

# Oxidation of Alcohols with Tetramethylammonium Fluorochromate in Acetic Acid

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Received January 21, 2005

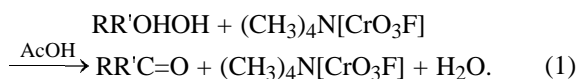
**Abstract**—A number of alcohols were oxidized to the corresponding carbonyl compounds in excellent yields using tetramethylammonium fluorochromate in acetic acid. The oxidant takes up two electrons, the reaction follows first-order kinetics with respect to the oxidant under pseudofirst-order conditions, and the concentration of alcohols changes according to the Michaelis–Menten dependence.

Chromium(VI) reagents are widely used in organic chemistry for oxidation of primary and secondary alcohols to carbonyl compounds. In the recent years, some new chromium(VI)-based reagents were proposed. Such compounds as Collins' reagent [1], chromium trioxide–3,5-dimethylpyrazole complex [2], pyridinium chlorochromate [3], pyridinium dichromate [4], and 2,2'-bipyridinium chlorochromate [5] have become quite popular and showed high efficiency as oxidants.

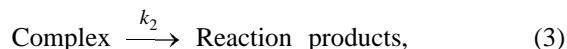
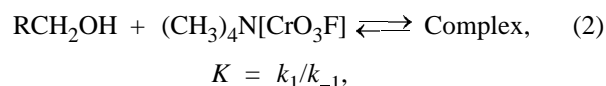
We recently reported on the synthesis of tetramethylammonium fluorochromate(VI) (TMAFC) and used this reagent for quantitative oxidation of several organic substrates [6, 7]. The present communication describes the results of oxidation of several alcohols with TMAFC in acetic acid medium. The data obtained may be useful for the following reasons: (1) Information on the kinetics of reactions involving complex metal ions in strongly acidic media are very limited, partly due to instability problems and difficult interpretation of the results; and (2) the reaction under study may serve as a model of enzymatic oxidation with alcohol dehydrogenases in acetic acid bacteria [8, 9].

The use of tetramethylammonium fluorochromate as oxidant for the transformation of alcohols into the corresponding carbonyl compounds was quite satisfactory. The results showed that TMAFC is a valuable addition to the existing oxidants. Figure shows the data obtained by spectrophotometric monitoring of the reaction course. The intensities of absorption maxima corresponding to the initial alcohols gradually decrease, while no shift of the maximum is observed.

The overall reaction is described by the following equation:



Insofar as the proposed oxidant is stable and soluble, the reaction can be carried out at room temperature, and isolation of the products is facile. During the process, the reaction mixture changes from orange to brown; therefore, the progress of oxidation can be monitored visually. Under pseudofirst-order conditions, the individual kinetic runs are of first order with respect to TMAFC. The rate constants do not depend on the initial oxidant concentration. In all cases, variation of the alcohol concentration conforms to the Michaelis–Menten dependence. The plot of  $1/k_1$  versus  $1/[\text{alcohol}]$  is a straight line ( $r = 0.995$ ) with a non-zero intercept on the y axis. The apparent rate constants  $k_{\text{ap}}$  (see table) were determined from the plots of  $\log[\text{TMAFC}]$  vs. time. The results indicated the following reaction mechanism:



$$v = k_2 K [\text{TMAFC}] [\text{alcohol}] / (1 + K [\text{alcohol}]). \quad (4)$$

Here,  $v$  is the reaction rate.

Oxo complexes of transition metals are also used as general-purpose stoichiometric oxidants in synthetic organic chemistry, and a variety of reaction pathways including both atom transfer and electron transfer are involved. The reaction of triphenylphosphine with TMAFC at a molar ratio of 1:1.1 in

acetonitrile at room temperature gave triphenylphosphine oxide in quantitative yield. This reactions represents a clear-cut example of oxygen transfer with participation of TMAFC, in keeping with the results obtained previously using pyridinium fluorochromate and chlorochromate [10, 11].

## EXPERIMENTAL

The IR spectra were recorded in KBr on a Shimadzu 420 spectrometer. The UV spectra were measured on a Uvicon 922 spectrophotometer. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were obtained on a Bruker Avance DRX-500 instrument at 500, 125, and 470.66 MHz, respectively; the chemical shifts were referenced to  $\text{SiMe}_4$  (external,  $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $\text{CFCl}_3$  (external,  $^{19}\text{F}$ ).

Chromium trioxide  $\text{CrO}_3$  (Merck, analytical grade) was used without additional purification. The solvents were purified by standard procedures.

The concentration of chromium was determined by iodometric titration. The concentration of Cr in the reduced oxidant was determined after oxidation with an acidic solution of potassium peroxodisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ). The elemental analyses for carbon, hydrogen, and nitrogen were obtained at the Microanalytical Laboratories, Department of Chemistry, OIRC (Tehran, Iran).

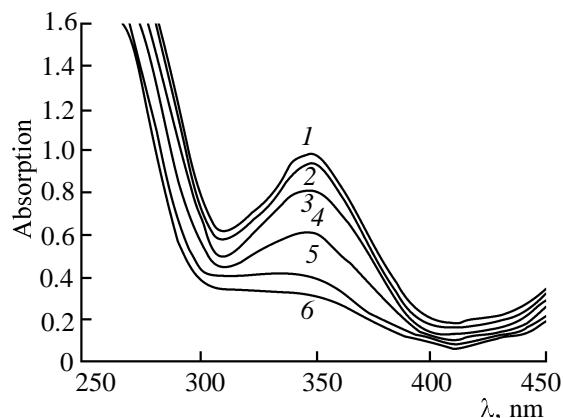
**Tetramethylammonium fluorochromate(VI)**  $(\text{CH}_3)_4\text{N}[\text{CrO}_3\text{F}]$ . The synthesis was carried out inside a glove box purged with argon. Chromium(VI) oxide, 1.07 g, was dissolved in 25 ml of anhydrous acetonitrile in a v polyethylene beaker, and a stoichiometric amount of tetramethylammonium fluoride (1 g) was added under stirring at room temperature. After 5 min, a transparent orange solution was formed, and crystals of tetramethylammonium fluorochromate separated on cooling. The product was filtered off, washed with anhydrous isopropyl alcohol and diethyl ether, dried for 1 h under reduced pressure, and purified by dissolution in acetonitrile, followed by slow evaporation of the solvent over a week. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 904 ( $\text{CrO}_3$ ), 636 ( $\text{CrF}$ ), 940 ( $\text{CrO}_3$ ). The electronic absorption and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were consistent with the TMAFC structure [6, 7]. Found, %: C 24.52; H 6.42; N 7.21.  $\text{C}_4\text{H}_{12}\text{CrFNO}_3$ . Calculated, %: C 24.85; H 6.21; N 7.25.

**General procedure for oxidation of alcohols with tetramethylammonium fluorochromate in acetic acid.** The progress of the reaction was monitored by UV/visible spectrophotometry. To determine the stoichiometry, excess of alcohol (10-fold or

Apparent pseudofirst-order rate constants for the oxidation of some alcohols to the corresponding carbonyl compounds with tetramethylammonium fluorochromate in acetic acid

Alcohol	$k_{\text{ap}} \times 10^4$	Alcohol	$k_{\text{ap}} \times 10^4$
Methanol	251	3-Pentanol	268
Ethanol	308	4-Methyl-1-pentanol	321
1-Propanol	312	1-Hexanol	305
2-Propanol	268	1-Heptanol	297
1-Butanol	326	1-Octanol	444
2-Butanol	364	2-Octanol	403
2-Methyl-1-propanol	357	Benzyl alcohol	433
1-Pentanol	308		

greater) was used in the reaction with TMAFC in 100 ml of acetic acid. The concentration of TMAFC was determined by spectrophotometry at  $\lambda$  350 nm. The results indicated a 1 : 1 stoichiometry in reactions of TMAFC with all alcohols. The reactions were carried out under pseudofirst-order conditions using a large excess of alcohol (0.01–0.2 M). The reaction mixtures were analyzed for the corresponding carbonyl compounds by the procedures reported previously [10, 11]. The temperature was maintained constant within  $\pm 0.1^\circ\text{C}$ . Spectrophotometric measurements were performed on a Uvicon-922 instrument equipped with a temperature control unit using 10-mm quartz cells. A very small magnetic stirrer was designed at the cell compartment just in the bottom of a sample cell. The



Electronic absorption spectra of the reaction mixture in the oxidation of 2-propanol with tetramethylammonium fluorochromate at  $30^\circ\text{C}$  in (1) 0.5, (2) 3, (3) 6, (4) 15, (5) 20, and (6) 25 min after the reaction started. Initial concentrations of 2-propanol and TMAFC 0.05 and 0.001 M, respectively.

reaction mixtures remain homogeneous under the given conditions.

**Oxidation of triphenylphosphine with tetramethylammonium fluorochromate.** The reaction was performed in a dry 100-ml round-bottomed flask under vigorous stirring in a nitrogen atmosphere. Triphenylphosphine, 1.5 g, was dissolved in 35 ml of acetonitrile, and 1.21 g of tetramethylammonium fluorochromate (substrate-to-oxidant ratio 1:1.1) was added in two portions over a period of 1 min. An exothermic reaction set in instantaneously and was complete in 5 min. The solution was cooled, the reduced oxidant was separated by centrifugation and washed with acetonitrile, and the mother liquor and the washings were passed through a short column charged with silica gel ( $7 \times 2$  cm). The sorbent was thoroughly washed with ether ( $3 \times 35$  ml), the filtrates were combined and evaporated on a water bath, and the residue was identified as triphenylphosphine oxide by the elemental analysis and IR spectrum. Yield 1.48 g (97%), mp  $155^{\circ}\text{C}$ ; published data: mp  $156\text{--}157^{\circ}\text{C}$ .

#### ACKNOWLEDGMENTS

The authors thank Dr. Gh. Rezaei Behbahani for valuable discussions and also thank the Azad University Saveh Center for performing some spectral analyses.

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