Advances in Environmental Biology, 4(3): 451-455, 2010
ISSN 1995-0756

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ORIGINAL ARTICLE

Comparative Study of Kinetics of Catalysed Oxidation of Glucose and Galactose by Hexacyanoferrate (III) Ion and Copper Sulphate in Alkaline Medium

Okeola F.O., Odebunmi E.O. and Olagoke O.A.

Chemistry Department University of Ilorin Ilorin,nigeria

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ABSTRACT

The kinetic study of catalytic oxidation of glucose and galactose by hexacyanoferrate(III) and copper sulphate have been investigated spectrophotometrically under pseudo first order condition, temperature of 313K – 353K and pH 9.60 – 11.20.The results show that the rate of oxidation of both glucose and galactose increased with increase in substrate concentration, temperature, ionic strength as well as pH. The Arrhenius activation energy at 313K for the uncatalysed glucose and galactose was found to be 63.18 and 12.3 $KJmol^{-1}$ respectively for hexacyanoferrate(III) and 124.5 and 13.4 $KJmol^{-1}$ respectively for copper sulphate,showing that Ea of the reaction was found to be higher with glucose than with galactose. The second order rate constantsobserved show the rate of reaction to be in order of galactose > glucose for hexacyanoferrate(III), and glucose > galactose for copper sulphate. The positive effect of catalyst was observed with Cu^{2+} in the reaction of galactose but not in glucose with hexacyanoferrate(III) as oxidant.. Oxidation of both sugars with $CuSO_4$ as oxidant was found not to enhance by Cr^{3+}.

Key words:

Introduction

Carbohydrates are one of three basic macronutrients needed to sustain life (the other two are proteins and fats). Carbohydrates serve as energy stores, fuels, and metabolic intermediate in biosynthesis. They also involve in the transport of energy and their derivatives include many important bimolecular that play key roles in the immune system, fertilization, pathogenesis, blood clotting, and development. [1]The kinetics of oxidation of sugars has been subject of extensive research in recent years. This is due to the increasing economic and biological importance of carbohydrate to living organisms. The oxidation of reducing sugar have been carried out in acidic and alkaline medium using such oxidants as transition metals ions, inorganic acids, organometallic complexes and enzymes [2]. Oxidation occurs under different conditions of pH, temperature and ionic strength giving products that depend on the reaction conditions used [3] The Kinetics and thermodynamics of glucose oxidase catalyzed oxidation reaction of glucose was studied over different reaction conditions. [4] kinetics and mechanism of Mn(ii) catalyzed oxidation of D-Arabinose and D-xylose by chromium(vi) ions in perchloric acid medium was also reported.[5] Oxidation of reducing sugars (aldo and keto hexoses) by alkaline potassium ferricyanide was carried out to study kinectics and transformation.[6]

The objective of this project work is to compare the kinetics of catalytic oxidation of two monosaccharides (glucose and galactose) with two oxidants (hexacyanoferrate (III) and copper sulphate) in alkaline medium under the different condition of substrate concentration, oxidant concentration, ionic

Corresponding Author
Okeola F.O., Chemistry Department University of Ilorin Ilorin,nigeria
Email: okeolaf@yahoo.com; okeola.of@unilorin.edu.ng
Phone Number: +2348058749768, +2348038626501

strength, pH and temperature on the rate of oxidation of glucose and galactose.

Experimental:

Chemical reagents of analytical grade,obtained from Merck and BDH.They were used as received and where necessary, some chemical reagents were subjected to further purification.

Stock solutions of the sugars as well as the oxidant were prepared using distilled water. Also fresh solutions of buffer were prepared for use when needed.

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 (0-120ºC) was used to check the temperature.

Kinetic Measurement:

The reaction rates was measure with different flasks containing each solution of the oxidants, substrates, catalysts, KNO_3 and buffer solution were arranged in a water bath. The water bath was allowed to attain a constant temperature of 40ºC. The oxidation reaction was initiated by mixing requisite quantities of the sugar solution and a mixture containing the oxidant, potassium nitrate, buffer solution and the catalyst.The kinectics of oxidation reaction were followed spectrophotometrially reported The absorbance which changes with time was recorded at at 600nm and 420nm for copper sulphate and hexacyannoferrate(III). All kinetic measurement was made under pseudo first order condition with the concentration of subsrate in large excess relative to the oxidant concentration for each of the reaction. [7]

Results and Discussion

The general kinetics features observed with the sugars (glucose and galactose) used are similar.The values of k_{obs} were determined from the slopes of the plot of log absorbance against time, Figure 1a-b shows such plot for glucose / hexacyannoferrate(III) and galactose/ hexacyannoferrate(III) reactions respectively. The values of k_{obs} in each sugar-oxidant reaction as shown in table 1 increases with increase in sugar concentration .This agree with literature reports.[8] The second order rate constant (k_2) was obtained from the slope of linear plot of pseudo- first order rate constant, k_{obs} against substrate concentration table 2. The order of the reactivity of the sugars are glucose > galactose for copper sulphate as oxidant and galactose > glucose for hexacyannoferrate(III) as oxidant Similar result where k_2 relative result of two substrate was affected by different oxidant.[3] The results in table 3 also show that the rates of the reaction are enhanced by the increase in pH of the reaction medium. This is in agreement with literature report [9]. The salt effect of KNO_3 as shown in table 4, increase the rate of the reaction as the salt increases suggesting that the reaction takes place between ions of similar charges.[10]

For the catalysed oxidation of sugars, the positive effect of catalysis was observed with Cu^{2+} as catalyst in the reaction of galactose,but not in glucose with hexacyannoferrate(III) as oxidant table 5a. This positive effect of Cu^{2+} on sugar oxidation was reported. [11] On the other hand Cr^{3+} inhibit reaction of both substrate with copper sulphate as the oxidant as shown in table 5b.The different in the catalytic ability of Cu^{2+} and Cr^{3+} has also being reported[12].

Table 1: Effect of Variation of Substrate Concentration on the rate of oxidation by $Fe(CN)_6^{-3}$ an$CuSO_4$ at 40ºC,pH==9.3

Concentration of substrate x 10^{-2} (M)	$K_{obs} \times 10^{-3}s^{-1}$		$K_{obs} \times 10^{-3}s^{-1}$	
	Glucose		Galactose	
	$Fe(CN)_6^{3-}$	$CuSO_4$	$Fe(CN)_6^{3-}$	$CuSO_4$
2	2.39	2.94	1.40	1.83
4	2.41	3.92	4.31	3.32
6	2.54	5.10	4.64	4.20
8	2.92	6.50	5.32	5.14
10	3.30	10.62	7.40	8.13

Table 2: Second Order Rate Constant of Sugar at 40ºC,pH==9.3,

Oxidant	Sugar	k_2 $dm^3mol^{-1}s^{-1}$
$CuSO_4$	Glucose	89.72
	Galactose	72.10
$Fe(CN)_6^{3-}$	Glucose	11.65
	Galactose	65.05

Table 3: Effect of pH on its Rate of Oxidation at 40ºC

pH	$CuSO_4$ Glucose $k_{obs} \times 10^{-3}S^{-1}$	$CuSO_4$ Galactose $k_{obs} \times 10^{-3}S^{-1}$	$Fe(CN)_6^{-3}$ Glucose $K_{obs} \times 10^{-3}S^{-1}$	$Fe(CN)_6^{-3}$ Galactose $K_{obs} \times 10^{-3}S^{-1}$
9.60	3.84	3.23	2.38	1.60
10.0	4.42	3.91	2.40	1.71
10.6	5.85	4.70	2.45	1.82
11.0	7.93	7.39	2.64	1.86
11.2	9.34	8.20	3.54	1.92

Table 4: Effect of Ionic Strenght on Rate of its Oxidation of Substrate at 40ºC sugar conc. 0.02M pH 9.3

$[KNO_3]$ (M)	$CuSO_4$ Glucose $K_{obs} \times 10^{-3}s^{-1}$	$CuSO_4$ Galactose $K_{obs} \times 10^{-3}s^{-1}$	$Fe(CN)_6^{-3}$ Glucose $K_{obs} \times 10^{-3}s^{-1}$	$Fe(CN)_6^{-3}$ Galactose $K_{obs} \times 10^{-3}s^{-1}$
0.03	3.41	2.53	3.90	3.82
0.06	3.64	3.45	4.42	4.33
0.09	5.23	5.01	5.20	5.12
0.12	7.24	6.30	5.29	5.20
0.15	9.81	7.98	5.40	5.71

Table 5a: Result of sugar oxidation by $Fe(CN)_6^{-3}$ with Cu(II) ion catalyst at 40ºC

Concentration (M)	$K_{obs} \times 10^{-3}s^{-1}$ Catalysed Glucose	$K_{obs} \times 10^{-3}s^{-1}$ Uncatalysed Glucose	$K_{obs} \times 10^{-3}s^{-1}$ Catalysed Galactose	$K_{obs} \times 10^{-3}s^{-1}$ Uncatalysed Galactose
0.02	1.83	2.20	1.49	1.40
0.04	1.90	2.34	5.00	4.31
0.06	2.15	2.71	5.13	4.64
0.08	2.43	3.10	7.51	5.32
0.10	2.64	3.18	7.74	7.40

Table 5b: Result of sugar oxidation by $CuSO_4$ with Cr(III) ion catalyst at 40ºC

Concentration (M)	$K_{obs} \times 10^{-3}S^{-1}$ Catalysed Glucose	$K_{obs} \times 10^{-3}S^{-1}$ Uncatalysed Glucose	$K_{obs} \times 10^{-3}S^{-1}$ Catalysed Galactose	$K_{obs} \times 10^{-3}S^{-1}$ Uncatalysed Galactose
0.02	2.30	2.94	1.80	1.83
0.04	2.74	3.92	1.92	3.32
0.06	3.00	5.10	2.10	4.20
0.08	3.42	6.50	2.28	5.14
0.10	3.93	10.6	2.44	8.13

Table 6a: Effect of Temperature on Rate of its Oxidation by $CuSO_4$ sugar conc. 0.02M pH = 9.3 $[KNO_3]$ = 0.2M

Temperature (ºC)	[Glucose] $k_{obs} \times 10^{-3}S^{-1}$	[Galactose] $K_{obs} \times 10^{-3}S^{-1}$
40	2.71	2.00
50	3.54	2.02
60	4.23	2.08
70	6.50	2.20
80	7.81	2.39

Table 6b: Effect of Temperature on Rate of its Oxidation by $Fe(CN)_6^{-3}$ sugar conc. 0.02M pH = 9.3 $[KNO_3]$ = 0.2M

Temperature (ºC)	[Glucose] $k_{obs} \times 10^{-3}S^{-1}$	[Galactose] $K_{obs} \times 10^{-3}S^{-1}$
40	1.83	1.00
50	2.41	1.11
60	2.62	1.24
70	3.50	1.38
80	4.29	1.51

Table 7a: Arrhenius And Thermodynamic Activation Parameter For The Oxidation Of Sugars By $CuSO_4$ at 40ºC sugar conc. 0.02M pH = 9.3 $[KNO_3]$ = 0.2M

Substrate	Ea $KJmol^{-1}$	A $dm^3mol^{-1}s^{-1}$	$\Delta H^{\#}$ $KJmol^{-1}$	$\Delta S^{\#}$ $KJmol^{-1}$	$\Delta G^{\#}$ $Kjmol^{-1}$
Glucose	124.5	0.68	-2477	-248.3	75.24
Galactose	13.40	0.07	-2588	-267.2	81.04

Table 7b: Arrhenius And Thermodynamic Activation Parameter For The Oxidation Of Sugars By Hexacyannoferrate (III) at 40ºC sugar conc. 0.02M pH = 9.3 $[KNO_3]$ = 0.2M

Substrate	Ea $KJmol^{-1}$	A $dm^3mol^{-1}s^{-1}$	$\Delta H^{\#}$ $KJmol^{-1}$	$\Delta S^{\#}$ $KJmol^{-1}$	$\Delta G^{\#}$ $KJmol^{-1}$
Glucose	63.18	0.29	-2539	-243.32	73.62
Galactose	12.30	0.10	-2589	-243.16	73.52

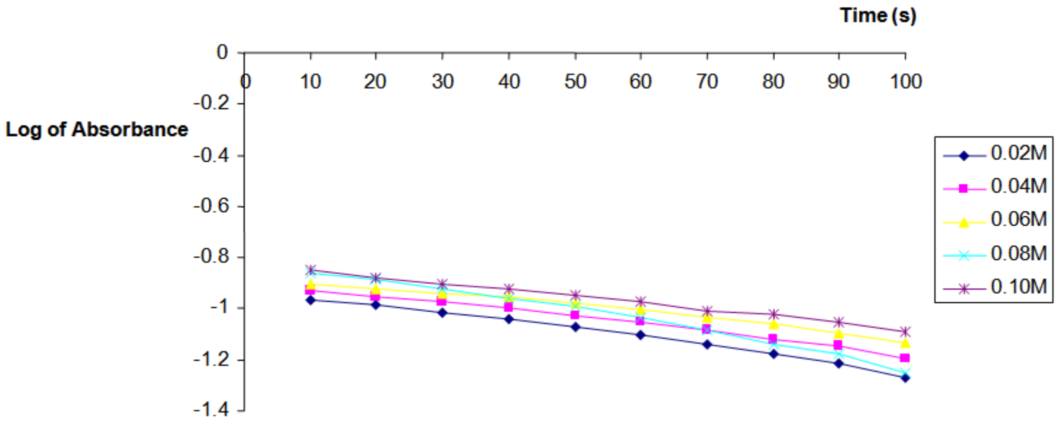

Fig. 1a: Effect of Glucose Concentration on the Rate of Oxidation by $Fe(CN_6)^3$

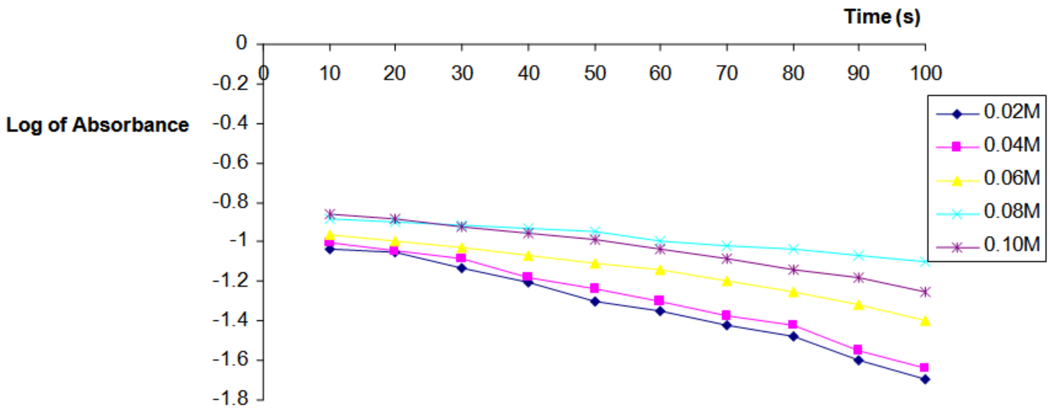

Fig. 1a: Effect of Glucose Concentration on the Rate of Oxidation by $Fe(CN_6)^3$

The oxidation of sugars was carried out at different temperatures from 40 – 50°C. The pseudo first order rate constants increased with increased with increase in temperature The thermodynamic parameters are given in table 7a-b. show that that the reactions of glucose with each of the oxidants give a higher Ea than that of galactose. This indicate that much energy has to be surmounted for the reaction of glucose for both oxidant used. In reaction involves glucose higher value of $\Delta H^{\#}$ was observed. The $\Delta S^{\#}$ is negative in all the reactions,. [4,9]

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