Kinetic and Mechanistic Study of Oxidation of Alcohols by Tetraethyl Ammonium Fluorochromate: A Versatile Oxidizing Agent

Syed Yousuf

Department of Chemistry, Kohinoor Arts, Commerce & Science College Khuldabad, Dist Aurangabad, Maharashtra 431101, India
sdyusufchem[at]gmail.com

Abstract: *The oxidation of alcohols with tetraethyl ammonium fluorochromate in acid medium was studied kinetically. The alcohols are oxidized under pseudo - first order keeping concentration of oxidant constant. It is observed that the reaction is catalyzed by the hydrogen ions. The rate of reaction at different concentrations of oxidant, acetic acid, temperature and using different solvents were evaluated and tabulated. The rate of reaction is found to be increasing with the increase in concentration of substrate and acid. Similarly it is observed to increase with the rise in the temperature. The probable mechanism for the oxidation is suggested and thermodynamic parameters are calculated.*

Keywords: Oxidation, Kinetics, Alcohols, Mechanism, Thermodynamics

1. Introduction

Oxidation is an important and most widely used chemical reaction in chemistry. Alcohols readily gets oxidized to carbonyl compounds with various oxidizing agents. Nowadays the chromium based reagents are used extensively for oxidation of organic compounds. There are large number of such compounds used for oxidation of alcohols by various researchers e. g. pyridine fluorochromate, pyridine chlorochromate, potassium dichromate, benzimidazolium dichromate, etc. Many workers have studied oxidation of alcohols using these reagents. [1] [2] [3]. Till now no one has reported the kinetics and mechanistic study of oxidation of alcohols using tetraethyl ammonium flurochromate. This is the attempt for the same. In this study we report the kinetic and mechanistic study of oxidation of methanol, ethanol, 1 - propanol and 1 - butanol using tetraethyl ammonium flurochromate. The reaction rate is calculated and probable mechanism is suggested.

2. Materials & Methods

The chemicals were purchased from a local dealer of reagent grade from Merck. The solvents were purified by standard methods. The oxidant i.e. tetraethyl ammonium flurochromate was prepared by the procedure reported earlier [4]. The stock solution of the oxidant was prepared by dissolving the required amount of tetraethyl ammonium flurochromate in the acetic acid. 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 350 nm. This is the λ_{max} of tetraethyl ammonium flurochromate. In controlling the experiments, in the absence of alcohols the concentration of tetraethyl ammonium flurochromate showed no appreciable changes. The observed first order rate constants, k_{obs}, with respect to [TEAFC] were calculated from the slopes of the linear plots of log_{abs} verses t (time) using the least squared method with a correlation coefficient greater than 0.99. The procedure was repeated three times and the resulting average values and corresponding deviations are noted in the tables.

3. Results and Discussion

In a flask a known amount of alcohols with twice the concentration of tetraethyl ammonium flurochromate in acetonitrile is taken. It is allowed to react completely in the presence of 7.5 mol dm^{-3} acetic acid at 25°C. The amount of tetraethyl ammonium flurochromate remained after completion of the reaction was measured spectrophotometrically at 350nm. Stoihchiometrically the ratio of alcohols to tetraethyl ammonium flurochromate obtained as 3: 2.

Initially the mixture of alcohol (0.1mol), acetic acid (0.2mol) and tetraethyl ammonium flurochromate (0.05mol) was taken in a flask then it is made up to 100 ml in acetonitrile. For completion of reaction the reaction mixture was kept in dark for 12 hours. The acetic acid was removed by distillation process. The remaining residue was reacted with excess of 2, 4 dinitro phenyl hydrazine in hydrochloric acid and kept at 4 - 5°C for completion. The precipitate of 2, 4 dinitro phenyl hydrazone was filtered, dried and recrystallized. The obtained yield of the product is 90% indicating the completion of the reaction. The oxidation of alcohols by tetraethyl ammonium flurochromate shows formation of corresponding aldehyde and the reaction may be represented stoichiometrically as

3R - CH2OH + 2Cr (VI) →3R - CHO + 6H$^+$ + 2Cr (III) (1)
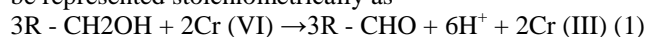
The similar results were reported before by oxidation of some of the alcohols by pyridinium fluorochromate and pyridinium chlorochromate [5] [6] [7]. The rate constants under pseudo - first order condtions and the individual kinetic runs are first order with respect to tetraethyl ammonium flurochromate. The rate constant is independent of initial concentration of the tetraethyl ammonium flurochromate reported in table 1. It is dependent on concentration of acetic acid table 2 showing that the reaction
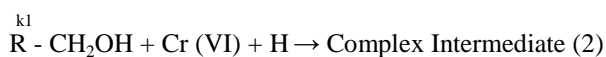
is catalyzed by the hydrogen ions. One can assume that the reaction is in between alcohols and protonated species of tetraethyl ammonium flurochromate because the reaction is dependent on the acetic acid indicating these species are involved in the oxidation of CrO_3 [8].

Table I: Dependence of the reaction rate on different [TEAFC] at 298K in acetonitrile ([Alcohol] = 6 x 10^{-2} mol/dm^3, [Acetic acid] = 4 mol/dm^3, Rate Constant $10^4 k_{obs}$ s^{-1})

[TEAFC] x 10^{-3}	1.0	1.5	2.0	2.5	3.0
Methanol	2.6	2.6	2.7	2.7	2.6
Ethanol	2.6	2.6	2.6	2.7	2.6
1 - propanol	2.8	2.8	2.7	2.7	2.8
1 - butanol	2.8	2.8	2.8	2.8	2.7

a) Effect of Concentration of Alcohol

The rate of reaction at different concentrations of alcohols was studied at various temperatures. It is observed that as the concentration of alcohol increased the rate constant increased slightly. A Michaelis - Menton type dependence was observed with respect to alcohol concentration as tabulated in table 3. A graph of $1/k_{obs}$ against $1/$[alcohol] is linear with a non - zero intercept on the rate ordinate. The probable mechanism suggested for the above reaction is as follows.

$$R - CH_2OH + Cr\ (VI) + H \xrightarrow{k1} Complex\ Intermediate\ (2)$$

$$Complex\ Intermediate \xrightarrow{k2} R - CHO + Cr\ (III) + H^+ + H_2O\ (3)$$

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

$$Rate = d\ [R - CHO] / dt = k2\ [Complex\ Intermediate]\ (4)$$

The formation rate of products is related to the loss of both oxidant and complex concentrations [9]. Applying the steady state approximation to the complex intermediate and substituting into equation (4), we get

Rate = $k_2 K$ [TEAFC] [R - CH_2OH]/ (1+ K [R - CH_2OH]) (5)

With

$k_{obs} = k_2$ K [R - CH_2OH] / (1+K [R - CH_2OH]) (6)

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

Table 2: Dependence of the Reaction Rate on Different [Alcohol] At 298k in Acetonitrile ([TEAFC] = 4 X 10^{-3} MOL/DM^3, [Acetic Acid] = 4 MOL/DM^3, Rate Constant $10^4 K_{OBS}$ S^{-1})

[Alcohol] x 10^{-2} mol/dm^3	1.0	2.0	3.0	4.0	5.0
Methanol	1.2	2.4	3.2	4.2	4.8
Ethanol	1.3	2.4	3.4	4.5	5.4
1 - propanol	1.5	2.8	3.6	4.6	5.8
1 - butanol	1.5	2.6	3.6	5.5	5.6

b) Effect of Solvent

The rate of reaction at different concentrations of acetic acid were evaluate and tabulated in table 2. The result shows sharp increase in the rate of reaction with the increase in the concentration of the acetic acid The rate of reaction is evaluated using different solvents. The solvents were selected on the basis of solubility of tetraethyl ammonium flurochromate and with different alcohols. The rate of reaction in different solvents was found similar. The values of kobs in different solvents were determined and are tabulated in table 4. The result shows that 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.

Table 3: Dependence Of The Reaction Rate On Different [Acetic Acid] at 298k In Acetonitrile ([TEAFC] = 4 X 10^{-3} MOL/DM^3, [ALCOHOL] = 6 MOL/DM^3, RATE CONSTANT $10^4 K_{OBS}$ S^{-1})

[Acetic acid] mol/dm^3	1.0	2.0	3.0	4.0	5.0
Methanol	1.0	1.8	2.8	3.8	4.6
Ethanol	1.1	2.2	3.2	3.8	4.9
1 - propanol	1.1	2.1	3.1	4.0	5.1
1 - butanol	1.0	2.0	3.2	4.2	5.1

Table 4: Dependence of the Reaction Rate on Different Solvents At 298k In Acetonitrile ([TEAFC] = 4 X 10^{-3} MOL/DM^3, [ALCOHOL] = 6 MOL/DM^3, [SOLVENT] =4 MOL/DM^3 Rate Constant $10^4 K_{OBS}$ S^{-1})

Solvent	Alcohols			
	Methanol	Ethanol	1 - propanol	1 - butanol
Acetone	2.4	2.6	2.6	2.7
Dimethyl formamide	1.8	1.8	1.8	2.0
Dimethyl sulfoxide	1.4	1.6	1.6	1.8

c) Effect of Temperature

The reaction was monitored at five different temperatures, 293K, 298K, 303K, 308K and 313K at constant [H+], [TEAFC] and [alcohol]. Arrhenius plot of log kobs versus 1/T gave a straight line with correlation of r= 0.99 with activation energy as Ea= 38.28 kJ/mol. The Eyring parameters were computed using the intercept and slope of logk2 versus 1/T plot and are ΔH 16.2 kJ/mol, ΔS = - 128 J/K mol and ΔG = 64.2 kJ/mol.

Table 5: Dependence of the Reaction Rate at Different Temperatures in Acetonitrile ([TEAFC] = 4 X 10^{-3} MOL/DM^3, [ALCOHOL] = 6 MOL/DM^3, [ACETIC ACID] =4 MOL/DM^3 Rate Constant $10^4 K_{OBS}$ S^{-1})

Temperature	293K	298K	303K	308K	313K
Methanol	1.5	2.8	3.2	3.8	4.6
Ethanol	1.5	2.7	3.2	3.8	4.5
1 - propanol	1.6	2.8	3.4	3.9	4.6
1 - butanol	1.5	2.7	3.2	3.8	4.6

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