Brief Communications

Kinetics of oxidation of alcohols with tetramethylammonium fluorochromate

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The oxidation of isopropyl, benzyl, and *n*-butyl alcohols to the corresponding aldehydes with tetramethylammonium fluorochromate was studied by spectrophotometry in acetonitrile solutions in the presence of *p*-toluenesulfonic acid. The reaction kinetics was studied under pseudo-first-order conditions with respect to the oxidizing agent. The Michaelis—Menten kinetics with respect to the substrate was observed, indicating the quasi-equilibrium formation of an oxidizing agent—alcohol complex. The formation constants and the rates of disproportionation of the complexes were determined. The temperature dependences of the reaction rates were studied, and the activation parameters were computed. A reaction scheme consistent with the observed results was proposed.

Key words: oxidation, alcohols, tetramethylammonium fluorochromate, *p*-toluenesulfonic acid, kinetics, mechanism.

The oxidation of organic substrates, such as amino acids, alcohols, thioethers, *etc.*, with inorganic compounds in solution have received considerable attention. In particular, pyridinium fluorochromate (PFC), being a complex of chromium trioxide, pyridine, and hydrofluoric acid, has long been studied.[1—7] It has been reported[8—11] that this complex converts alcohols into aldehydes at room temperature and this oxidizing agent is better than its analogue, pyridinium chlorochromate (PCC). Recently,[12] we synthesized another oxidizing agent, *viz.*, tetramethylammonium fluorochromate (TFC), which should be suitable for alcohol oxidation. This compound has additional advantages over PFC and PCC, namely, lower acidity, ability to more selective oxidation under mild conditions, higher solubility in nonaqueous solvents, *etc.*

The kinetics and mechanism of alcohol oxidation with chromic acid have been studied in detail.[13,14] These reactions were found[13,14] to involve a change in the chromium oxidation state from Cr^{VI} to Cr^{III}. The oxidation of primary alcohols with the Collins reagent affords the desired aldehydes in moderate yields.[15] Our studies show that TFC oxidizes efficiently a wide spectrum of alcohols to aldehydes.

To our knowledge, no published report on alcohol oxidation with TFC and the kinetics and mechanism are available. In this work, we studied the kinetics of oxida-

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tion of some alcohols with TFC, determined the reaction rate constants and temperature dependences of the reaction rates, and proposed a probable mechanism of oxidation.

Experimental

Materials. Alcohols (Pr^iOH, $PhCH_2OH$, and Bu^nOH, analytical grade, Merck) were distilled *in vacuo*. Their purity was checked by comparing their boiling points with the literature values.[16] Acetonitrile (analytical grade, Fluka) was purified and dried by distillation over P_2O_5. Tetramethylammonium fluorochromate was prepared by a previously described procedure.[12] *p*-Toluenesulfonic acid (analytical grade, Merck) was used as a source of hydrogen ions.

Stoichiometry. To determine the stoichiometry, a specified amount of each alcohol was treated with TFC in acetonitrile (100 mL). The amount of the unreacted oxidizing agent after the reaction completion was measured spectrophotometrically at λ = 350 nm. According to the obtained results, the experimental ratio of the reacted substances (substrate : oxidizing agent) is 3 : 2, *i.e.*, corresponds to the stoichiometry

$$3\ RR'CHOH + 2\ Cr^{VI} \rightarrow 3\ RR'CO + 6\ H^+ + 2\ Cr^{III}. \quad (1)$$

R = Ph, R′ = H; R = R′ = Me; R = Pr, R′ = H

Kinetic measurements. The reactions were carried out in acetonitrile as solvent under pseudo-first-order conditions with respect to TFC by keeping a large excess of alcohol (from 0.01 to 0.2 mol L^{-1}), being at least tenfold over TFC (0.01 mol L^{-1}), at a constant temperature (±0.1 °C) and monitored spectrophotometrically by the absorption band at λ = 350 nm. This wavelength corresponds to the absorption maximum of TFC. The absorption of the other reaction species is negligible at this wavelength. Spectrophotometric measurements were performed on a UV-Vis Uvicon 922 spectrophotometer with a Pentium IV computer and using two temperature-controlled 10-mm quartz cells. A small magnetic stirrer was designed at the cell compartment just in the bottom of the sample cell in the spectrophotometer to stir up the solution under study in the cell. The reaction mixture remained homogeneous in the solvent system used. The rate constants (k_1) were calculated from the plots of logarithm of absorbance *vs*. time.

In control experiments, in the absence of alcohols, the TFC concentration shows no appreciable changes. Repetitive scans of the spectra during the reaction course showed only a decrease in the absorbance with no evidence of any shift in the peaks (Fig. 1). In all cases, the procedure was repeated at least two times. The resulting average values and corresponding standard deviations are presented in the text.

Analysis of products. In a typical experiment, a mixture of Pr^iOH (0.1 mol), *p*-toluenesulfonic acid (0.005 mol), and TFC (0.02 mol) was dissolved in MeCN (100 mL). The reaction mixture was allowed to stand in dark to ensure completion of the reaction (10 h). The most portion of the solvent was distilled off under reduced pressure. The residue was treated with an excess (250 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *M* HCl, and the mixture was kept for 10 h at 5 °C. The precipitate of 2,4-dinitrophenylhydrazone was filtered off, dried, recrystallized from EtOH, and weighed. The product was identified by melting point comparing it with that of an authentic sample of acetone 2,4-dinitrophenylhydrazone. The measured yield of the product corresponded to the 89% conversion. In similar experiments with other alcohols, the yields of 2,4-dinitrophenylhydrazones were 88—90%.

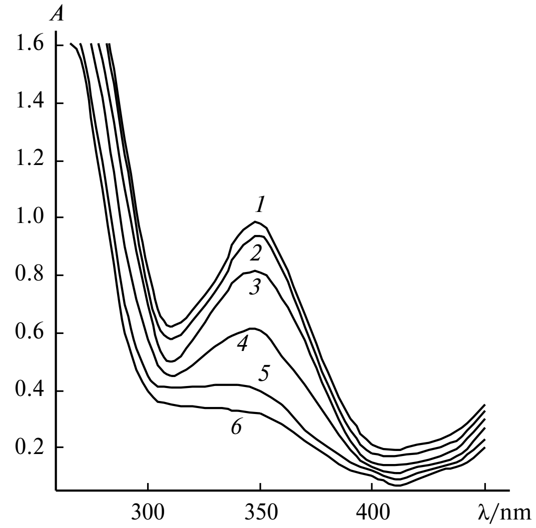

Fig. 1. Sequential scans of the absorption spectrum during the reaction of isopropyl alcohol with TFC in MeCN at 30 °C at the reaction time: 0.5 (*1*), 3 (*2*), 6 (*3*), 10, 15 (*4*), 20 (*5*), and 25 min (*6*) ($[Pr^iOH]$ = 0.05 mol L^{-1}, [TFC] = 0.001 mol L^{-1}, [TsOH] = 0.005 mol L^{-1}).

Results and Discussion

The oxidation of alcohols with tetramethylammonium fluorochromate afforded the corresponding aldehydes (ketones). The overall reaction can be presented by Eq. (1).

Similar observations have been reported earlier for the oxidation of some alcohols with PFC and PCC.[17—19] The oxidizing agent TFC undergoes a three-electron reduction. This is in an accord with the earlier observations for the analogues PFC and PCC.[17—19] Under the pseudo-first-order conditions, the individual kinetic runs are first-order with respect to TFC. The rate constants are independent of the initial concentration of the oxidizing agent (Table 1).

A Michaelis—Menten type dependence was observed for each alcohol used (Table 2).

Table 1. First-order reaction rate constants (k_1) of isopropyl alcohol oxidation with TFC at different oxidizing agent concentrations ($[Pr^iOH]$ = 0.05 mol L^{-1}, [TsOH] = 0.005 mol L^{-1}, 30 °C)

$[TFC] \cdot 10^3$/mol L^{-1}	$k_1 \cdot 10^3/s^{-1}$
0.1	7.21±0.05
0.2	7.24±0.04
0.5	7.21±0.06
1.0	7.27±0.03
2.0	7.33±0.05

Table 2. Dependence of the first-order rate constants (k_1) of alcohol oxidation with TFC on the alcohol concentration at different temperatures ([TFC] = 0.001 mol L^{-1})

Alcohol	T/°C	$k_1 \cdot 10^3$ */s^{-1} at different [ROH]/mol L^{-1}							
		0.01	0.015	0.02	0.025	0.05	0.08	0.1	0.2
Pr^{i}OH	25	5.73	5.86	5.89	6.00	6.02	6.15	6.27	6.39
	30	6.78	6.93	6.95	7.11	7.21	7.31	7.57	7.65
	35	7.43	7.75	7.86	8.06	8.23	8.41	8.57	8.71
	40	8.60	9.45	9.86	10.32	10.97	11.39	11.70	11.79
PhCH$_2$OH	25	3.93	4.08	4.15	4.22	4.33	4.38	4.41	4.43
	30	4.19	4.57	4.80	4.94	5.14	5.39	5.55	5.60
	35	4.45	4.98	5.18	5.55	6.03	6.30	6.55	6.59
	40	4.85	5.49	5.76	6.19	6.76	7.13	7.45	7.65
Bu^{n}OH	25	5.65	5.83	5.86	6.03	6.16	6.24	6.63	6.73
	30	6.69	6.76	6.94	7.31	7.26	7.71	8.27	8.43
	35	7.19	7.45	7.56	7.70	7.77	7.97	8.13	8.55
	40	7.42	7.55	7.65	7.84	7.98	8.21	8.59	8.98

* The standard deviation from the average value is 0.02—0.09.

Table 3. Formation constants of complexes with TFC and alcohols (K) at different temperatures

Alcohol	K			
	25 °C	30 °C	35 °C	40 °C
Pr^{i}OH	1049.48±0.31	1001.55±0.24	623.42±0.19	251.57±0.29
Bu^{n}OH	768.91±0.25	489.39±0.32	422.90±0.23	234.90±0.21
PhCH$_2$OH	746.91±0.22	289.15±0.28	190.78±0.34	168.11±0.22

Plots in the $1/k_1$—1/[ROH] coordinates are linear (correlation coefficient 0.99) with non-zero intercepts on the ordinate (Fig. 2). This indicates the overall mechanism

$$\text{ROH} + \text{TFC} \overset{K}{\rightleftharpoons} \text{Complex}, \tag{2}$$

$$\text{Complex} \xrightarrow{k_2} \text{Products} \tag{3}$$

and results in the following equation for the reaction rate (W):

$$W = k_2K[\text{TFC}][\text{ROH}]/(1 + K[\text{ROH}]). \tag{4}$$

The equilibrium constants (K) and rate constants (k_2) of the complexes for all substrates were determined from the slopes and intercepts, respectively (see Fig. 2), and are presented in Tables 3 and 4.

To determine the activation parameters, the reaction was carried out at several temperatures (25, 30, 35, and 40 °C) and constant concentrations of the hydrogen ion, oxidizing agent, and each alcohol. The Arrhenius plots $\log k_2$—$1/T$ are linear for all substrates. The linear correlation coefficient ($r = 0.99$) of the plots show that all alcohols are oxidized *via* the same mechanism.[20,21] The Eyring parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$) calculated from the in-

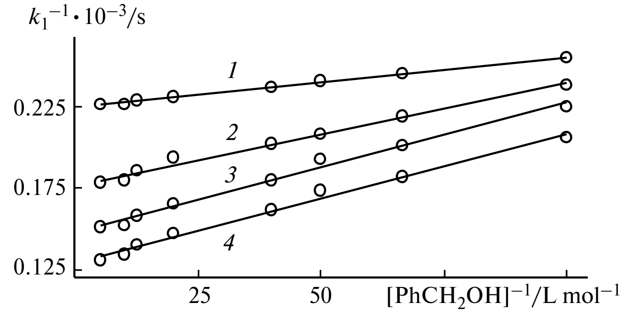

Fig. 2. Michaelis—Menten plots of the k_1 rate *vs*. alcohol concentration for the oxidation of PhCH$_2$OH with TFC ([TFC] = 0.001 mol L^{-1}, [catalyst] = 0.005 mol L^{-1}) at 25 (*1*), 30 (*2*), 35 (*3*), and 40 °C (*4*).

Table 4. Rates of decomposition of the alcohol—TFC complexes (k_2) at different temperatures

Alcohol	$k_2 \cdot 10^3$/s^{-1}			
	25 °C	30 °C	35 °C	40 °C
Pr^{i}OH	6.22±0.05	7.40±0.06	8.58±0.02	12.00±0.10
PhCH$_2$OH	4.45±0.05	5.62±0.03	6.72±0.06	7.66±0.09
Bu^{n}OH	6.34±0.04	7.91±0.04	8.10±0.08	9.17±0.07

Table 5. Activation parameters for the oxidation of alcohols with TFC at 25 °C ([ROH] = 0.01 mol L^{-1}, [TFC] = 0.001 mol L^{-1})

Alcohol	$\Delta H^{\neq}$ /kJ mol^{-1}	$-\Delta S^{\neq}$ /J mol^{-1} K^{-1}	$\Delta G^{\neq}$ /kJ mol^{-1}
Pr^iOH	20.34±0.18	277.47±0.31	103.03±0.37
$PhCH_2OH$	10.72±0.20	313.00±0.29	103.99±0.33
Bu^nOH	13.88±0.15	299.05±0.28	103.00±0.25

tercepts and slopes of the $\log k_2$—$1/T$ plots are shown in Table 5.[22—24]

The Michaelis—Menten kinetics of alcohol oxidation with PFC differs from the data reported for PCC and TFC. The differences are possibly due to the higher electronegativity of the F atom compared to Cl atom that may cause the central metal atom to be more electron deficient; also the difference can be due to a higher acidity of PFC compared to TFC.

The kinetic isotope effect for benzyl alcohol (k_H/k_D = 6.4 at 30 °C)* suggests the rate-determining step to involve the cleavage of the C—H bond at the C atom linked to the OH group. The observed dependence of the reaction rate on acidity suggests that the reaction occurs between the alcohol molecules and a protonated chromium(VI) species. This view is in accord with the well established involvement of these species in oxidation with chromium trioxide.[7] However, this implies that hydrogen transfer is the essence of the mechanism of such reactions in the presence of an acid. The results point to a hydride ion transfer in the rate-determining step. The hydride transfer can take place either directly or through the preliminary formation of a chromate ester (Scheme 1). This is in accordance with the results obtained for the oxidation of benzyl alcohol with PFC.[6] The present data do not enable one to distinguish between the two mechanisms (see Scheme 1).

Scheme 1

$$\mathrm{CrO_3FNMe_4 + H^+ \longrightarrow HOCr^+O_2FNMe_4}$$

$$\mathrm{R{-}CH_2OH \xrightarrow{HOCr^+O_2FNMe_4} R{-}C^+HOH + H^+ \longrightarrow}$$

$$\mathrm{\longrightarrow R{-}CHO + H^+}$$

$$\mathrm{R{-}CH_2OH \xrightarrow{HOCr^+O_2FNMe_4} R{-}CHO + 2\,H^+}$$

A near constancy of the free activation energy (see Table 5) shows that the same mechanism is operative for all the alcohols. The changes in the activation enthalpy are useful for interpretation of the structure of transition states.

The calculated K and k_2 values (see Tables 3 and 4) clearly show that the formation and dissociation parameters of the ROH • TFC complexes are very sensitive to steric hindrance related to the substrate volume. It follows from the data in Table 3 that benzyl alcohol has the lowest equilibrium constant of complex formation, likely, due to its lower rate of formation. This is possibly caused by the interaction of the amino group in the TFC molecule with the π-electrons of the aromatic ring.[13] The reaction rates of the alcohols studied in this work (especially at elevated temperatures) can be arranged in the following order: $Pr^iOH > Bu^nOH > PhCH_2OH$. The results suggest that the smallest substrate is transformed with the highest reaction rate.

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