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**Research Article**

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# Oxidation of isopropyl alcohol by tripropylammonium fluorochromate: A kinetic and mechanistic study

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**ABSTRACT**

*The Kinetics of oxidation of isopropyl alcohol by Tripropylammonium fluorochromate {TPAFC} has been Studied spectrophotometrically in presence of Sulphuric acid in aqueous acetic acid medium . The reaction is first order with respect to isopropyl alcohol, TPAFC and fractional order with respect to Acid. The Reaction rate has been determined at different temperatures and activation parameters were calculated. The solvent effect was analyzed using Tafts & Swains multiparametric equation. A suitable mechanism has been proposed.*

**Key words:** Isopropyl alcohol, Tripropylammonium fluorochromate, oxidation, kinetics.

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## 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 improvement were achieved by the use of new oxidizing agents such as quinolinium fluorochromate (QFC) [1-3], pyridinium Fluorochromate (PFC) [4-6], pyridinium Chlorochromate [7], 2,2-Bipyridinium Chlorochromate (BPCC)[8,9], Pyridinium bromochromte (PBC) [10] , Quinolium Chlorochromate (QCC) [11], Quinolium Bromochromate (QBC) [12], Quinolium Dichromate (QDC) [13], Imidazolium Fluorochromate (IFC) [14], benimidazolium flurochromate(BIFC) [15], N-methyl benzylammonium fluorochromate (MBAFC) [16], tributylammonium chlorochromate (TBACC) [17], imidazolium dichromate [18], isoquinolium bromochromate [19] for the study of kinetics and mechanism of various organic compounds. Most of these reagents have been developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, hygroscopicity, low selectivity, long reaction time. To overcome these difficulties 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 isopropyl alcohol by TPAFC; hence we have considered it to study the kinetics and mechanism of oxidation of isopropyl alcohol 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 [20] 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 $0^oC$. 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 $0^oC$. The orange colored precipitate was filtered, washed with petroleum ether and dried in vacuum for 2 hours at room temperature [21]. Yield was 28 g (97%); mp was $142^oC$ .

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 isopropyl alcohol in 20% acetic acid by using 0.1N $H_2SO_4$. 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, isopropyl alcohol (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 isopropyl alcohols 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-o.999) plots of log [TPAFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within +/- 3%.

## RESULTS AND DISCUSSION

The results of oxidation of isopropyl alcohol by TPAFC are represented in table 1-7.

**Effect of variation of concentration isopropyl alcohol:-**
The oxidation of isopropyl alcohol with TPAFC in 20% of acetic acid in presence of sulphuric acid yields acetone. By keeping constant [TPAFC] and [$H_2SO_4$], the increase in [isopropyl alcohol] increases the rate of reaction. The plot of log of $k_{obs}$ versus log [isopropyl alcohol] for different initial concentration of isopropyl alcohol is linear with unit slope demonstrate the first –order dependence of rate on isopropyl alcohol(table-1).

**Effect of variation of concentration of TPAFC:-**
At constant [isopropyl alcohol] and [$H_2SO_4$], the increase in [TPAFC] increases the rate of reaction. The plot of log $k_{obs}$ 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 concentration of $H^+$:-**
In order to study the effect the $H^+$ion concentration on the rate of oxidation reaction of isopropyl alcohol, the dependence of reaction rate has been investigated at different initial concentration of $H_2SO_4$. The rate of reaction increases with increase in [$H_2SO_4$]. The plot of log $K_{obs}$ verses log [H+]are also straight line with slope less than unity, Indicating a fractional order dependence on [H+]. (table-3).

**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 $CaCl_2$ , $Ca(NO_3)_2$, $Al(NO_3)_3$ and $K_2SO_4$. 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 isopropyl alcohol 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 [22] by interaction between $Cl^-$ ion and protonated TPAFC.

**Effect of solvent composition:-**
At fixed ionic strength and $[H^+]$, the rate of oxidation of isopropyl alcohol with TPAFC increases with decrease in polarity of solvent. This is due to polar character of transition state as compared to the reactant. The plot of log $k_{obs}$ verses 1/D is linear with positive slope indicating ion- dipole type of reaction[23].(table 5)

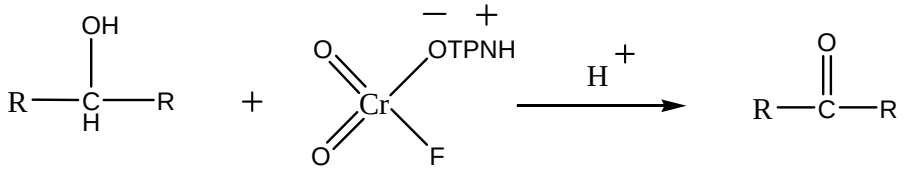
**Effect of temperature:-**
The study of effect of temperature on rate of oxidation of isopropyl alcohol by TPAFC has been subjected to different temperature range 293K to 313K by keeping the concentration of isopropyl alcohol and reagent constant. Rate constants are given in table 6. The plots of log of $K_{obs}$ verses 1/T are linear. 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 ΔG value indicates that similar mechanism is operative for the oxidation of isopropyl alcohol(table 7).

**Energy-entropy relationship:-**
The entropy of activation and heat of reaction are correlated by equation 1.

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

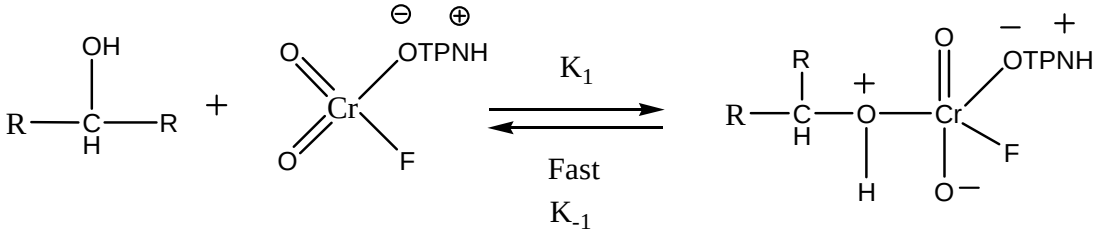
Where β is the isokinetic temperature, the isokinetics temperature for the reactions between isopropyl alcohol and TPAFC in aqueous acetic acid and which is greater than experimental temperature. The values of entropy of activation also suggested that the reaction is entropy as well as enthalpy controlled. 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 [24]. The linear relationship in Exner plot [25, 26] at 3+log $k_{303k}$ and 3+log $K_{308k}$ is observed.

**Mechanism of oxidation of isopropyl alcohol by TPAFC:**
**Reaction:**




Secondary alcohol Ketone

**Mechanism:**




**I**

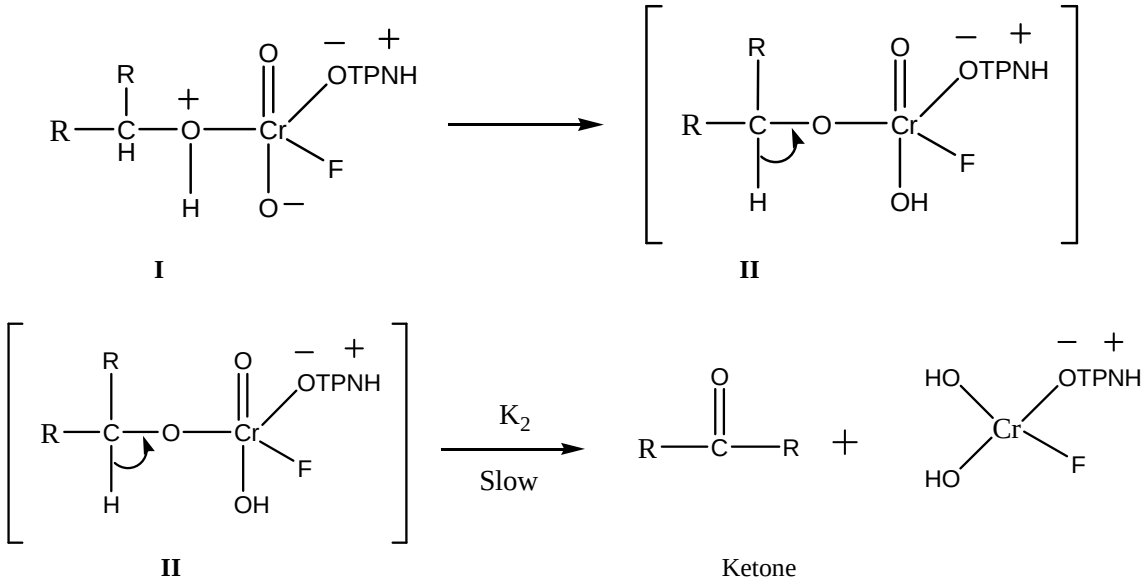



**Table 1: Effect of variation of [isopropyl alcohol] on reaction rate**
**[TPAFC]= 0.001 M, [$H_2SO_4$] = 0.1 N, Temperature =303 k, AA = 20% (v/v)**

| [Isopropyl alcohol] | K x $10^4$ $sec^{-1}$ |
|---|---|
| 0.01M | 2.98 |
| 0.02M | 5.96 |
| 0.03M | 9.36 |
| 0.04M | 12.48 |
| 0.05M | 14.48 |
| 0.06M | 16.36 |
| 0.07M | 18.38 |
| 0.08M | 20.45 |

**Table 2: Effect of variation of [TPAFC] on reaction rate**
**[Isopropyl alcohol]= 0.01 M, [$H_2SO_4$] = 0.1 N, Temp =303 k, AA = 20% (v/v)**

| [TPAFC] | K x $10^4$ $sec^{-1}$ |
|---|---|
| 0.001M | 5.98 |
| 0.0015M | 7.96 |
| 0.002M | 9.37 |
| 0.0025M | 11.48 |
| 0.003M | 13.48 |
| 0.0035M | 14.36 |
| 0.004M | 16.38 |
| 0.0045M | 18.45 |

**Table 3: Effect of variation of [$H_2SO_4$] on reaction rate**
**[TPAFC]= 0.001 M, [IPA] = 0.01 N, Temperature =303 k, AA = 20% (v/v)**

| [$H_2SO_4$] | K x $10^4$ $sec^{-1}$ |
|---|---|
| 0.1M | 2.97 |
| 0.2M | 4.92 |
| 0.3M | 5.38 |
| 0.4M | 6.47 |
| 0.5M | 7.41 |
| 0.6M | 8.34 |
| 0.7M | 9.36 |
| 0.8M | 10.50 |

**Table 4: Effect of variation of [salts] on reaction rate**
**[TPAFC]= 0.001 M, [$H_2SO_4$] = 0.1 N, Temperature =303 k, AA = 20% (v/v)**

| [salts] | K x $10^4$ $sec^{-1}$ |
|---|---|
| KCl | 2.98 |
| KBr | 5.96 |
| KI | 5.36 |
| $CaCl_2$ | 6.48 |
| $Ca(NO_3)_2$ | 6.78 |
| $Al(NO_{3)3}$ | 7.06 |
| $K_2SO_4$ | 6.38 |

**Table5: Effect of variation of Acetic Acid % on reaction rate**
**[TPAFC]= 0.001 M, [$H_2SO_4$] = 0.1 N, [IPA] =0.01M, Temperature =303 k**

| Acetic Acid % | K x $10^4$ $sec^{-1}$ |
|---|---|
| 10% | 2.75 |
| 20% | 5.96 |
| 30% | 9.67 |
| 40% | 13.06 |
| 50% | 14.86 |
| 60% | 16.78 |
| 70% | 18.76 |
| 80% | 19.69 |

**Table 6: Effect of variation of Temperatures on reaction rate**
**[TPAFC]= 0.001 M, [IPA] =0.01M, [$H_2SO_4$] = 0.1 N, AA = 20% (v/v)**

| Temperatures(k) | K x $10^4$ $sec^{-1}$ |
|---|---|
| 293 | 2.70 |
| 298 | 5.56 |
| 303 | 9.36 |
| 308 | 14.24 |
| 313 | 22.78 |

**Table 7: Activation Parameters**
**[TPAFC]= 0.001 M, [$H_2SO_4$] = 0.1 N, Temperature =303 k, AA = 20% (v/v)**

| Activation Parameters | K x $10^4 sec^{-1}$ |
|---|---|
| $\Delta E_a$ kJ $mole^{-1}$ | 69.92 |
| $\Delta H^{\#}$ kJ$mole^{-1}$ | 67.44 |
| $-\Delta S^{\#}$KJ $mole^{-1}$ | 284.65 |
| $\Delta$G# KJ $mole^{-1}$ | 140.37 |

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