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# Kinetics and Mechanism of Oxidation of n-Pentanol by Tetramethylammonium Fluorochromate

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## ABSTRACT

The oxidation of n-pentanol by tetramethylammonium fluorochromate in acidic solution was studied using spectrophotometric technique. The reaction was arranged to be under pseudo first-order conditions respect to the oxidant. A Michaelis-Menten type kinetic was observed respect to the substrate. The reaction is catalyzed by hydrogen ions. Dependences of the reaction rates on temperature and different solvents have been studied. The solvent effect was analyzed using Kamlet-Taft's and Swain's multiparametric equations. Finally, a mechanism consistent with the observed results has been proposed and discussed.

**Keywords:** Kinetics; Mechanism; Michaelis_Menten

## INTRODUCTION

The selective oxidation of alcohols to the corresponding aldehyde compounds is a frequently used transformation in organic synthesis, and hence a wide variety of methods has been developed. Among them, chromium(VI) containing reagents have been extensively studied [1]. The most popular of them, the Collins reagent, showed several difficulties. It should be used in large excess and it is unstable, hygroscopic, and finally it shows a poor selectivity in oxidation of primary alcohols to their aldehydes [2].

Tetramethylammonium fluorochromate, TMAFC, is a complex of chromium trioxide and tetramethylammonium fluoride. It has been reported that this complex converts alcohols into aldehyde products smoothly at room temperature and is a better oxidant than its homologous pyridinium chlorochromate, PCC, and pyridinium fluorochromate , PFC [3] . Some preliminary observation about the oxidation of Primary alcohols by TMAFC have been published which indicate there are some differences in kinetics of oxidation by TMAFC and PCC or PFC [4].

In this work we report the kinetics of oxidation of n-pentanol by TMAFC, evaluate the reaction rate constant at different temperatures and various solvents, and finally the mechanistic aspects are discussed and a probable mechanism has been proposed.

## EXPERIMENTAL

### Reagents

All chemicals were of reagent grade materials from Merck. The solvents were purified and dried by distillation over $P_2O_5$. TMAFC, $(CH_3)_4NFCrO_3$, was prepared by the procedure reported before [3]. The stock solution of the oxidant was prepared by dissolving the requisite amount of TMAFC in each solvent, and it was found to be stable at room temperature at least for two days.

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### Kinetics Measurements

The reaction was arranged to be under pseudo first order conditions by keeping a large excess of pentanol, 5 to $35\times10^{-4}$ mol, five hundred times or greater over TMAFC ($10^{-6}$ mol) in each solvent. The reaction vessel was thermostated in a water bath maintained at the desired temperature, 20-40 °C, within ± 0.1 °C. The reaction was followed spectrophotometrically by monitoring the absorption band at 350 nm. This wavelength is the maximum absorption due to TMAFC, the absorption due to the other reaction species being negligible. Spectrophotometric measurements were performed on a UV-Vis Shimadzu 2100 double-beam spectrophotometer supported with a Pentium IV computer, using quartz cells of path-length 10 mm. The reaction mixtures remain homogenous in the solvent system used.

In controlling the experiments, in the absence of pentanol, the concentration of TMAFC showed no appreciable changes. Repetitive scans of the spectra during the course of the reaction showed only decrease in the absorbance with no evidence of any shift in the peaks, Fig. 1. The observed first-order rate constants, $k_{obs}$, with respect to [TMAFC] were calculated from the slopes of the linear plots of logarithm of absorbance versus time, using the least-squared method with a correlation coefficient greater than 0.99. The reaction was followed beyond two half-lives. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding deviations are shown in the text and Tables.

## RESULTS AND DISCUSSION

### Stoichiometry and Product Analysis

Reaction mixture containing a known amount of n-pentanol with 2 fold excess of TMAFC in acetonitrile (100 ml) in the presence of 7.5 mol $dm^{-3}$ acetic acid was allowed to react completely at 25 °C. The remaining of the oxidant when the reaction completed was measured spectrophotometrically at 350 nm. The result indicates a ratio of substrate and oxidant as 3:2 stoichiometry, according to equation 1.

In a typical experiment a mixture of n-pentanol (0.1 mol), acetic acid (0.2 mol), and TMAFC (0.05 mol) 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. Most of the solvent was removed by distillation under reduced pressure. The residue was then treated with an excess (250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol $dm^{-3}$ HCl and kept in 5 °C for 10 hours. The precipitated 2,4-dinitrophenylhydrazone was filtered off, dried, recrystallized and weighed. The product was identical in melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of butyl aldehyde. The measuring yield of the product showed 96 percent completion of the reaction. So, the oxidation of pentanol by TMAFC resulted in the formation of corresponding aldehyde and the overall reaction may be represented as

$$3C_5H_{11}OH + 2Cr(VI) \rightarrow 3C_4H_9CHO + 6H^+ + 2Cr(III) \quad (1)$$

Similar observations have been reported before in oxidation of some alcohols by PFC and PCC [5-7]. The oxidant, TMAFC, undergoes a three-electron change. This is in accordance to the earlier observations for the other homologous, PFC and PCC [5-7]. Under the pseudo first-order conditions, the individual kinetic runs are first-order with respect to TMAFC. Further, the rate constant is independent of the initial concentration of the oxidant, Table 1, but dependent on concentration of acid, Table 2. This result shows that the reaction is catalyzed by hydrogen ions. The plot of [alcohol] versus [acetic acid] indicates the hydrogen ion dependence has the following form $k_{obs} = a + b[\text{acetic acid}] + c[\text{acetic acid}]^2$.

### Effect of Concentration on pentanol

The reaction rate was studied at different concentrations of pentanol and various temperatures, at constant acetic acid and oxidant concentrations. At this condition the rate constant slightly increased with increasing the concentration of alcohol, Table 3. A Michaelis-Menten type dependence was observed with respect to pentanol concentration, Table 3. A plot of $1/k_{obs}$ against 1/[alcohol] is linear (r is more than 0.99) with a non-zero intercept on the rate ordinate. This indicates the following overall mechanism, eqs 2 and 3, leads to the rate equation, eq 5.

$$RCH_2OH + TMAFC \underset{}{\overset{K}{\rightleftharpoons}} complex \qquad (2)$$

$$complex \xrightarrow[k_2]{slow} products \qquad (3)$$

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

$$rate = d[product]/dt = k_2[complex] \qquad (4)$$

The formation rate of the products is related to the loss of both oxidant and complex concentrations [8]. Applying the steady state approximation to the complex species, solving for complex and substituting into eq 4, we get

$$rate = k_2K[TMAFC][alcohol]/(1 + K[alcohol]) \qquad (5)$$

with

$$k_{obs} = k_2K[alcohol]/(1 + K[alcohol]) \qquad (6)$$

The values of equilibrium constant, K, for decomposition of pentanol 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.

## Solvent Effect

The oxidation of the pentanol was studied in different solvents. The choice of the solvent was limited to the solubility of TMAFC and its reaction with the substrates. There was no reaction with the solvents chosen. The kinetics was similar in all the solvents. The values of $k_{obs}$ were determined in different solvents and are listed in Table 4. Decrease in the rate constant of the reaction with an increase in the polarity of the medium suggests that the transition state is less polar than the reactants, Tables 4.

From idealized theories, the dielectric constant of a solvent is often predicted to serve as a quantitative measure of the solvent polarity. However, this approach is often inadequate since these theories regard solvent as a non-structured continuum, not composed of individual solvent molecules with their own solvent-solvent interactions and it does not take into account specific solute-solvent interactions, such as hydrogen bonding, electron pair donor, and electron pair acceptor interactions, which often play a dominant role in solute-solvent interactions. No single macroscopic physical parameter could possibly account for the multitude of solute-solvent interactions on the molecular microscopic level [9]. Thus, bulk solvent properties, like dielectric constant and ionizing power can only poorly describe the micro-environment around the reacting species, which govern the stability of the transition state and thus the rate of reaction. Hence, there have been a variety of attempts to quantity different aspects of solvent polarity and then use the resultant parameters to interpret solvent effects on reactivity through multiple regression.

In order to obtain a deeper insight into the specific interactions which influence the reactivity, an attempt was made to adopt the solvatochromic comparison method developed by Kamlet and Taft [10-12]. Kamlet and Taft's solvatochromic parameters have been used in one, two, or three-parameter correlation involving different combination of the parameters which are called linear solvation energy relationships. In general, all these parameters constitute more comprehensive measures of solvent polarity than the dielectric constant or any other single physical characteristic, since they reflect more reliably the complete picture of all intermolecular forces acting between solute and solvent molecules. Using the solvatochromic solvent parameters, the multi-parameter equation 7 has been proposed.

$$\log k_2 = A_0 + p\pi^* + a\alpha + b\beta \qquad (7)$$

Where $A_0$ represents the regression value, $\pi^*$ is the index of the solvent dipolarity/polarizability, the $\alpha$ coefficient represents the solvent hydrogen-bond donor (HBD) acidity and $\beta$ coefficient is a measure of a solvent hydrogen-bond acceptor (HBA) basicity. The regression coefficients, p, a, and b in eq 7 measure the relative susceptibilities of the solvent-dependent of $\log k_2$ to the indicated solvent parameters.

In order to explain the obtained $\log k_2$ values through Kamlet and Taft's solvent parameter, the rate constants were correlated with solvent properties by means of single and multiple linear regression analysis by a suitable computer program [13]. We used the Gauss-Newton nonlinear least-squares method in the computer program to refine the $\log k_2$ by minimizing the error squares sum, U, from eq 8,

$$U = \sum(a_i - b_i)^2 \qquad (8)$$

where $a_i$ and $b_i$ are the experimental and calculated values of $\log k_2$, respectively.

The rate of oxidation of pentanol failed to yield any significant correlation in terms of the linear solvation energy relationship of Kamlet and Taft's equation. Similar observations have been reported before in oxidation of some alcohols by PFC and PCC [14-16].

$\log k_2 = A_0 + a\alpha + b\beta + p\pi^*$ (9)

$\log k_2 = 0.02 - 0.02\alpha - 0.03\beta + 0.01\pi^*$ ($n = 6$, $r = 0.92$) (9a)

So, the data on the solvent effect was analyzed in terms of Swain's equation of cation and anion solvating concept of the solvents, eqs 10 and 11.

$\log k_2 = aA + bB + c$ (10)

$\log k_2 = aA + bB + s(A+B) + c$ (11)

Where A and B represent the anion and cation solvating power of the solvent, respectively, and a, b, c and s are regression coefficients. The rates in different solvents were analyzed in terms of eqs 10 and 11, separately with A and B and also with (A+B), solvent polarity.

$\log k_2 = 0.02A - 0.005B + 0.13$ ($n = 6$, $r = 0.98$) (10a)

$\log k_2 = -0.015A - 0.019B + 0.013(A+B) + 0.13$ ($n = 6$, $r = 0.99$) (11a)

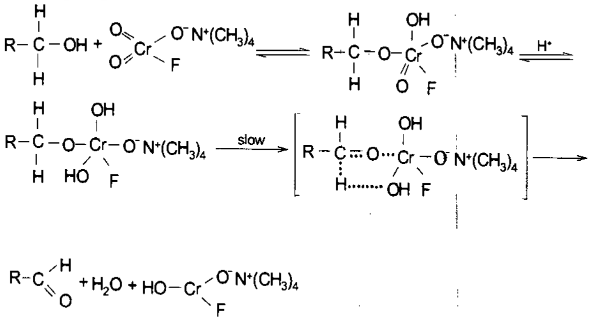
The rate of oxidation of pentanol in different solvents showed an excellent correlation in Swain's equation, eq 11. From the magnitude of coefficients a, b, and s the percentage contributions of A, B, and (A+B) to the reactivity were calculated and are as: 32 %, 40 %, and 28 %, respectively. The excellent correlation indicates the existence of specific local electrostatic solute-solvent interactions. In all the solvent, the cation solvating tendency plays the major role. The negative sign of the coefficients of the terms A and B show that the magnitude of the specific interaction between the reactants and the solvent is greater than that of the transition state-solvent interactions [17].

Cation solvation is closely related to the electron pair donor capacity or Lewis basicity of solvents and tends to become stronger with the increase in donor number. On the other hand, the anion solvation is closely related to the electron pair acceptability or Lewis acidity of solvents and tends to become stronger with increase in acceptor number. Acetonitrile has relatively small donor number and usually solvates weakly to a cation [18], and this should possibly be responsible for the greater $k_{obs}$ in acetonitrile in comparison to the other solvents, although the dielectric constant of acetonitrile is greater than acetone, 2-butanone, and cyclohexanone.

**Temperature effect**

To determine the activation parameters, 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 $\log k_{obs}$ versus 1/T gave a straight line with correlation of $r = 0.99$ with activation energy as $E_a = 49.68$ (kJ/mol). The Eyring parameters were computed using the intercept and slope of $\log k_2$ versus 1/T plot, and are: $\Delta H^{\#} = 26.3$ (kJ/mol), $\Delta S^{\#} = -197.2$ (J/K mol), and $\Delta G^{\#} = 85.1$ (kJ/mol).

The Michaelis-Menten kinetics of oxidation of the alcohols by PFC differs from those reported for PCC and both differ with TMAFC. The differences are possibly due to the more electronegativity of fluorine than chlorine that may cause the central metal atom to be more electrons deficient and also because of more acidity of PFC than TMAFC in the reaction. The observed acid dependence of the reaction suggests that the reaction may be one between the alcohols and a protonated species of chromium(VI). This view is in accordance with the involvement of such species well established in chromium trioxide oxidation [19]. However, this implies that transfer of hydrogen nucleus is the essence of the mechanism of such reactions in the presence of an acid. The results point to a proton transfer in the rate-determining step, scheme 1. This is in accordance with the result obtained in the oxidation of benzyl alcohol by PFC [20].



**scheme 1**

The values of enthalpy of activation are useful for interpretation of the structure of transition states. In essence, it is related to energy changes along the reaction coordinate and can be interpreted in terms of bond strengths. The positive enthalpy of activation for the substrate resulted in this work is clearly denotes to the loose bonds in the corresponding complex.

The entropy of activation provides one of the best indications of the nature of transition state. For reactions that occur in solution a negative $\Delta S^{\#}$ might be expected because the complex is formed by association of two individual molecules, and there is a loss of translational and rotational freedom.

**Table 1**. Dependence of the reaction rate of n-pentanol, $9.20\times10^{-4}$ (mol), [acetic acid] =5.0 (mol/dm$^3$) on different oxidant concentrations at 25 °C in acetonitrile

| $10^4$ [TMAFC] (mol/dm$^3$) | 1.43 | 2.14 | 2.86 | 3.57 | 4.28 | 5.71 |
|---|---|---|---|---|---|---|
| $10^3 k_{obs}$ (s$^{-1}$) $^a$ | 5.39 | 5.40 | 5.40 | 5.41 | 5.42 | 5.41 |

(a) The standard deviation from the average is between 0.04-0.10.

**Table 2**. Dependence of the reaction rate of n-pentanol, 0.38 (mol/dm$^3$), [TMAFC] = $2.86\times10^{-4}$ (mol/dm$^3$) on different [acetic acid] at 25 °C in acetonitrile

| [acetic acid] (mol dm$^{-3}$) | 3.0 | 4.0 | 5.0 | 6.0 | 7.5 | 9.0 | 9.75 |
|---|---|---|---|---|---|---|---|
| $10^3 k_{obs}$ (s$^{-1}$) $^a$ | 0.07 | 1.85 | 3.64 | 5.34 | 5.84 | 6.83 | 11.21 |

(a) The standard deviation from the average is between 0.05-0.11.

**Table 3**. Dependence of the reaction rate of TMAFC, $2.86\times10^{-4}$ (mol/dm$^3$), on different concentrations of n-pentanol, at constant acetic acid, 7.5 (mol/dm$^3$), and temperature, 25 °C in acetonitrile

| [n-pentanol] (mol/dm$^3$) | 0.13 | 0.21 | 0.26 | 0.32 | 0.39 | 0.53 |
|---|---|---|---|---|---|---|
| $10^3 k_{obs}$ (s$^{-1}$) $^a$ | 4.36 | 5.11 | 5.40 | 5.63 | 5.93 | 6.29 |

(a) The standard deviation from the average is between 0.04 – 0.13.

**Table 4**. Dependence of the reaction rate of n-pentanol by TMAFC, $2.86\times10^{-4}$ (mol/dm$^3$), at different mediums, 25 °C, [acetic acid] = 7.5 (mol/dm$^3$)

| | $10^3 k_{obs}$ (s$^{-1}$) $^a$ | | | | | |
|---|---|---|---|---|---|---|
| solvent | concentration of n-pentanol (mol/dm$^3$) | | | | | |
| | 0.13 | 0.21 | 0.26 | 0.32 | 0.39 | 0.53 |
| DMSO | 3.57 | 4.15 | 4.45 | 4.66 | 4.95 | 5.21 |
| DMF | 4.18 | 4.89 | 5.21 | 5.44 | 5.72 | 6.08 |
| acetone | 5.02 | 5.78 | 6.11 | 6.32 | 6.64 | 7.02 |
| 2-butanone | 5.55 | 6.32 | 6.59 | 6.74 | 6.95 | 7.36 |
| cyclohexanone | 6.27 | 7.06 | 7.35 | 7.46 | 7.75 | 8.09 |

(a) The standard deviation from the average is between 0.03 – 0.14.

**Table 5**. The values of K and $k_2$ at different solvents, according to eq 6

| solvent | $10^3 k_2$ (s$^{-1}$) $^a$ | K (dm$^3$/mol) |
|---|---|---|
| DMSO | 6.08 | 4.02 |
| DMF | 7.05 | 2.76 |
| acetonitrile | 7.26 | 5.18 |
| acetone | 7.95 | 3.67 |
| 2-butanone | 8.10 | 9.38 |
| cyclohexanone | 8.83 | 7.15 |

(a) The standard deviation from the average is between 0.03 – 0.08.

**Table 6**. The Kamlet and Taft's solvatochromic and Swain's parameters

| solvent | $\pi^{*\,a}$ | $\alpha^{a}$ | $\beta^{b}$ | $A^{c}$ | $B^{c}$ | $A+B^{c}$ |
|---|---|---|---|---|---|---|
| DMSO | 1.0 | 0.0 | 0.76 | 0.34 | 1.08 | 1.41 |
| DMF | 0.88 | 0.0 | 0.69 | 0.30 | 0.93 | 1.23 |
| acetonitrile | 0.75 | 0.19 | 0.31 | 0.37 | 0.86 | 1.22 |
| acetone | 0.71 | 0.08 | 0.48 | 0.25 | 0.81 | 1.06 |
| 2-butanone | - | - | - | 0.23 | 0.74 | 0.97 |
| cyclohexanone | 0.76 | - | 0.53 | - | - | - |

a, b, and c were obtained from references 17, 14, and 9, respectively

**Table 7**. The rate of decomposition of the complexes, $k_2$, at different temperatures, [TMAFC] = $2.86\times10^{-4}$ (mol/dm$^3$), [acetic acid] = 7.5 (mol/dm$^3$) in acetonitrile

| 20 °C | 25 °C | 30 °C | 35 °C | 40 °C |
|---|---|---|---|---|
| 6.48 | 7.26 | 9.45 | 11.24 | 13.40 |

The standard deviation from the average is between 0.03 – 0.1.

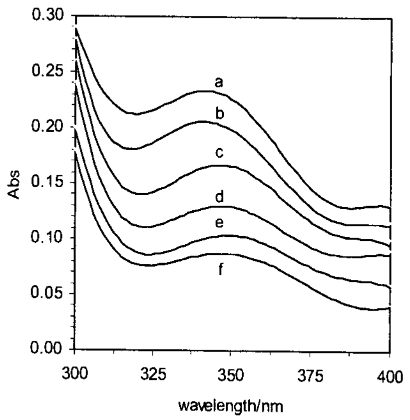


**Fig. 1**. Sequential scans of the absorption spectrum during the reaction of n-pentanol with TMAFC at 25 °C, [n-pentanol] 0.38 (mol dm$^{-3}$), [acetic acid] 7.5 (mol dm$^{-3}$), [TMAFC] =$2.86\times10^{-4}$ (mol dm$^{-3}$) in acetonitrile, at reaction time, (a) 0.1, (b) 0.5, (c) 1.1, (d) 1.5, (e) 3.0, and (f) 6.0 minutes.

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