sugars has many uses. (Odebunmiet al., 2006) Some industrial processes use this oxidation to prepare some input materials for chemical industries. Carbohydrates perform numerous roles in living organisms and are also sources of energy for vital metabolism processes. (Collinson and Thielemans, 2010; Donald and George, 1977). The biological and economical importance of carbohydrates is due to their reactivities and their biochemical and physiological properties. These reactivities and properties depend largely on their redox behavior (Hudlicky, 1990). Works have been carried out on sugar oxidation and various kinetics studies on the oxidation reaction were embarked upon.

A vast amount of literature is available on the kinetic of oxidation of carbohydrates, using various oxidants. Different methods and reaction media include alkaline

(mostly), acidic and micellar were embarked upon. These were subjected to different reaction conditions such as the effect of pH, temperature, ionic strength, oxidant and substrate concentrations (Okoro and Odebunmi, 2009; Parvataneni et al., 2008; Odebunmi et a.,l 1991; Odebunmi et al., 2009; Owalude, 2004; Okeola et al., 2010; Gupta and Bhathacharya, 1983; Green, 1948).

In spite of these, much works are yet to be done on catalytic oxidation, especially, using homogenous transition metal catalyst. There are of course limited information on catalysed oxidation of reducing sugar using the transitiom metals such as Mn(II), Ir (III), Ru(III), Ruthenate ion ,Os (VIII), Pb (II),V(V), Ru (VIII) and Hg(II) as homogenous catalysts. (Ogunlaja et a.,l 2009; Ashok et a.,l 2007; Singh et al., 2007; Rahmani et al., 2005; Tripathi and Upadhyay, 2004; Singh et al., 1998; Olavi et al., 1985; Singh et al., 1992).

The present work seek to study the kinetics of oxidation of two monosaccharide isomers D-glucose and D-galactose by potassium heptaoxodichromate (VI) in alkaline buffer under the influence of homogenous catalyst, Fe (III).

Ex perimental:

Chemical Reagents

The chemical reagents used in this study were obtained from Merck and BDH. They were of analytical grade. They were used as received and where necessary subjected to further purification. Fresh solutions of buffer were prepared from its components in distilled water. Stock solutions of the substrates and the oxidant were prepared in appropriate buffer solutions

Instrumentation

The instrument used for this experiment includes a UV-visible spectrophotometer (Camspec M106), a thermostat, and pH-meter (Crison micropH 2000).The weighing balance (Mettler P165) was also used to measure the entire chemical reagent used and thermometer (0-120°C) was used to monitor the temperature.

Spectral measurement:

The absorption spectra of different concentrations of the chromium (VI) were measured in the visible region between 300-600nm. The value λmax of 350nm obtained in agreement with literature (Stroh and West, 1982; Sen-Gupta et al 1985).

Kinetic studies:

All kinetic runs should be achieved under pseudo-first order conditions by keeping the concentration of substrate in large excess relative to the oxidant concentration for each of the reaction. The reaction rates was measured with different flasks containing each solution of the oxidants, substrates, catalysts (for catalysed reaction), KNO_3 and buffer solution were arranged in a water bath. The water bath was allowed to attain a constant temperature of 40°C. The oxidation reaction was initiated by adding requisite quantities of the oxidant solution placed separately into the mixture containing the substrate, potassium nitrate, buffer solution and the catalyst.The kinetics of oxidation reaction were followed spectrophotometrically as reported. (Okoro and Odebunmi, 2010). The rate of reaction was monitored by measuring the decrease in absorbance of $K_2Cr_2O_7$ at a wavelength of 350nm. Plots of logarithm of different absorbances versus time gave the pseudo-first order rate constans for the reaction (Shamle et al., 2010).

RESULTS AND DISCUSSION

Effects of variation of reactant concentration

The reactions were studied at various initial sugar concentration but at constant initial concentration of the oxidant $[oxidant]_0$, constant pH, ionic strength and temperature.The pseudo -first-order rate constant k_{obs} was determined from a logarithmic plot of absorbance as a function time (figure 1 and 2). The data in table-1 shows that the pseudo-first-order rate constants increased as the concentration of each sugar increased.

The k_{obs} measurement was repeated but at different initial concentrations of the oxidants and at constant initial concentration of the sugar. The results in table 2 show the pseudo-first order rate constants exhibit a steady increase with increase in the oxidant concentration, suggesting pseudo-first order dependence of reaction rate on $K_2Cr_2O_7$ concentration. This agrees with the observation of (Odebunmi and owalude, 2007; Gupta and Basu, 1979).

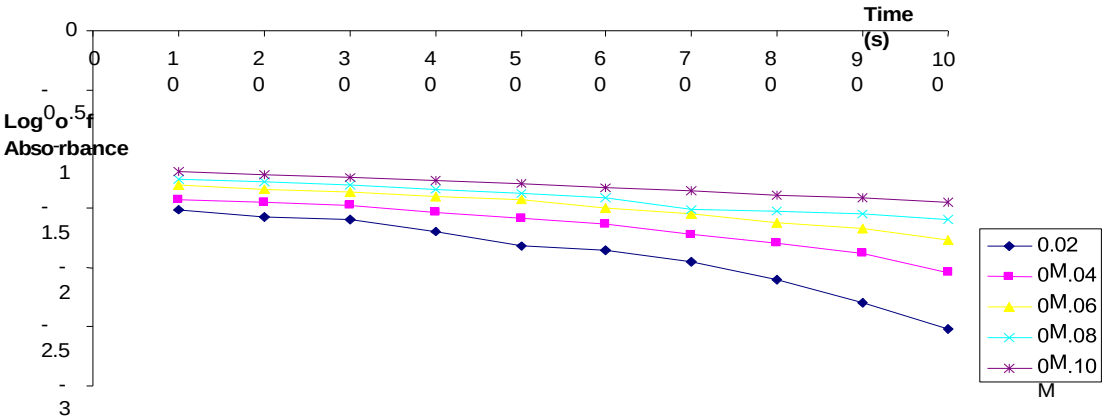

Figure1. Plots of log of absorbance versus time for effect of variation of Gloucose concerntration

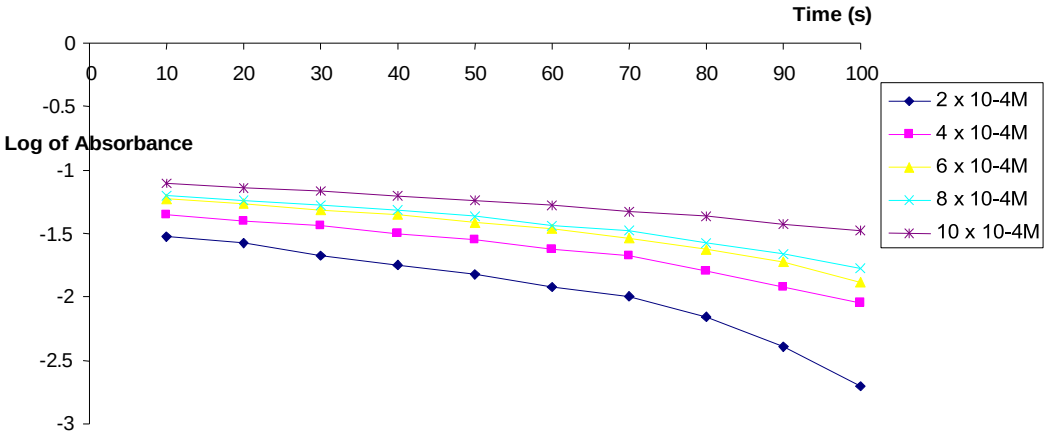

Figure 2. plots of log of absorbance versus time for effect of variation of Galactose concentration on the rate oxidation

Table1. Effect of sugar concentration on rate of reaction at Temp = 40°C, pH= 11, [KNO_3] =0.2M, [$K_2Cr_2O_7$] = 1.0 x 10^{-3}M.

[SUGAR] x 10^{-2}M	Galactose	Glucose
	10^2k_1, s^{-1}	10^2k_1, s^{-1}
1.0	1.89	1.99
2.0	3.32	3.65
3.0	3.90	4.21
4.0	5.62	5.63
5.0	6.78	6.96

Table 2. Effect of oxidant concentration on rate reaction at Temp = 40ºC, [sugar] = 5.0 x 10^{-2}M, pH= 11, [KNO_3] = 0.2M

[OXIDANT] x 10^{-3}M	Glucose	Galactose
	10^2k_1, s^{-1}	10^2k_1, s^{-1}
2.0	1.60	0.57
3.0	1.66	0.60
4.0	1.97	0.87
5.0	2.37	1.33
6.0	2.50	1.49

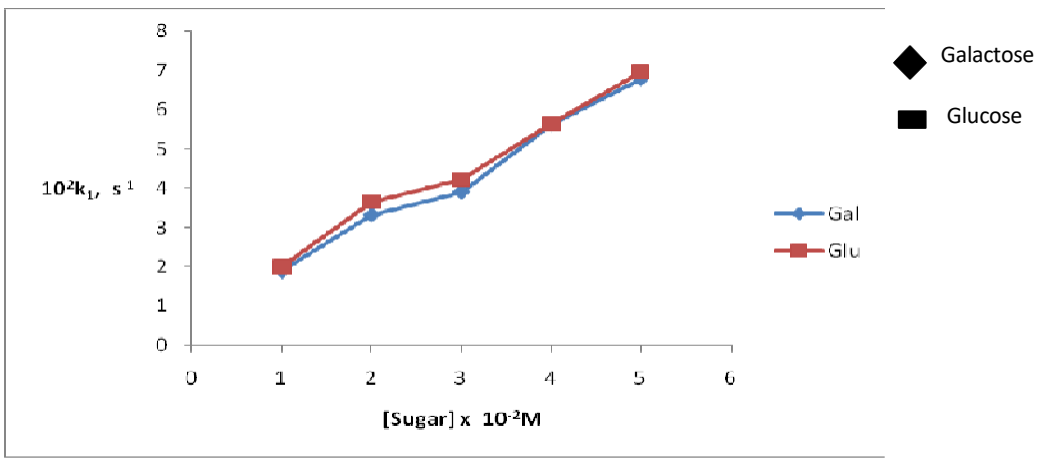

Figure 3. A plot of k obs against Sugar concentration

The plots of k_{obs} against sugar concentration were linear for both sugars, the second order rate constants (k_2) were determined from these plots. These results suggest that the reactions were first order with respect to the reducing sugar and oxidant concentrations.

The second order rate constants k_2 obtained from the slope of the plot of log of pseudo-first order rate constant k_{obs}, against substrate concentration (figure 3) were linear for each sugar, suggesting that the reactions were pseudo first order with respect to the reducing sugar concentrations. The average second-order rate constants have been determined to be 0.023$M^{-1}s^{-1}$ and 0.022$M^{-1}s^{-1}$ for glucose and galactose respectively for the catalyzed reaction. The r elative reactivity of the sugars is thus Glucose ≈ Galactose

Effect of salt concentration

The effect of variation of the concentration of KNO_3 on the rate of oxidation of the sugar was studied at constant concentration of oxidant, sugar, pH and temperature.

The concentration of KNO_3 was varied between 0.02M and 0.10M. The results presented in table 3 shows that the oxidation rate was found to increase with increase in [KNO_3]. This same trend was observed by Rafia *et al. (2006).* This suggests that the reactions

Table 3. Effect of KNO_3 concentration at Temp = 40°C, pH =11.0, [oxidant] = 1.0 x 10^{-3}M, [Sugar] = 5.0 x 10^{-2}M

[KNO_3] M	Glucose	Galactose
	10^2k_1, s^{-1}	10^2k_1, s^{-1}
0.02	1.60	1.58
0.04	1.62	1.60
0.06	1.64	1.62
0.08	2.08	2.04
10.0	2.22	2.18

Table 4. Effect of pH on rate ofreaction at Temp=40°C, [Oxidant] =1.0 x 10^{-3}M, [KNO_3]=0.2M, [Sugar] = 5.0 x 10^{-2}M

pH	Glucose	Galactose
	10^2k_1, s^{-1}	10^2k_1, s^{-1}
9.6	0.72	0.69
9.8	0.90	0.88
10.0	1.33	1.30
10.4	1.64	1.58
10.8	1.86	1.84
11.0	2.10	2.07

occur between ions of similar charges (Puri et al., 2007).

Effect of variation of pH

The effect of pH on the rate of oxidation of sugars was studied at 40°C in the pH range 9.60 to 11.0, and at constant ionic strength, constant concentrations of oxidant and substrate. The results in table 4: how that the rate of oxidation increased with increase in the pH of the reaction medium for both reactions. The plots of log k_{obs} against pH were linear for all the reactions. The same trend was observed by Shankar and Bihari (1991). These results suggest that the hydrogen ion and hydroxyl ions may be involved in the rate determining step of the oxidation reaction. It also shows that the reactions were base catalyzed (Odebunmi et al., 2006).

Effect of the catalyst in the sugar oxidation

The experiment on the effect of variation of reactant concentration was repeated, with the reaction carried out with the inclusion of constant concentration catalyst, [$FeCl_3$] in the reacting mixture. The data in table 5a and 5b show k_{obs} for catalysed reaction to be greater than of corresponding non catalysed reaction.

From the plots, the values of the second order rate constant k_2 for the catalyzed reaction are 0.023$M^{-1}S^{-1}$ and 0.022$M^{-1}s^{-1}$ for glucose and galactose respectively, as against the uncatalyzed reaction of 0.019$M^{-1}s^{-1}$ and 0.015$M^{-1}s^{-1}$, for glucose and galactose respectively, whereas. The relative reactivity of the sugars are Glucose ≈ Galactose still remains. A similar result was observed in Mn(II) catalysed sugar oxidation (15)It was also used as homogenous catalyst and in the first transition series as Fe (III)

Effect of variation of temperature

The oxidation of the sugars were carried out at different temperatures from 35°C to 55°C.This was done at constant, the concentrations of oxidant, KNO_3, sugar, pH and catalyst (for a catalyzed reaction). The pseudo-first order rate constant was observed to increase with

Table 5a. Effect of sugar concentration on rate for the catalyzed reaction at Temp = 40°C, pH= 11, [KNO_3] =0.2M, [$FeCl_3$] = 6.0x10^{-4}M, [Oxidant] = 1.0 x 10^{-3}M

	GALACTOSE		GLUCOSE	
[Sugar] x 10^{-2}M	**Catalysed**	**Uncatalysed**	**Catalysed**	**Uncatalysed**
	10^2k_1, s^{-1}	10^2k_1, s^{-1}	10^2k_1, s^{-1}	10^2k_1, s^{-1}
1.0	3.39	1.89	3.49	1.99
2.0	4.82	3.32	5.15	3.65
3.0	5.44	3.90	5.71	4.21
4.0	7.12	5.62	7.13	5.63
5.0	8.28	6.78	8.30	6.96

Table 5b. Effect of oxidant concentration on rate for catalyzed and uncatalysed reaction at Temp = 40°C, [sugar] = 5.0 x 10^{-2}M, pH= 11, [KNO_3] = 0.2M, [$FeCl_3$] = 6.0 X 10^{-4}M.

	GLUCOSE		GALACTOSE	
[Oxidant] x 10^{-3}M	**Catalysed**	**Uncatalysed**	**Catalysed**	**Uncatalysed**
	10^2k_1, s^{-1}	10^2k_1, s^{-1}	10^2k_1, s^{-1}	10^2k_1, s^{-1}
2.0	3.10	1.60	2.07	0.57
3.0	3.16	1.66	2.10	0.60
4.0	3.47	1.97	2.37	0.87
5.0	3.87	2.37	2.83	1.33
6.0	4.00	2.50	2.99	1.49

Table 6. Effect of temperature variation on the rate at pH =11, [Sugar] = 5.0 x 10^{-2}M, [Oxidant] = 1.0 x 10^{-3}M, [KNO_3] =0.2M, [$FeCl_3$] = 6.0 X 10^{-4}M for the catalyzed and uncatalysed reaction

	Galactose		Glucose	
Temperature °C	Catalysed	Uncatalysed	Catalysed	Uncatalysed
	10^2k_1, s^{-1}	10^2k_1, s^{-1}	10^2k_1, s^{-1}	10^2k_1, s^{-1}
35	2.98	5.89	3.00	6.01
40	3.00	6.00	3.02	6.04
45	3.00	6.80	3.04	6.85
50	3.02	6.96	3.06	7.01
55	3.04	7.00	4.00	7.02

increase in temperature as shown in table 6. The logarithmic plot of the second order rate constant k_2 against the reciprocal of the temperature 1/T in Kelvin. This is shown in figure 4. The Arrhenius parameters (i.e. Ea and A) shown in table 7 were determined from from the plots the values of the Arrhenius activation energy Ea, for the catalysed oxidation of glucose and galactose obtained from the slopes of the linear plots are 68.9kJ/mol and 55.5kJ/mol respectively and the values of A are 3.1$Lmol^{-1}s^{-1}$ and 1.6 $Lmol^{-1}s^{-1}$ for glucose and galactose respectively. On the other hand, for the uncatalyzed reaction, the values of Ea for glucose and galactose are 139.8kJ/mol and 110.0$kJmol^{-1}$ respectively and the values of A are 6.50$L/mol^{-1}$and 3.60L/mol^{-1} for glucose and galactose respectively.

The other thermodynamic activation parameters ($\Delta H^{\neq}$,$\Delta S^{\neq}$ and $\Delta G^{\neq}$) (table 7) were determined as in the literature (Puri et al., 2007; Frost and Pearson, 1970), It is being observed that the rate of reaction for the oxidation of the sugars was enhanced by an increase in the temperature of the reaction medium. Also, Ea of the

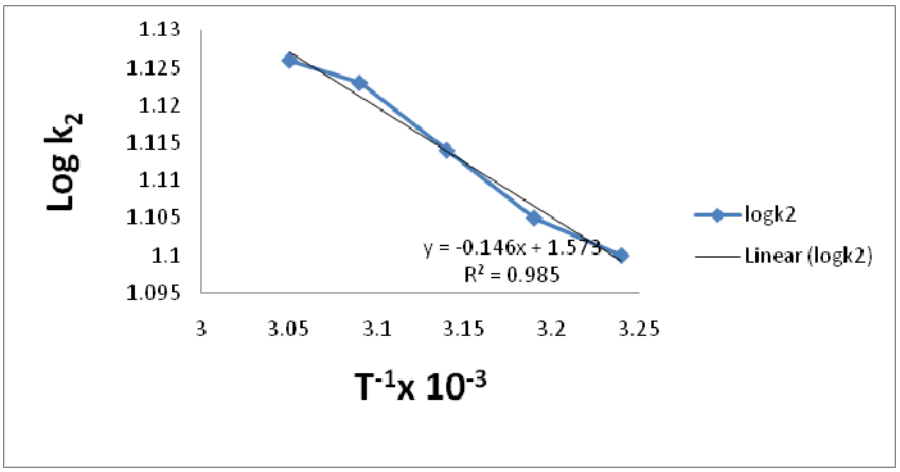

Figure 4. Arrhenius plot of Log k_2 against 1/T for oxidation of Glucose

Table 7. Arrhenius and thermodynamic activation parameters for the oxidation of sugars by alkaline $K_2Cr_2O_7$ at 313K for the catalyzed reaction

Sugar	Ea (kJmol^{-1})	$\Delta H^{\neq}$ (kJmol^{-1})	$\Delta S^{\neq}$(Jmol^{-1}K^{-1}	$\Delta G^{\neq}$ (kJmol^{-1})	A (Lmol^{-1}S^{-1}
Glucose	68.9	63.7	-235.90	137.54	3.6
Galactose	55.5	50.3	-241.40	139.26	1.6

For the uncatalyzed reaction

Sugar	Ea (kJmol^{-1})	$\Delta H^{\neq}$ (kJmol^{-1})	$\Delta S^{\neq}$ (Jmol^{-1}K^{-1}	$\Delta G^{\neq}$ (kJmol^{-1})	A (Lmol^{-1}S^{-1}
Glucose	139.8	134.6	-229.74	206.51	6.5
Galactose	110.0	104.8	-234.66	178.24	3.6

reaction with glucose is slightly greater than Ea with galactose for both catalyzed and uncatalyzed reaction, which implies that the energy barriers of glucose is higher than that of galactose. The liberated energy, $\Delta H^{\neq}$, is also, fairly higher in the case of glucose. The values of Ea of uncatalysed reaction is greater than the Ea of catalysed reaction which suggest an indication of positive catalysis (Odebunmi et al., 2010).

CONCLUSION

During the course of this work, some factors were observed to enhance the rate of the sugar oxidation. These include increase in either of the reactants concentration, increase in temperature, ionic strength, and pH. The oxidation of glucose and galactose when the reaction was carried out using Fe (III) as a homogenous catalyst, the rate of reaction was enhanced. This was the result of alternative route of lower activation energy.

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