



RESEARCH ARTICLE

OXIDATION OF ALCOHOLS BY TETRAMETHYLAMMONIUM FLUOROCHROMATE : A KINETIC STUDY

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ABSTRACT

The oxidation of different alcohols by tetramethyl ammonium fluorochromate in acidic medium is studied kinetically. The reaction was arranged to be pseudo-first order with respect to oxidant for all alcohols. The reaction is found to be catalyzed by the hydrogen ions. The effect of change in temperature, concentration of substrate, oxidant and acid medium is studied kinetically. On the basis of results obtained the mechanism of the reaction is proposed and discussed.

Key words:

Kinetics, Alcohols, Oxidation,
Oxidizing agent, Mechanism.

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INTRODUCTION

In organic synthesis conversion of alcohols to aldehydes, ketones and carboxylic acids is widely used reaction. This oxidation is done using different oxidizing agents. Among these chromium based oxidizing agents are extensively used (Gaur *et al.*, 2011). There are large number of such reagents available but many of these are not practically useful while doing the reactions on large scale (O'Brien, 1980). The tetramethyl ammonium fluorochromate is one of the chromium based mild oxidizing agent (Shahriar Ghammamy and Sajjad Sedaghat, 2012). This compound has additional advantages over pyridine fluorochromate and pyridine chlorochromate with reference to lower acidity, ability to more selective oxidation under mild condition, higher solubility in non aqueous solvents, etc (Corey and Suggs, 1975). Tetramethyl ammonium fluorochromate (TMAFC) is a complex of chromium trioxide and tetramethyl ammonium fluoride (Mahjoub *et al.*, 2000). In this work we report the kinetics of oxidation of 1-propanol, 2-propanol, n-pentanol, n-hexanol and n-octanol by tetramethyl ammonium fluorochromate, evaluate the reaction rate constant at different temperature and various solvents and finally the mechanistic aspects are discussed and a probable mechanism has been proposed.

MATERIALS AND METHODS

All chemicals were of reagent grade materials from Merck. The solvents were purified by standard methods. The tetramethyl ammonium fluorochromate was prepared by the procedure reported by Mahjoub *et al.* (2000). The stock solution of the oxidant was prepared by dissolving the required amount of tetramethyl ammonium fluorochromate in each solvent. The reaction was arranged to be under pseudo-first order conditions by keeping a large excess of alcohols. The reaction vessel was thermostated in a water bath maintained at 20-40°C. The reaction was followed spectrophotometrically at 350nm. This is the λ_{max} of tetramethyl ammonium fluorochromate. In controlling the experiments, in the absence of alcohols the concentration of tetramethyl ammonium fluorochromate showed no appreciable changes. The observed first order rate constants, k_{obs} , with respect to (TMAFC) were calculated from the slopes of the linear plots of log of absorbance versus time using the least squared method with a correlation coefficient greater than 0.99. The procedure was repeated at least three times and the resulting average values and corresponding deviations are shown in the tables.

RESULTS AND DISCUSSION

A vessel containing a known amount of alcohols with twice the concentration of tetramethyl ammonium fluorochromate in acetonitrile in the presence of 7.5 mol dm⁻³ acetic acid was

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allowed to react completely at 25°C. The amount of oxidant remained on completion of the reaction was measured spectrophotometrically at 350nm. The stoichiometry of the equation 1 indicates the ratio of substrate to oxidant as 3:2. When a mixture of n-hexanol (0.1mol), acetic acid (0.2mol), and tetramethyl ammonium fluorochromate (0.05mol) were made up to 100 ml in acetonitrile. The reaction mixture was allowed to stand in dark for 10 hours to ensure completion of the reaction. The solvent was removed by distillation. The residue was treated with excess of 2,4-dinitrophenylhydrazine in HCl and kept at 4-5°C for conversion. The precipitated 2,4-dinitrophenylhydrazone was filtered, dried, recrystallized. The yield of the product is 90% showing the completion of the reaction. The oxidation of n-hexanol by tetramethyl ammonium fluorochromate shows formation of corresponding aldehyde and the reaction may be represented stoichiometrically as



The results of oxidation of some of the alcohols by pyridinium fluorochromate and pyridinium chlorochromate reported before are similar (Banerji, 1988; Brown *et al.*, 1979; Banerji, 1978). The rate constant under pseudo-first order conditions, the individual kinetic runs are first-order with respect to tetramethyl ammonium fluorochromate.

Table 1. Dependence of the reaction rate of alcohols, 6×10^{-4} (mol/dm³), (acetic acid) = 4 (mol/dm³) on different oxidant concentrations at 25°C in acetonitrile

(TMAFC) 10 ³ (mol/dm ³)	1.64	2.18	2.68	3.42	4.16
1-propanol 10 ³ k _{obs} (s ⁻¹)	3.18	3.19	3.18	3.20	3.19
2-propanol 10 ³ k _{obs} (s ⁻¹)	3.21	3.21	3.22	3.22	3.22
n-pentanol 10 ³ k _{obs} (s ⁻¹)	3.16	3.18	3.18	3.19	3.19
n-hexanol 10 ³ k _{obs} (s ⁻¹)	3.18	3.19	3.18	3.20	3.19
n-octanol 10 ³ k _{obs} (s ⁻¹)	3.18	3.18	3.18	3.18	3.19

Table 2. Dependence of the reaction rate of alcohols, 0.2 (mol/dm³), (TMAFC) = 1.4 x 10⁻⁴ (mol/dm³) on different acetic acid concentration at 25°C in acetonitrile

(acetic acid) (mol/dm ³)	2.0	2.5	3.0	3.5	4.0
1-propanol 10 ³ k _{obs} (s ⁻¹)	0.8	1.2	1.6	2.2	3.4
2-propanol 10 ³ k _{obs} (s ⁻¹)	0.6	1.0	1.8	2.0	2.6
n-pentanol 10 ³ k _{obs} (s ⁻¹)	0.5	1.0	1.6	3.0	4.0
n-hexanol 10 ³ k _{obs} (s ⁻¹)	0.5	1.2	1.9	3.2	4.6
n-octanol 10 ³ k _{obs} (s ⁻¹)	0.6	1.6	2.0	2.8	3.8

Table 3. Dependence of the reaction rate of TMAFC, 1.8 x 10⁻⁴ (mol/dm³), on different concentrations of alcohols, at constant (acetic acid) = 4.0 (mol/dm³) and temperature, 25°C in acetonitrile

(alcohol) (mol/dm ³)	0.1	0.2	0.3	0.4	0.5
1-propanol 10 ³ k _{obs} (s ⁻¹)	1.6	2.2	3.4	3.8	4.6
2-propanol 10 ³ k _{obs} (s ⁻¹)	2.2	3.4	4.0	4.6	5.0
n-pentanol 10 ³ k _{obs} (s ⁻¹)	2.8	3.6	4.2	4.8	5.0
n-hexanol 10 ³ k _{obs} (s ⁻¹)	2.8	3.5	4.1	4.6	5.2
n-octanol 10 ³ k _{obs} (s ⁻¹)	2.6	3.2	3.8	4.4	5.2

Table 4. Dependence of the reaction rate of alcohols by tetramethyl ammonium fluorochromate using different solvents at 25°C. (TMAFC) 1.6x10⁻⁴ (mol/dm³), (acetic acid) 4 (mol/dm³)

Solvent	10 ³ k _{obs} (s ⁻¹)				
	Concentration of alcohol (0.1 mol/dm ³)				
	1-prop anol	2-prop anol	n-pent anol	n-hex anol	n-oct anol
Acetone	2.26	4.10	3.60	4.25	3.80
Cyclohexanone	3.80	4.68	4.04	5.13	4.72
Dimethyl Formamide	1.8	2.47	2.12	2.61	2.33
Dimethyl Sulfoxide	1.0	0.80	0.23	0.17	0.67

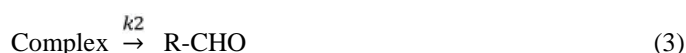
Table 5. The values of k and K₂ for different solvents calculated as per the equation 6

Solvent Alcohol		Acet one	Cyclohex anone	Dimethyl Formamide	Dimethyl Sulfoxide
1-propanol	k ₂	7.68	8.16	7.12	6.86
	K	4.66	7.84	3.23	5.20
2-propanol	k ₂	6.55	8.00	7.68	7.34
	K	3.92	5.74	2.30	4.92
n-pentanol	k ₂	7.66	8.32	7.52	6.10
	K	6.25	7.56	5.24	2.80
n-hexanol	k ₂	6.26	7.30	6.54	5.32
	K	7.68	6.18	4.62	3.62
n-octanol	k ₂	6.88	5.94	7.66	4.88
	K	6.76	5.00	3.94	6.44

The rate constant is independent of initial concentration of the oxidant, Table 1, but dependent on concentration of acid, Table 2 indicating that the reaction is catalyzed by the hydrogen ions. As the reaction is dependent on the acid it can be assumed that the reaction is in between alcohol and protonated species of chromium reagent. It indicates that these species are involved in the oxidation of chromium trioxide (Bhattacharjee *et al.*, 1987).

Effect of concentration of substrate

The rate of reaction at different concentrations of alcohols was studied at various temperatures. The rate constant slightly increased with increasing the concentration of alcohols. A Michaelis-Menton type dependence was observed with respect to alcohol concentration, Table 3. A plot of 1/k_{obs} against 1/(alcohol) is linear with a non-zero intercept on the rate ordinate. The following overall mechanism can be proposed.



Under the pseudo first-order conditions the reaction rate equation is given by

$$\text{Rate} = d(R-CHO)/dt = k_2(\text{complex}) \quad (4)$$

The formation rate of the products is related to the loss of both oxidant and complex concentrations (Wilkins, 1991). Applying the steady state approximation to the complex and substituting into equation 4, we get

$$\text{Rate} = k_2 K (\text{TMAFC})(\text{R-CH}_2\text{OH}) / (1 + K(\text{R-CH}_2\text{OH})) \quad (5)$$

With

$$k_{\text{obs}} = k_2 K (\text{R-CH}_2\text{OH}) / (1 + K(\text{R-CH}_2\text{OH})) \quad (6)$$

The values of equilibrium constant, K, for decomposition of alcohol and the rate constants, k_2 , for decomposition of the complexes in different solvents were determined from the slope and intercept of the double reciprocal plots and are shown in Table 5.

Effect of solvent

Using different solvents the oxidation reaction was monitored. On the basis of the solubility of tetramethyl ammonium fluorochromate and with substrate solvents were selected. The kinetics of oxidation reaction in different solvents was found similar. The values of k_{obs} in different solvents were determined are tabulated in table 4. With the increase in the polarity of the solvent the rate constant of the reaction decreases indicating the transition state less polar than the reactants.

Effect of temperature

The reaction was carried out at five temperatures, 20, 25, 30, 35 and 40°C at constant hydrogen ion concentration, oxidant and alcohol concentration. Arrhenius plot of $\log k_{\text{obs}}$ versus $1/T$ gave a straight line with correlation of $r = 0.99$ with activation energy as $E_a = 43.36$ (kJ/mol). The Eyring parameters were computed using the intercept and slope of $\log k_2$ versus $1/T$ plot, and are : $H = 18.8$ (kJ/mol), $S = -163.6$ (J/K mol), and $G = 72.4$ (kJ/mol).

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