Kinetic and Mechanistic Study of Oxidation of D-galactose and D-glucose by Quinolinium Fluorochromate in Aqueous Acetic Acid

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ABSTRACT

The present work deals with the kinetics of oxidation of D-Glucose and D-Galactose by Quinolinium fluorochromate (OFC) in aqueous acetic acid 50% (v/v) medium has been investigated. The reaction has been found to be first order with respect to each of the substrate and oxidant under pseudo first order conditions. The reaction is catalyzed by acid and follows a first order dependence H^+ concentration. The decrease in dielectric constant of the medium increases the rate of reaction. The rate of reaction was not influenced by ionic strength.   The stoichiometry of reactions is 1:1. The effect of temperature   is studied and the various activation parameters are determined. A probable reaction mechanism is proposed.

Key words: Kinetics, Oxidation, D-Glucose, D-Galactose, Quinolinium fluorochromate.

INTRODUCTION

A variety of compounds containing chromium (VI) have proved to be versatile reagents capable of oxidizing every oxidiasable functional group. A number of new chromium(VI) containing compounds like Quinolinium fluorochromate (QFC) has been used as mild and selective oxidizing agent in synthetic organic chemistry[1]. It oxidizes secondary alcohols to corresponding ketones in dimethyl sulphoxide (DMSO)[2-3] and also oxidizes Atrolactic acid to the ketones[4].

The kinetics of oxidation of reducing sugars which contain a large number of functional groups is of considerable interest from the mechanistic point of view and have been studied fairly well[5-9]. The oxidation of carbohydrates was widely studied by many researchers[10-12]. Sharma *et al*[13].,

reported oxidation of monosaccharides such as D-xylose, D-galactose. Kinetics of dextrose and serbose in sulphuric medium follows first order rate constant by Ce (IV) and zero order with glucose, fructose and galactose by ammonium metavandate in H_2SO_4 medium. Oxidation of sugars and non sugar by hexa cyanoferrate (III) in alkaline medium were investigated by Nath and Singh[10]. The kinetics of arabinose, galactose, xylose, fructose, lactose, maltose by chloramines-*T* exhibit first order kinetics with respect to substrate, [Chloramines-T] and $[OH^-]$[14]. The kinetics of oxidation of D-glucose[15] with QCC in acetic acid medium have been studied at constant ionic strength. The reaction is first order each in [oxidant] and [D-glucose]. Arabinose and formic acid have been identified as the main product of the reaction. The present investigation is concerned with the kinetics and oxidation of D-Glucose and D-Galactose by Quinolinium fluorochromate in aqueous acetic acid medium.

EXPERIMENTAL

Quinolinium fluorochromate (QFC) was prepared by the method described in literature[1], and its purity was checked by melting point, TLC and an iodometric method. All chemicals used were of Merck and BDH, AR grade quality. Acetic acid (AR grade) laboratory reagent was dried and distilled by method of Orton and Bradfield[16] . Solutions of D-Glucose and D-Galactose were freshly prepared in 1:1 aqueous acetic acid. All the kinetic measurements were carried out at constant temperature ($\pm 0.1^oC$).

KINETICS MEASUREMENTS

The reactions were carried out as QFC react iodometrically as a function of time. Equal volumes of QFC and aldoses of required concentration in 50% acetic acid were taken into two separate iodine flasks and placed in thermostatic bath at required temperature. After half an hour carbohydrate (aldose) solution is quickly added to QFC solution. The kinetics of the oxidation was followed by taking aliquots of 10 ml of reaction mixture into a stoppered flask containing 10 ml of KI solution to arrest the reaction. The rate of oxidation was measured by titrating the liberated iodine against sodium thiosulphate solution iodometrically using starch as an indicator. The reaction was followed by taking burette readings at different time intervals up to 70-80% completion of reaction. The concentration of QFC remaining unreacted at the various time intervals can be determined. First order rate constants were determined by calculation and graphical method.

RESULTS AND DISCUSSION

Stoichiometry and product analysis:-

The stoichiometry of the oxidation reaction was carried out by taking excess of QFC than carbohydrate and was kept for several hours at 308K for the reaction to go for completion. The unconsumed oxidant was estimated iodometrically at the end of reaction. The stoichiometry was found to 1:1,

For the product analyses, the reaction mixture containing hexose and QFC in the stoichiometry proportion of 1:1 was left as to equilibrate at 308K for 24 hours. The product of oxidation of D-glucose and D-galactose was found to be five membered aldopentoses like D-arabinose D-lyxose along with formic acid. The formations of aldopentoses were confirmed by phenylhydrazone formation[17]. The presence of formic acid was confirmed by spot test[18]. The oxidation state of chromium in completely reduced mixtures, determined by iodometric method.

Effect of variation of [Aldohexoses] on rate of oxidation:-

The pseudo first order rate constants were determined at various initial concentrations of reactants. It has been found that, reaction rate increases with increase in concentration of hexose.

TABLE –1: EFFECT OF CONCENTRATION OF HEXOSES ON RATE OF REACTION

$[QFC]$ = 1 $\times$ 10^{-3}M;   [$Na_2S_2O_3.5H_2O$] = 1 $\times$ 10^{-2}M; solvent = 50% (v/v) Acetic acid; Temp. 308K.

[Aldohexose] 10^2 moldm^{-3}	Rate constant K $\times$ 10^3 (min^{-1})	
	D-Glucose	D-Galactose
1.0	2.32	1.98
2.0	3.94	2.81
3.0	5.45	4.03
4.0	6.88	4.87
5.0	8.39	5.71

Effect of variation of [QFC] on reaction rate:

Rate constants increases with increase in concentration of QFC, indicates that the reaction is first order with respect to [QFC].

TABLE –2: EFFECT OF CONCENTRATION OF QFC ON REACTION RATE

[Aldohexose] = 3 $\times$ 10^{-2}M;   [$Na_2S_2O_3.5H_2O$] = 1 $\times$ 10^{-2}M, Solvent = 50% Acetic acid; Temperature = 308K

[QFC] 10^3 moldm^{-3}	Rate constant K 10^3 (min^{-1})	
	D-Glucose	D-Galactose
1.0	6.12	7.31
2.0	9.15	13.86
3.0	12.42	14.43
4.0	15.53	24.05
5.0	17.54	29.71

Effect of variation of [H$^+$] on reaction rate:

Rates of oxidation were found to be increase with increase in [H$^+$] and that the reaction is acid catalyzed and follows the first order dependence in [H$_2$SO$_4$].

TABLE –3: EFFECT OF [H$^+$] ON REACTION RATE

[Aldohexose] = 3 10^{-2}M; [QFC] = 1 10^{-3}M; [Na$_2$S$_2$O$_3$.5H$_2$O] = 1 10^{-2}M
[H$_2$SO$_4$] = 1 10^{-2} to 3 10^{-2} moldm^{-3}; Solvent : 50% (v/v)Acetic acid; Temperature : 308K

[H$^+$] 10^2 moldm^{-3}	Rate constant K 10^3 (min^{-1})	
	D-Glucose	D-Galactose
1.0	4.17	3.93
1.5	4.74	4.32
2.0	6.14	5.04
2.5	8.11	5.01
3.0	10.3	6.50

Effect of ionic strength (Salt effect):-

The reaction rate was not influenced by ionic strength when KCl was initially added to the reaction mixture over the range of 1 10^{-1} to 5 10^{-1} Moldm^{-3}. Similar observations were also reported earlier in the oxidations of diols by some oxochromium (VI) reagents[19] and chromic acid[20].

Effect of solvent:

The reaction has been studied under various compositions of acetic acid-water mixture. It has been observed that, the reaction rate increases

with increase of CH_3COOH in acetic acid-water mixture (Table-4). Which suggests an interaction between ions

formed during reaction and developing dipole moment[21].

TABLE –4: DEPENDENCE OF RATE ON SOLVENT COMPOSITION

[Aldohexose] = 3 $\times$ 10^{-2}M; [QFC] = 1 $\times$ 10^{-3}M; [Na$_2$S$_2$O$_3$.5H$_2$O] = 1 $\times$ 10^{-2}M
Solvent : 40% - 80% Acetic acid ; Temperature : 308K

Composition CH_3COOH : H_2O	$\dfrac{1}{D}$	K $\times$ 10^3 (min^{-1})	
		D-Glucose	D-Galactose
40:60	0.020	2.79	3.88
50:50	0.024	3.55	4.56
60:40	0.028	4.12	5.30
70:30	0.036	4.93	6.98
80:20	0.048	6.38	9.43

Effect of Temperature:-

The reaction rates at different temperatures were determined. The data in Table-5 shows that, the rate of reaction increases with increase in temperature and these reactions are characterized by high negative value of entropy of activation (ΔS^*). This indicates that solvation effects are predominant in the reaction, which suggests the formation of changed and rigid transition state. Furthermore, the high positive values of energy of activation and enthalpy of activation indicate that the intermediate is highly solvated.

TABLE-5: DEPENDENCE OF RATE ON TEMPERATURE AND ACTIVATION PARAMETERS OF OXIDATION OF ALDOHEXOSES BY *QFC*.

[Aldohexose] = 3 $\times$ 10^{-2}M; [QFC] = 1 $\times$ 10^{-3}M; Solvent : 50% Acetic acid; Temp. 293 K – 318 K

Substrate	K $\times$ 10^3 (min^{-1}) Temperature (K)					E_a (Kcal)	$\Delta H*$ (Kcal)	$\Delta S*$ (Kcal)	$\Delta G*$ (Kcal)
	293	303	308	313	318				
D-Glucose	4.29	4.87	5.12	5.47	6.06	2.167	1.551	-70.25	21.64
D-Galactose	3.08	3.60	4.03	4.51	5.14	3.316	2.700	-66.15	20.37

Mechanism:-

On the basis of the results, the following reaction mechanism is proposed. The oxidation D-Galactose proceeds via hydride ion transfer   involving the specific cleavage of C_1-C_2 bond of the substrate to give D-lyxose and formic acid.
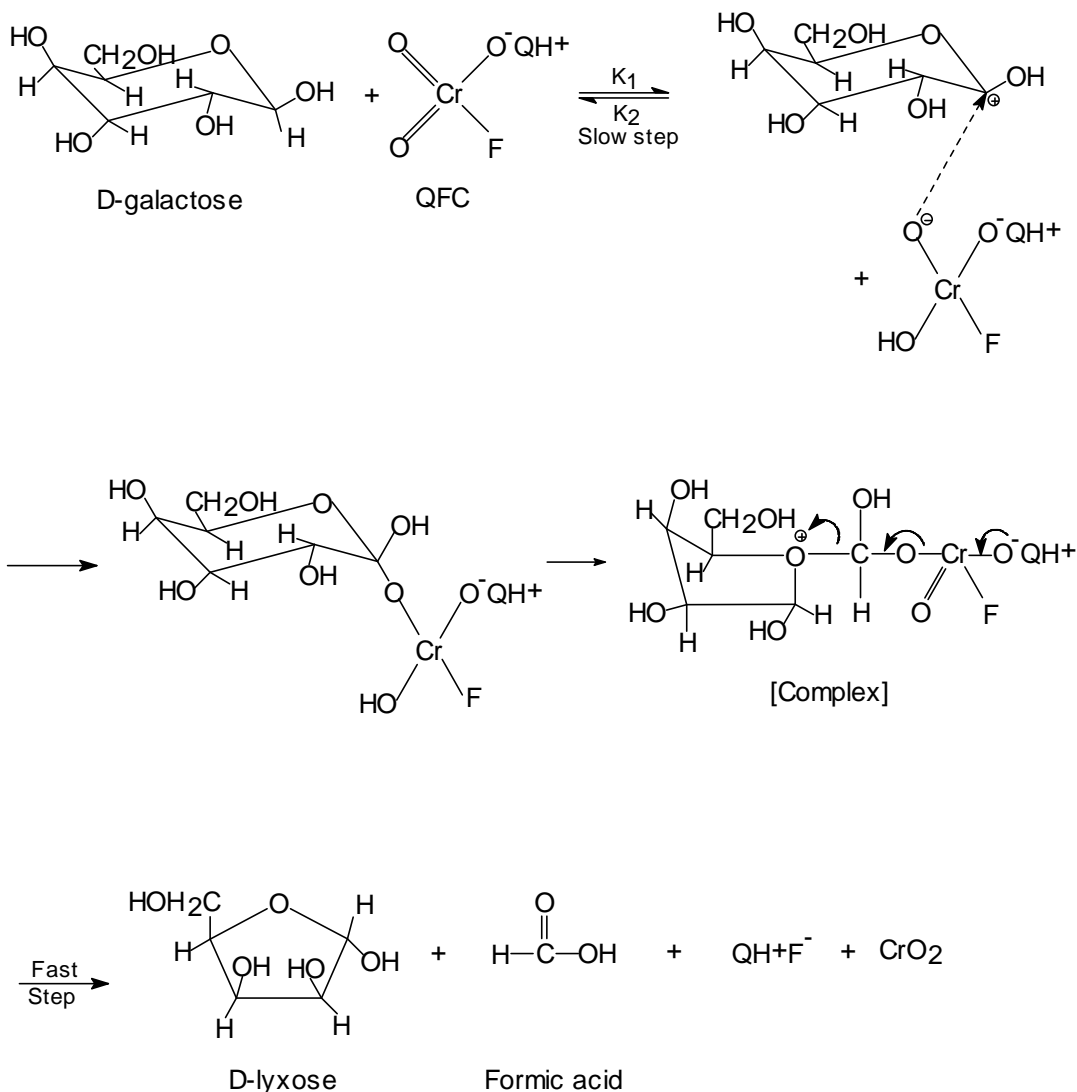
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