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Kinetics and Mechanism of Oxidation of Benzyl Alcohol by Benzimidazolium Fluorochromate

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Abstract: The kinetics of oxidation of benzyl alcohol (BzOH) by benzimidazolium fluorochromate (BIFC) has been studied in 50% aqueous acetic acid medium at 308 K. The reaction is first order with respect to [oxidant] and [benzyl alcohol]. The reaction is catalysed by hydrogen ions. The decrease in dielectric constant of the medium increases the rate of the reaction. Addition of sodium perchlorate increases the rate of the reaction appreciably. No polymerization with acrylonitrile. The reaction has been conducted at four different temperature and the activation parameters were calculated. From the observed kinetic results a suitable mechanism was proposed.

Keywords: Benzyl alcohol, Kinetics and mechanism, Oxidation, Benzimidazolium fluorochromate

Introduction

Chromium compounds have been used in aqueous and non-aqueous medium for the oxidation of a variety of organic compounds¹. Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups²⁻⁴. Numerous reagents and experimental procedures have been developed to carry out this transformation⁵, in particular reagents containing chromium(VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds^{6,7}. Benzimidazolium fluorochromate has been used as on mild selective oxidant in synthetic organic chemistry⁸. Kinetics of oxidation of benzyl alcohol by various oxidising reagents have been well documented⁹⁻¹¹. The literature survey reveals that the kinetics and mechanism of oxidation of benzyl alcohol by BIFC has not been reported. Hence, in the present investigation, we have carried out the oxidation of benzyl alcohol by BIFC in aqueous acetic acid medium and the corresponding mechanistic aspects are discussed in this research paper.

Experimental

Materials and reagents

BIFC was prepared by the method described in the literature⁸. Benzyl alcohol, 2,2'-bipyridyl, 1,10-phenanthroline (E. Merck) and oxalic acid (Qualigens) were used as supplied without further purification and the other chemicals used in this experiment are all of AnalaR grade samples.

Procedure and kinetic measurement

The reaction were performed in aqueous acetic acid medium under pseudo-first order conditions by maintaining a large excess of substrate over chromium(VI). The reaction mixture was homogeneous throughout the course of the reaction. The progress of the reaction was monitored for at least two half-lives by iodometric estimation of unchanged oxidant at regular time intervals. The pseudo-first order rate constants were calculated from the slopes of linear plots of log titre *versus* time.

Product analysis

The reaction mixture was kept for 48 h to ensure completion of the reaction. The solution was extracted with chloroform and the organic layer was washed with water, dried over anhydrous sodium sulphate. Benzaldehyde is formed as the main product under kinetic conditions and it was identified by the formation of 2,4-dinitrophenyl hydrazone (m.p. 234–236°C, lit. 237°C).

Results and Discussion

Oxidation of benzyl alcohol by BIFC has been conducted in 50% (v/v) acetic acid-water medium at 308 K, under the pseudo-first order conditions and the observed results were discussed in the subsequent pages.

Effect of varying oxidant concentration

The concentration of BIFC was varied in the range 7.5×10^{-4} to 1.75×10^{-3} mol dm⁻³ and keeping all other reactant concentrations as constant and the rate were measured (Table 1). The non-variation in the pseudo-first order rate constants at various concentrations of [BIFC] indicates that the order with respect to [BIFC] is unity. This was also confirmed from the linearity of plots of log titre *versus* time (*r* = 0.999) (Figure 1) up to 70% completion of the reaction.

Effect of varying substrate concentration

The substrate, BzOH was varied in the range of 2.00×10^{-2} to 6.00×10^{-2} mol dm⁻³ at 35°C and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The plot of log *k*_{obs} *versus* log [BzOH] gave the slope of 0.996 (*r* = 0.995) (Figure 2) shows that this oxidation reaction was first order with respect to [BzOH].

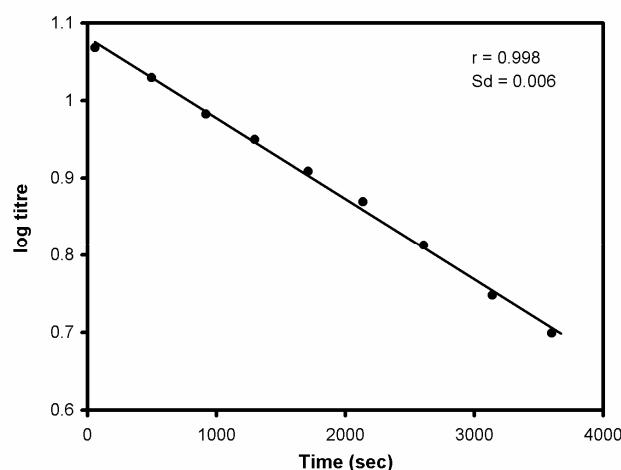
Effect of perchloric acid concentration

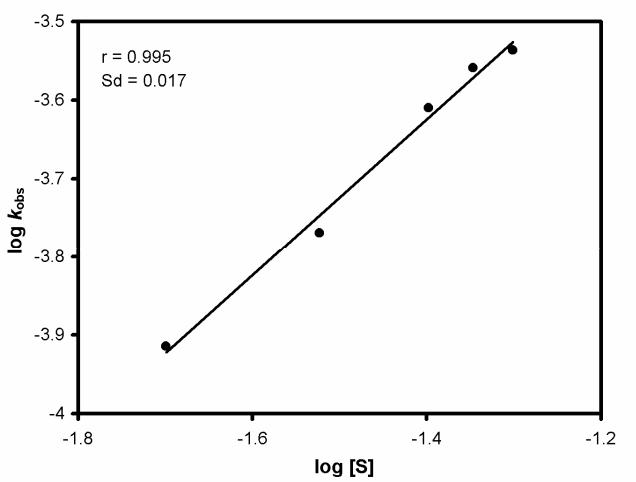
The perchloric acid concentration was varied in the range of 12.50×10^{-4} to 22.50×10^{-4} mol dm⁻³ and keeping the concentrations of all other reactant concentrations as constant and the rates were measured (Table 1). The rate of oxidation increases with increase in perchloric acid concentration. Added hydrogen ions had very significant effect on the rate of reaction showing that the hydrogen ions provided by the solvent molecules were not adequate for the protonation of the oxidant.

Table 1. Effect of variation of [BIFC], [BzOH], [HClO₄], solvent composition and temperature on the reaction rates

[BIFC] 10 ³ mol dm ⁻³	[BzOH] 10 ² mol dm ⁻³	Solvent AcOH-H ₂ O %, v/v	[HClO ₄] 10 ⁴ mol dm ⁻³	Temperature K	$k_{\text{obs}} \times 10^4$ s ⁻¹
0.75	4.00	50-50	-	308	2.60
1.00	4.00	50-50	-	308	2.45
1.25	4.00	50-50	-	308	2.51
1.50	4.00	50-50	-	308	2.40
1.75	4.00	50-50	-	308	2.35
1.00	2.00	50-50	-	308	1.27
1.00	3.00	50-50	-	308	1.70
1.00	4.50	50-50	-	308	2.76
1.00	5.00	50-50	-	308	2.90
1.00	6.00	50-50	-	308	3.50
1.00	4.00	50-50	12.50	308	3.00
1.00	4.00	50-50	15.00	308	3.35
1.00	4.00	50-50	20.00	308	3.50
1.00	4.00	50-50	22.50	308	4.53
1.00	4.00	40-60 (50.8)*	-	308	1.71
1.00	4.00	45-55 (47.1)*	-	308	2.16
1.00	4.00	55-45 (43.4)*	-	308	2.69
1.00	4.00	60-40 (39.7)*	-	308	4.63
1.00	4.00	65-35 (36.0)*	-	308	5.13
1.00	4.00	50-50	-	303	1.70
1.00	4.00	50-50	-	313	3.36
1.00	4.00	50-50	-	318	4.41

* Dielectric constant values

**Figure 1.** Plot of time *versus* log titre

**Figure 2.** Plot of $\log[S]$ versus $\log k_{\text{obs}}$ *Effect of ionic strength, $MnSO_4$ and solvent polarity*

The effect of ionic strength was studied by varying the NaClO_4 concentration in the reaction medium. The ionic strength of the reaction medium was varied from 2.50×10^{-4} to 10×10^{-4} mol dm^{-3} and keeping all other reactant concentration as constant. It was found that the rate constants increased with increase in concentration of NaClO_4 (Table 2). Permittivity values are calculated approximately from the values of pure solvents. The low dielectric constant of the medium favors the oxidation process as shown in Table 1. The effect of ionic strength and solvent polarity suggests that the participation of an ion and a neutral molecule in the mechanistic steps¹². Addition of manganous sulphate enhances the rate of the reaction (Table 2) shows that added Mn^{2+} shows catalytic activity in this oxidation reaction¹².

Table 2. Effect of variation of $[\text{MnSO}_4]$, $[\text{NaClO}_4]$ and [acrylonitrile] on reaction rates*

$[\text{MnSO}_4] \times 10^3$ mol dm^{-3}	$[\text{NaClO}_4] \times 10^4$ mo dm^{-3}	$[\text{Acrylonitrile}] \times 10^4$ mol dm^{-3}	$k_{\text{obs}} \times 10^4$ s^{-1}
0	-	-	2.45
2.50	-	-	2.56
5.00	-	-	2.69
7.50	-	-	2.73
10.00	-	-	3.05
-	2.50	-	3.55
-	5.00	-	4.08
-	7.50	-	4.17
-	10.00	-	4.42
-	-	2.50	2.34
-	-	5.00	2.58
-	-	7.50	2.38
-	-	10.00	2.57

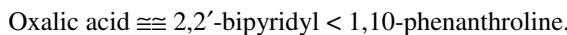
*Condition: $[\text{BIFC}] = 1.00 \times 10^{-3}$ mol dm^{-3} ; $[\text{BzOH}] = 4.00 \times 10^2$ mol dm^{-3} ; $\text{AcOH-H}_2\text{O} = 50-50$ (v/v); Temperature = 308 K

Polymerization study

The possibility of radical formation and its involvement in the reaction has been ruled out as the addition of acrylonitrile in the reaction mixture developed no turbidity and hence the reaction rates was not affected even the [acrylonitrile] was at 2.50×10^{-4} to 10.00×10^{-4} mol dm⁻³ (Table 2).

Effect on different catalyst

We have also employed the complexing agents like oxalic acid, 1,10-phenanthroline and 2,2'-bipyridyl under identical experimental conditions and the reactivities are compared (Figure 3). The order of catalytic efficiency is as follows



More pronounced activity in the presence of 1,10-phenanthroline as a catalyst is observed. This may probably due to the formation of more reactive electrophile in between oxidant and 1,10-phenanthroline and the corresponding transition state is well stabilized^{13, 14}.

Table 3. Effect of different catalyst on reaction rates*

Catalyst	[Catalyst] 10^3 mol dm ⁻³	$k_{\text{obs}} \times 10^4$ s ⁻¹
1,10-Phenanthroline	5.00	8.78
Oxalic acid	5.00	3.73
2,2'-Bipyridyl	5.00	3.67

*Condition: M[BIFC] = 1.00×10^{-3} mol dm⁻³; [BzOH] = 4.00×10^{-2} mol dm⁻³; AcOH-H₂O = 50-50 (v/v); Temperature = 308 K

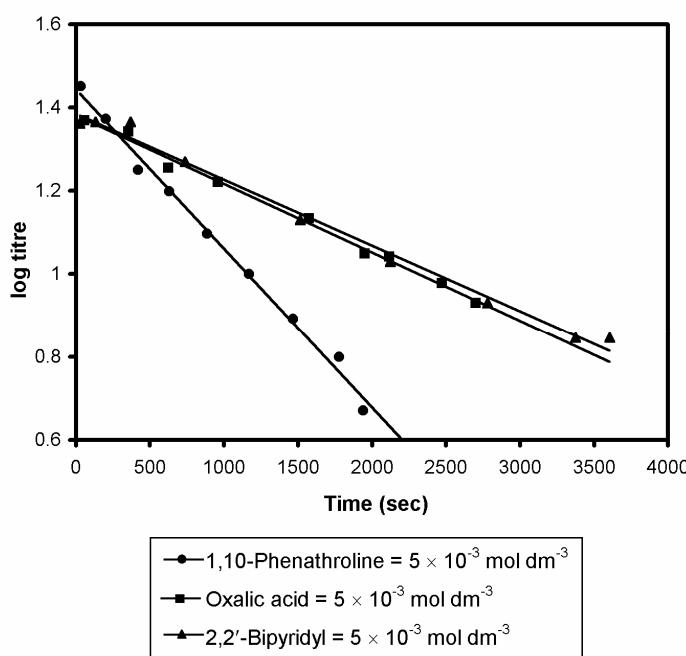
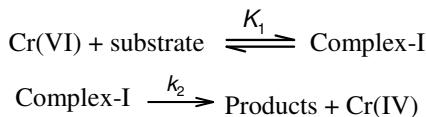


Figure 3. Catalytic activities of different catalyst.

Effect of temperature

This oxidation reaction was conducted at four different temperatures *viz.*, 303, 308, 313 and 318 K and the measured rate constant values were given in Table 1. Eyring's plot of $\ln k_{\text{obs}}/T$ versus $1/T$ were linear ($r = 0.999$) (Fig. 4) and the activation parameters $\Delta H^\# = 47.31 \text{ kJ mol}^{-1}$ and $\Delta S^\# = -160.81 \text{ J K}^{-1} \text{ mol}^{-1}$ were obtained from the slope and intercept of the Eyring's plot.

Mechanism and rate law



The proposed mechanism was substantiated by the following rate law

$$\begin{aligned} \text{Rate} &= K_1 k_2 [\text{Cr(VI)}] [\text{substrate}] \\ k_{\text{obs}} &= K_1 k_2 [\text{substrate}] \end{aligned}$$

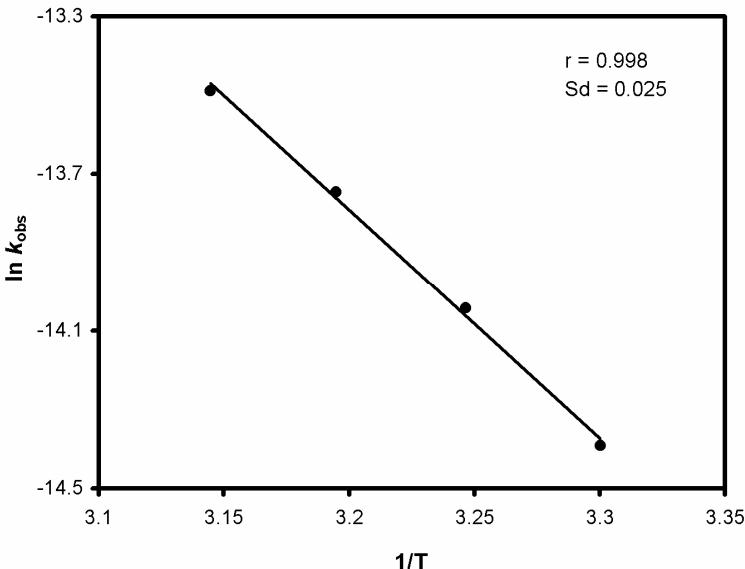


Figure 4. Plot of $\ln k_{\text{obs}}$ versus $1/T$

Conclusion

Oxidation of benzyl alcohol by BIFC is an acid catalysed reaction. The oxidation of benzyl alcohol yields the corresponding benzaldehyde as the product. The effects of ionic strength and solvent polarity suggest the participation of an ion and a neutral molecule in the mechanistic steps. Addition of Mn^{2+} shows catalytic activity in this oxidation reaction. The negative value of entropy adds additional support for the formation of the intermediate complex (C_1). More pronounced activity in the presence of 1,10-phenanthroline as a catalyst is observed.

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