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1

Kinetic and Mechanism of Oxidation of 2-Methoxy-1-Butanol By Tripropylammonium Fluorochromate

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Research Paper : Chemistry

ABSTRACT

The Kinetics of oxidation of 2-methoxy-1-butanol by tripropylammonium fluorochromate {TPAFC} has been Studied Spectrophotometrically in presence of Sulphuric acid in aqueous acetic acid medium in the temperature range 292-318K.The reaction is first order with respect to both 2-methoxy-1-butanol and TPAFC. The activation parameters for the slow step were computed and calculated. Effect of ionic strength and dielectric constant of medium has also been reported. A suitable mechanism has been proposed.

Key words: 2-methoxy-1-butanol, tripropylammonium fluorochromate, oxidation, kinetics.

Introduction :

Selective oxidation of alcohols to their corresponding aldehydes and ketones is an important transformation in organic chemistry which has received the most attention over years, especially in the search of versatile and selective reagent for this purpose. Halochromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry. Chromic acid being one of the most versatile and selective available oxidizing reagent. The synthesis of newer chromate (VI) reagent for the oxidation of organic substrates continues to be interest. In recent years, significant improvements were achieved by the use of new oxidizing agents [1-16] for the study of kinetics and

mechanism of various organic compounds. We have synthesized new reagent TPAFC which is mild, efficient, selective, and stable oxidizing reagent. Literature survey reveals that there no report is available on kinetics and mechanism of oxidation of 2-methoxy-1-butanol by TPAFC; hence we have considered it to study the kinetics and mechanism of oxidation of 2-methoxy-1-butanol by TPAFC.

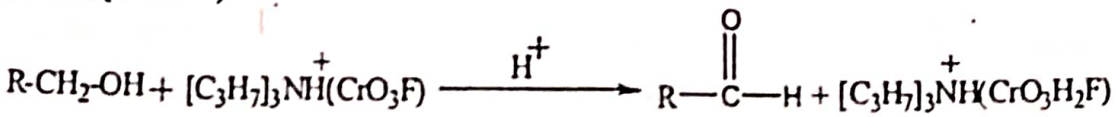
EXPERIMENTAL SECTION:-

All the chemicals and reagents were of analytical grade. All the solutions used in the study were prepared by using distilled acetic acid [17] and doubly distilled water. Tripropylammonium Fluorochromate was prepared by the following method: chromium (VI) oxide (15.0g, o.150 mol) was dissolved in water in a polyethylene beaker and 40% hydrofluoric acid (11.3 ml, 0.225 mol) was added with stirring at 0oC. To the resultant orange solution, tripropylammine (28.3 ml, 0.150 mol) was added drop wise with stirring to this solution over a period of 30 minutes and stirring was continued for 30 minutes at 0oC. The orange colored precipitate was filtered, washed with petroleum ether and dried in vacuum for 2 hours at room temperature [18]. Yield was 28 g (97%); mp was 142oC .

The Tripropylammonium Fluorochromate was stored in polyethylene bottle for long period of time. TPAFC was soluble in water, DMF, acetonitrile, acetone and DCM and was sparingly soluble in benzene, chloroform and hexane.

DETERMINATION OF STOICHIOMETRY AND PRODUCT ANALYSIS:-

The Stoichiometry of the reaction was determined by carrying out several sets of experiment with varying amount of (TPAFC) largely in excess over 2-methoxy-1-butanol in 20% acetic acid by using 0.1N H2SO4. The remaining (TPAFC) was then analyzed Spectrophotometrically. The result indicated that 1 mole of alcohols react with 1 mole (TPAFC).



The product analysis was carried out under kinetic conditions. In a typical experiment, 2-methoxy-1-butanol (0.05 mol) and TPAFC (0.01) were made up to 50

ml in 20% acetic acid and kept in dark for about 24 hours to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 mol dm-3 HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystalized from ethanol and weighed again. The yield of DNP before and after recrystallisation was 2.0 g (90%) and 1.7 g (75%) respectively. The DNP was found identical with the DNP of acetone by meting point. The products were also characterized by TLC, IR, and NMR spectra.

KINETIC MEASUREMENTS:-

The reactions were followed under pseudo-first-order conditions by keeping large excess (x 10 or greater) of the 2-methoxy-1-butanol over TPAFC. The temperature was kept constant to +/- 0.1 K. The solvent was acetic acid. The reactions were followed by monitoring the decrease in the concentration of TPAFC spectrophotometrically at 345 nm for 80% completion of the reaction. The pseudo-first-order rate constants K obs, were evaluated from the linear (r=0.990-0.999) plots of log [TPAFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within +/- 3%.

RESULT AND DISCUSSION:-

The results of oxidation of 2-methoxy-1-butanol by TPAFC are represented as follows.

Effect of variation of concentration 2-methoxy-1-butanol:-

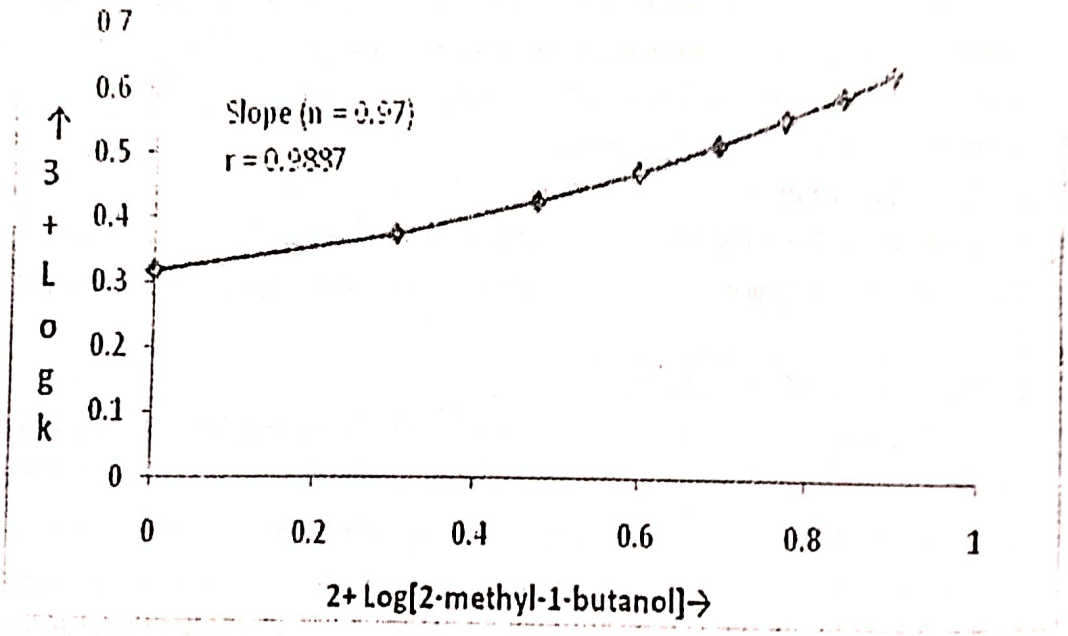
The oxidation of 2-methoxy-1-butanol (MB) with TPAFC in 20% of acetic acid in presence of sulphuric acid yields acetone. By keeping constant [TPAFC] and [H2SO4]. the increase in [2-methoxy-1-butanol] increases the rate of reaction (Table-1). The plot of log of kobs versus log [2-methoxy-1-butanol] for different initial concentration of 2-methoxy-1-butanol is linear with unit slope demonstrate the first order dependence of rate on 2-methoxy-1-butanol (Figure: 1).

Table 1: Effect of variation of [2-methoxy-1-butanol] on reaction rate

[TPAFC]= 0.001 M, [H2SO4] = 0.1 N, Temperature =303 k, AA = 20% (v/v)

[MB]	0.01M	0.02M	0.03M	0.04M	0.05M	0.06M	0.07M	0.08M
k x 10^3sec^{-1}	2.06	2.35	2.64	2.94	3.22	3.50	3.78	4.08

Figure: 1: Plot of 2+ Log [2-methoxy-1-butanol] Vs 3 + Logk'



Effect of variation of concentration of TPAFC:-

At constant [2-methoxy-1-butanol] and [H2SO4], the increase in [TPAFC] increases the rate of reaction (Table-2). The plot of log kobs verses log [TPAFC] for different initial concentration of TPAFC is linear with unit slope present the first-order dependence of rate on TPAFC.

Table 2: Effect of variation of [TPAFC] on reaction rate

[2-methoxy-1-butanol]= 0.01 M, [H2SO4] = 0.1 N, Temp =303 k, AA = 20% (v/v)

[TPAFC]

[TPAFC] Mole	0.001	0.0015	0.002	0.0025	0.003	0.0035	0.004	0.0045
$k \times 10^{3} sec^{-1}$	2.06	2.33	2.58	2.84	3.08	3.31	3.55	3.79

Effect of variation of concentration of H+:-

In order to study the effect the H+ion concentration on the rate of oxidation reaction of 2-methoxy-1-butanol, the dependence of reaction rate has been investigated at different initial concentration of H2SO4. The rate of reaction increases with increase in [H2SO4] (Table-3). The plot of log Kobs verses log [H+]are also straight line with slope less than unity, Indicating a fractional order dependence on [H+].

Table 3: Effect of variation of [H2SO4] on reaction rate

[TPAFC]= 0.001 M, [2-methoxy-1-butanol] = 0.01 M, Temp. =303 k, AA = 20% (v/v)

$[H_2SO_4]$	0.1M	0.2M	0.3M	0.4M	0.5M	0.6M	0.7M	0.8M
$k \times 10^{3} sec^{-1}$	2.06	2.26	2.43	2.60	2.75	2.91	3.06	3.24

Effect of ionic strength:-

In the present investigation effect of salt on the rate of reaction is carried out. The salts selected are KCl, KBr, and KI. These will give effect of anion particularly halides on the rate of reaction. The divalent and trivalent cationic salt were also used such as CaCl2 , Ca(NO3)2, Al(NO3)3 and K2SO4. The experiments were carried out under pseudo- first- order condition. These results were used to determine first order rate constant. The rate constants for the oxidation of 2-methoxy-1-butanol in presence of different salt are shown in [Table 4]. From table it is clear that, the rate increases with increase in cationic charge and decreases with increase in anionic charge. In case of KCl the rate of reaction decreases with the addition of KCl, this is due to the formation of less

reactive species [19] by interaction between Cl- ion and protonated TPAFC.

Table 4: Effect of variation of [salts] on reaction rate

[TPAFC]= 0.001 M, [MB] = 0.01 M, [H2SO4] = 0.1 N, Temp. =303 k, AA = 20% (v/v)

Salts 0.1M	KCl	KBr	KI	$CaCl_2$	$Ca(NO_3)_3$	$Al(NO)_3$	K_2SO_4
$k \times 10^3 sec^{-1}$	2.07	2.38	2.38	2.47	2.76	2.98	2.34

Effect of solvent composition:-

At fixed [MB], [TPAFC] and [H+], the rate of oxidation of 2-methoxy-1-butanol with TPAFC increases with decrease in polarity of solvent (Table 5). This is due to polar character of transition state as compared to the reactant. The plot of log kobs verses 1/ D is linear with positive slope indicating ion- dipole type of reaction [20].

Table5: Effect of variation of Acetic Acid % on reaction rate

[TPAFC]= 0.001 M, [H2SO4] = 0.1 N, [2-methoxy-1-butanol] =0.01M, Temp=303 k

Acetic acid	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %
$k \times 10^3 sec^{-1}$	1.95	2.06	2.21	2.34	2.46	2.58	2.72	2.86

Effect of temperature:-

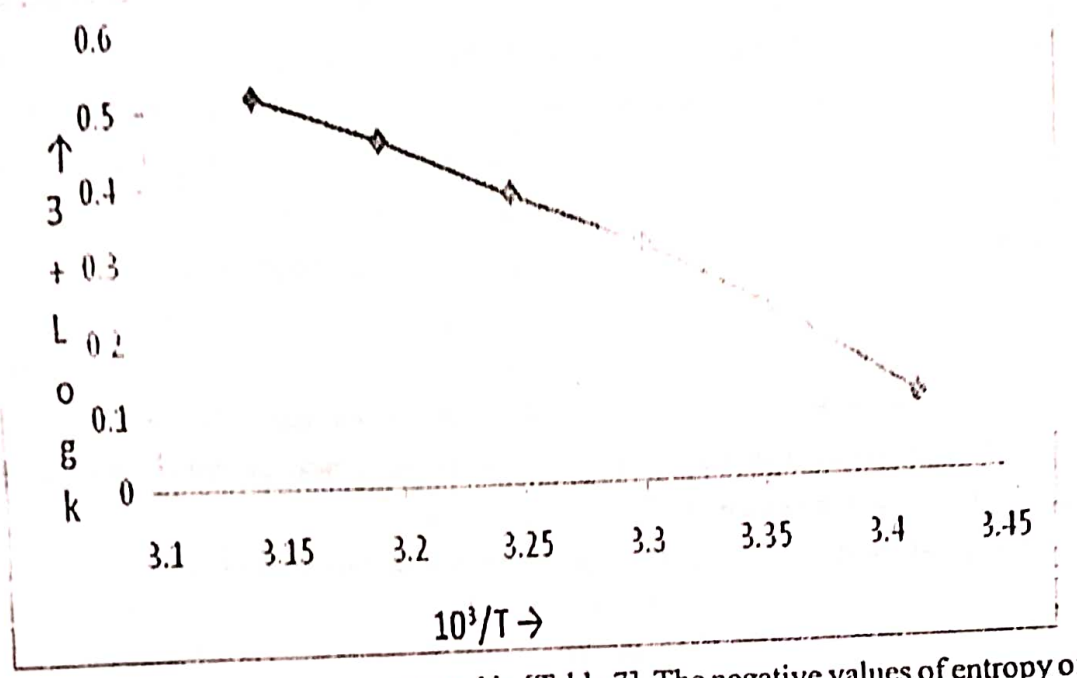
The study of effect of temperature on rate of oxidation of 2-methoxy-1-butanol by TPAFC has been subjected to different temperature range 293K to 313K by keeping the concentration of 2-methoxy-1-butanol and reagent constant. Rate constants are given in [Table 6]. The plots of log of Kobs verses 1/T are linear (Figure: 2)

Table 6: Effect of variation of Temperatures on reaction rate

[TPAFC]= 0.001 M, [2-methoxy-1-butanol] = 0.01 M, [H2SO4] = 0.1 N, AA = 20% (v/v)

Temperatures (K)	293	298	303	308	313	318
$k \times 10^3 sec^{-1}$	1.27	1.69	2.06	2.44	2.88	3.28

Figure: 2: Arrhenius plot of oxidation of 2-methoxy-1-butanol



Activation parameters are presented in [Table 7]. The negative values of entropy of activation reflect that the transition state is more rigid than initial state. The nearly constant ?G value indicates that similar mechanism is operative for the oxidation of 2-methoxy-1-butanol.

Table 7: Activation Parameters

[TPAFC]= 0.001 M, [MB] = 0.01 M. [H2SO4] = 0.1 N, Temp. =303 k, AA = 20 % (v/v)

Activation parameters	ΔE_a KJ mole^{-1}	$\Delta H^{\#}$ KJmol^{-1}	$\Delta S^{\#}$ JK^{-1}mole^{-1}	$\Delta G^{\#}$ KJ mole^{-1}
	25.67	23.15	-220.06	89.83

Energy-entropy relationship:-

The entropy of activation and heat of reaction are correlated by equation 1.

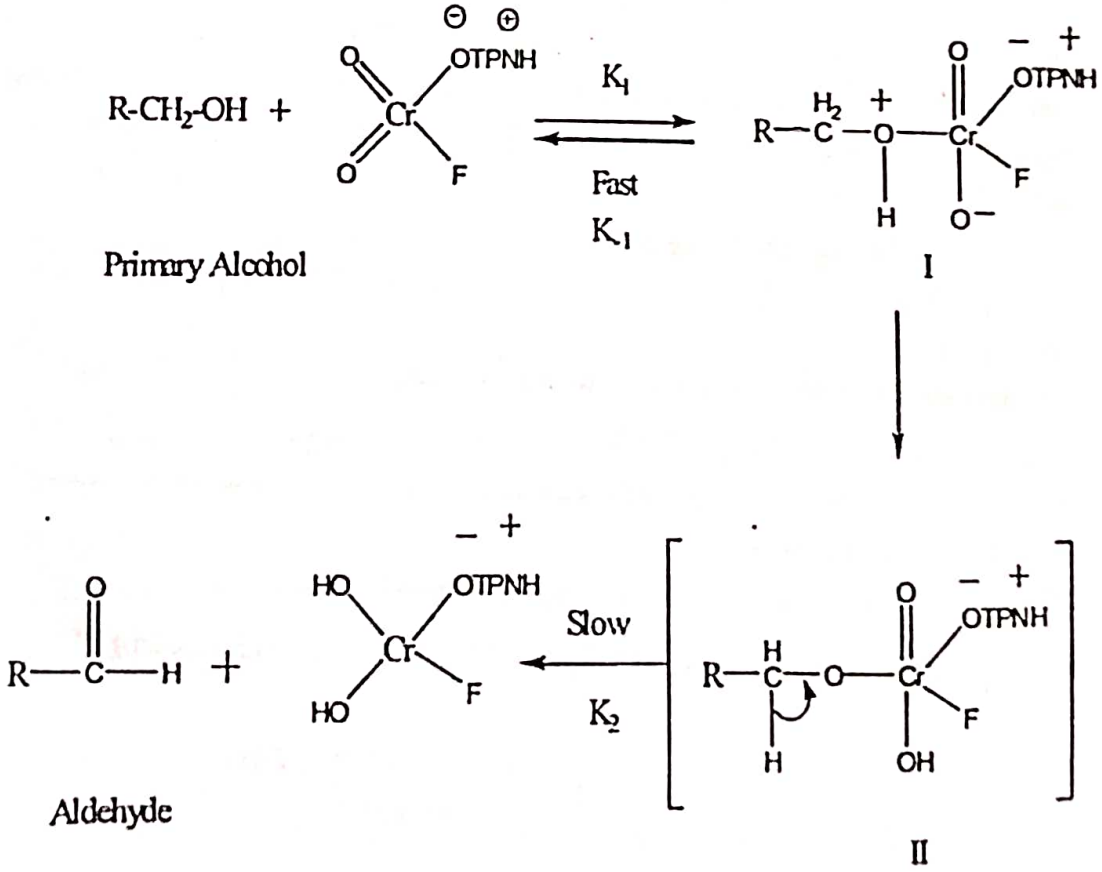
$$\Delta H^{=} = \Delta H^{o} - \beta \Delta S^{=} \quad \text{----------(1)}$$

Where ? is the isokinetic temperature, the isokinetic temperature for the reactions between 2-methoxy-1-butanol and TPAFC in aqueous acetic acid is 404K, which is greater than experimental temperature. The values of entropy of activation also suggested that the reaction is entropy as well as enthalpy controlled. The values of free energies of activation of reaction were found to be more or less similar. These trends also support the identical reaction mechanism being followed in these reactions [21].

CONCLUSION:-

The rate constants of the slow step involved in the mechanism were evaluated. Activation parameters were also computed. The negative value of ?S# provides support to the formation of rigid transition state. The overall mechanism described here is consistent with product and kinetic studies.

Mechanism of oxidation of 2-methoxy-1-butanol by TPAFC:-



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