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Kinetics of oxidation of maltose by pyridinium fluorochromate in aqueous acetic acid

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ABSTRACT

The kinetics of oxidation of maltose by pyridinium fluorochromate in aqueous acetic acid inpresence of perchloric acid has been studied. The reaction shows fractional order dependence on [maltose]. The rate of reaction increases with increase in [$HClO_4$]. An increase in rate constant was observed with decrease in dielectric constant of the medium. Addition of salt has positive effect on the rate. The activation parameters were calculated from Arrhenius plot.

KEYWORDS

Kinetics;
Oxidation;
Maltose;
Pyridinium fluorochromate.

INTRODUCTION

Oxidation is one of the fundamental reactions in synthetic organic Chemistry. Kinetics of oxidation of some organic substrates such as organic sulfides, benzaldehydes, phenols, glucose etc.[1-5] by Pyridinium Fluorochromate has already been reported. Pyridinium fluorochromate (PFC) is a mild and selective oxidizing agent. Kinetics of oxidation of maltose by various oxidants have been reported[6,7]. However, literature survey reveals that there are no reports so far about the kinetics of oxidation of maltose by Cr (VI) compound with heterocyclic base such as Pyridinium fluorochromate. So we have taken up the systematic kinetic study of oxidation of maltose by PFC. The present work reports the kinetics of oxidation of maltose by PFC.

MATERIALS AND METHODS

Materials

All the chemicals used were of AR grade. Acetic acid was purified by the method of Orton and Bradfield. Pyridinium Fluorochromate (PFC) was prepared from Pyridine, Hydrofluoric acid (40 %) and chromium oxide all were (AR Grade) used in the ratio 1:1.5:1. The bright orange solid which was isolated by filtration and dried in vacuum, yield 93-94%. Re-crystallized the product from water (M P 106-108 °C) and further used for oxidation of maltose.

Kinetic measurements

The reactions were followed under pseudo first order conditions by maintaining a large excess of maltose over PFC. Rate studies were carried out at the desired temperature with an accuracy of ± 0.5 °C. The reactions were followed by monitoring decrease in concentration of PFC spectrophotometrically at 370 nm. The pseudo first order rate constants were evaluated from the linear plots of log(Absorbance) against time. Duplicate kinetic runs showed that the rate constants are reproducible to within ± 5.0%

Stoichiometry & product analysis

The stoichiometric analysis of oxidation of maltose by pyridinium fluorochromate indicate that one mole of oxidant reacts with one mole of substrate. Formic acid and arbinonic acid were the main oxidation products. The reaction may be represented stoichiometrically as:

$$C_{12}H_{22}O_{11} + C_5H_5NHFCrO_3 + 4H_2O \longrightarrow$$

$$2C_5H_{10}O_6 + 2HCOOH + 2CrO2 + C_5H_5NHF + 6H^+$$

The products were confirmed by TLC. The presence of carboxylic acid group in the given compound is confirmed by the addition of product in 1ml of 5% sodium bicarbonate solution, evolution of CO_2 with effervescence indicates the presence of acidic group.

RESULT AND DISCUSSION

The kinetic runs of oxidation maltose by PFC in aqueous acetic acid (50:50) at 298 K were followed at different initial concentrations of substrate, oxidant and $HClO_4$ keeping all other concentrations constant. The observed pseudo first order rate constants are given in TABLE 1.

Effect of varying reactant concentration

The concentration of oxidant [PFC] was varied in the range 2 x 10^{-4} to 2 x 10^{-3} mol dm^{-3} keeping all other reactant concentrations constant and rates were measured (TABLE 1). The pseudo first order rate constants (k_{obs}) obtained with different [PFC] were nearly similar, confirming the first order dependence of rates on [PFC].

TABLE 1 : Effect of variation of [PFC], [Maltose] and [$HClO_4$] on the oxidation of maltose by PFC in aqueous acetic acid (50:50) at 298 K and [KCl] = 0.2 mol dm^{-3}

10^3 [PFC] Mol dm^{-3}	10^2 [Maltose] Mol dm^{-3}	[$HClO_4$] Mol dm^{-3}	10^5 Kobs S^{-1}
0.2	3	1	3.62
0.4	3	1	3.65
1.0	3	1	3.60
1.5	3	1	3.60
2.0	1	1	1.58
2.0	1.5	1	2.12
2.0	2	1	2.55
2.0	2.5	1	3.19
2.0	3	1	3.55
2.0	3	1.5	5.50
2.0	3	2	7.10
2.0	3	2.5	9.36

The concentration of substrate [maltose] was varied in the concentration range 1 x 10^{-2} to 3 x 10^{-2} moldm^{-3} at 298 K and keeping all other reactant concentrations constant.

The pseudo first order rate constants were calculated from the plot of log [absorbance] against time (TABLE 1). The rate constant was found to increase with increase in concentration of maltose. The plot of log k_{obs} against log [Maltose] was linear with slope 0.77 (Figure 1) shows fractional order dependence with respect to [Maltose].

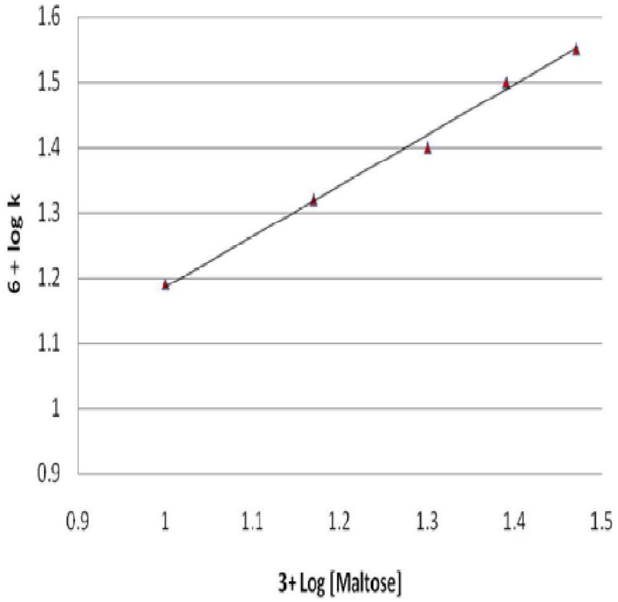

Figure 1 : Plot of 6+ log k_{obs} vs. 3+log [Maltose]

Effect of perchloric acid concentration

The effect of perchloric acid concentration on the reaction was studied at constant [Maltose] and [PFC] keeping constant ionic strength of 0.2 mol dm^{-3} at 298 K and the rates were measured (TABLE 1). The increase in [$HClO_4$] increases the rate of reaction and shows a first order dependence on [$HClO_4$]. A plot of log k_{obs} against log [$HClO_4$] is linear with slope 1.1 (Figure 2).

Effect of ionic strength

The effect of addition of salt on the rate of reaction was studied by adding various concentrations of KCl by keeping concentration of PFC, maltose,

$HClO_4$, constant. It was observed that the rate constant increases with increase in KCl concentration and two fold increase in rate constant in 1.6 mol dm^{-3} KCl was observed.

TABLE 2 : Effect of solvent on the rate of oxidation

[Maltose] = 0.03 mol dm^{-3} [PFC] = 2 x 10^{-3} mol dm^{-3}
[$HClO_4$] = 1 mol d [KCl] = 0.2 mol dm^{-3}

CH_3 COOH :H_2O	D	k_{obs} x 10^5 S^{-1}
50 : 50	37.50	3.55
55 : 55	34.75	4.25
60 : 40	31.50	5.22
65 : 35	28.50	6.45
70 : 30	27.10	7.94

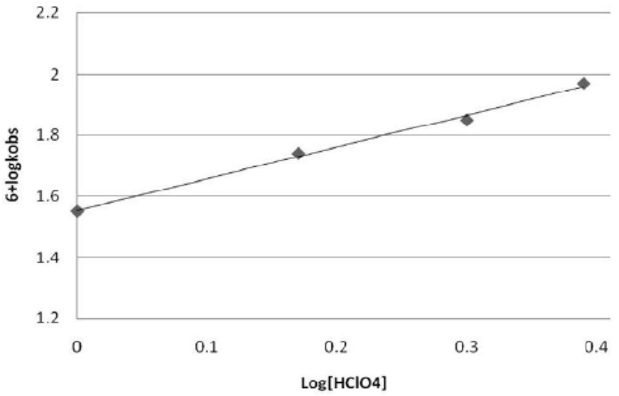

Figure 2 : Plot of 6+log k_{obs} vs. log of [$HClO_4$]

Effect of solvent

The effect of solvent composition on the rate was studied by varying concentration of acetic acid from 50% to 70%. An increase in the rate constant was observed with increase in percentage of acetic acid. It suggests that decrease in dielectric constant of medium increases the rate of reaction (TABLE 2). The plot of log k_{obs} against 1/D, where D is dielectric constant of the medium gives straight line with positive slope[9]. (Figure 3)

Effect of temperature

The effect of temperature on the rate of reaction was studied at different temperatures. The Arrhenius plot of log k_2 against 1/T were linear (Figure 4). The activation parameters Ea, ?H$^{\#}$, ?S$^{\#}$, ?G$^{\#}$ and log A were calculated[10]

Reaction mechanism and rate law

The plot between 1/k_{obs} against 1/[Maltose] were linear with positive intercept indicates formation of intermediate complex between maltose and PFC. A large increase in rate with [H^+] suggests that the protonated Cr(VI) may be involved in the rate determining step[11]. Thus a mechanism involving hydride ion transfer in the rate determining step is suggested.

TABLE 3 : Activation parameters for oxidation of maltose by PFC at 298 K

[PFC] = 0.002 mol dm^{-3} [Maltose] = 0.03 mol dm^{-3}
[$HClO_4$] = 1 mol dm^{-3} [KCl] = 0.2 mol dm^{-3}

Second order rate constants $10^3 k_2$ dm^3 s^{-1} mol^{-1}					Ea KJ mol^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ Jk^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}	log A
298K	303K	308K	313K	318K					
1.18	1.55	2.21	3.08	4.34	40.47	37.97	-166.99	88.62	5.46

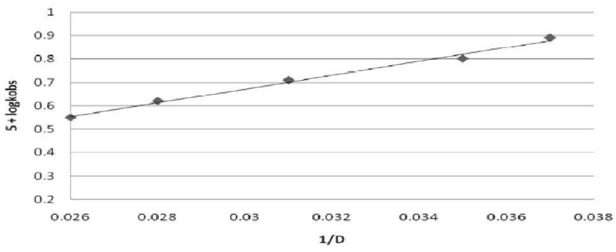

Figure 3 : Plot of 5+ log k_{obs} vs. 1/D

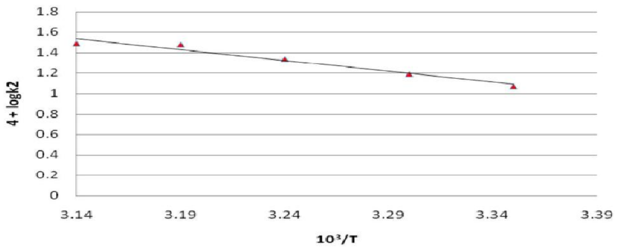

Figure 4 : Plot of 4+log k_2 vs. 10^3/T K^{-1}

$$\text{Maltose} + \text{PFC} \underset{k_2}{\overset{K}{\rightleftharpoons}} \text{Intermediate}$$

$$\text{Intermediate} \longrightarrow \text{Product}$$

The above mechanism leads to the rate equation

$$\frac{-d[PFC]}{dt} = \frac{kK[PFC][Maltose]}{1+K[Maltose]}$$

The plot of log k_{obs} against 1/D is linear with a positive slope indicates the reaction follows an ionic mechanism between positive ion and a dipole[12]. Rate constant increases with increase in ionic strength suggests the reaction occurs between ions of similar charges. Relatively small positive values of $\triangle H^{\#}$ and large negative values of $\triangle S^{\#}$ indicates the formation of intermediate complex in the rate determining step.

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