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Oxidation of Aliphatic Alcohols by Pyridinium Fluorochromate: A Kinetic Study

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The oxidation of aliphatic primary alcohols by pyridinium fluorochromate (PFC), to the corresponding aldehydes, is first order with respect to PFC but the order with respect to the alcohol is less than one. The initial formation of a complex between the alcohol and PFC is thus indicated. The oxidation of [1,1-$^2H_2$]ethanol indicated the presence of a substantial primary kinetic isotope effect. The formation constants of the alcohol–PFC complex and the rate of its disproportionation have been determined. The rate of decomposition of the complex is susceptible to both polar and steric effects of the substituent. The reaction involves a hydride-ion transfer in the rate-determining step.

Pyridinium fluorochromate (PFC) is a complex of chromium trioxide, pyridine, and hydrofluoric acid.[1] It has been reported that this complex converts alcohols into carbonyl products smoothly at room temperature and is a better oxidant than pyridinium chlorochromate (PCC).[2] Some preliminary observations about the oxidation of alcohols by PFC have been published,[3] which showed that kinetics of the oxidations by PCC[4] and PFC are different. In continutation of our work on PCC,[4] the kinetics of the oxidation of nine aliphatic alcohols by PFC are reported.

Results

The oxidation of ethanol of PFC in dimethyl sulphoxide (DMSO) results in the formation of acetaldehyde. The overall reaction corresponds to equation (1).

$$3RCH_2OH + 2Cr^{VI} \longrightarrow 3RCHO + 6H^+ + 2Cr^{III} \quad (1)$$

Rate Laws.—Under the pseduo-first-order conditions, the individual kinetic runs are first order with respect to PFC. Further, the rate constants are independent of the initial concentration of PFC (Table 1).

A Michaelis–Menten-type dependence was observed with respect to the alcohol concentration (Table 2). A plot of 1/[Alcohol] against $1/k_1$ is linear (r 0.9993) with a non-zero intercept on the rate ordinate. This indicated the following mechanism [equations (2) and (3)] and leads to the rate law (4).

$$RCH_2OH + PFC \overset{K}{\rightleftharpoons} [Complex] \quad (2)$$

$$[Complex] \xrightarrow[\text{slow}]{k_2} Products \quad (3)$$

$$\frac{-d[PFC]}{dt} = \frac{k_2[PFC][Alcohol]}{1 + K[Alcohol]} \quad (4)$$

The dependence of the reaction rate on the concentration of alcohol was determined at different temperatures. The values of the equilibrium constant (K) and the rate of decomposition of the complex (k_2) were computed from the slope and intercept of the double reciprocal plots. The activation parameters of the decomposition of the complex were calculated (Tables 3 and 4).

Kinetic Isotope Effect.—The oxidation of [1,1-$^2H_2$]ethanol was studied to ascertain the importance of cleavage of the α-C–H bond in the rate-determining step. The results showed the presence of a substantial primary kinetic isotope effect (*cf.* Table 4).

Induced Polymerization of Acrylonitrile.—The oxidation of ethanol, under nitrogen, failed to induce polymerization of acrylonitrile. One-electron oxidation is thus unlikely. In control experiments, with the alcohol absent, the concentration of PFC does not show any appreciable change.

Discussion

A linear correlation (r 0.9989) between the log k_2 at 298—313 K for the nine alcohols indicates that all the alcohols are oxidized by the same mechanism.[5]

The substantial kinetic isotope effect (k_H/k_D = 6.56) indicates that the rate-determining step involves C–H bond cleavage from the carbon atom bearing the hydroxy group.

The Michaelis–Menten kinetics of the oxidation of the alcohols by PFC differs from those reported for PCC.[4] This difference is not easily explained. Fluorine is more electronegative than chlorine and may cause the central metal atom to be more electron-deficient. This might explain the formation of a kinetically detectable complex in the oxidation mechanism by PFC.

Table 1. Dependence of the reaction rate on the oxidant concentration; [EtOH] 0.10M; T 303 K

10^3[PFC]/M	1.0	2.0	4.0	6.0	8.0	10.0
$10^4k_1/s^{-1}$	4.48	4.59	4.50	4.67	4.59	4.63

Table 2. Dependence of the reaction rate on the concentration of the alcohol; [PFC] 0.002M, T 303 K

[EtOH]/M	0.04	0.06	0.08	0.10	0.12
$10^4k_1/s^{-1}$	2.10	3.00	3.80	4.59	5.33
[EtOH]/M	0.15	0.20	0.50	1.00	
$10^4k_1/s^{-1}$	6.23	7.71	12.7	16.5	

Table 3. Formation constants of the complex between PFC and the primary alcohols.

	K			
Compound	298 K	303 K	308 K	313 K
Methanol	2.32	2.14	1.90	1.73
Ethanol	2.13	2.00	1.92	1.87
Propan-1-ol	2.22	2.07	1.81	1.65
Butan-1-ol	1.97	1.82	1.63	1.43
Pentan-1-ol	2.07	1.90	1.75	1.55
2-Methylpropan-1-ol	2.42	2.25	1.98	1.77
2-Methoxyethanol	3.00	2.64	2.33	1.93
2-Chloroethanol	2.52	2.18	1.97	1.60
2,2-Dimethylpropan-1-ol	2.30	2.16	1.90	1.78
[1,1-$^2H_2$]Ethanol	2.45	2.20	2.01	1.87

Table 4. Rate of decomposition of PFC–alcohol complex and the activation parameters[a]

Compound	$10^5k_2/s^{-1}$ 298 K	303 K	308 K	313 K	$\Delta H^*/$ kJ mol^{-1}	$\Delta S^*/$ J K^{-1} mol^{-1}	$\Delta G^*/$ kJ mol^{-1}
Methanol	3.64	5.37	8.00	11.0	54.9	−145	98.1
Ethanol	164	227	318	475	51.9	−124	88.7
Propan-1-ol	304	417	590	731	43.5	−147	87.2
Butan-1-ol	504	708	988	1 480	52.5	−113	85.6
Pentan-1-ol	480	692	980	1 230	46.5	−133	86.0
2-Methylpropan-1-ol	657	851	1 100	1 630	43.5	−141	85.4
2-Chloroethanol	5.21	7.95	11.8	17.5	59.7	−126	97.2
2-Methoxyethanol	48.8	63.0	81.5	120	45.1	−167	91.8
2,2-Dimethylpropan-1-ol	5 120	6 760	9 000	12 500	43.5	−125	80.2
[1,1-$^2H_2$]Ethanol	25.0	37.0	55.4	81.0	56.5	−123	93.2

[a] Error limits $\Delta H^* \pm 1.8$ kJ mol^{-1}; $\Delta S^* \pm 2$ J K^{-1} mol^{-1}; ΔG^* (at 298 K) $\pm$ 2.8 kJ mol^{-1}.

Table 5. Temperature dependence of the reaction constants

T/K	ρ^*	δ	R	s.d.
298	−1.55	−0.69	0.9981	0.07
303	−1.50	−0.69	0.9987	0.06
308	−1.51	−0.67	0.9963	0.08
313	−1.50	−0.67	0.9992	0.06

Structure–Reactivity Correlation.—It is apparent that the formation constants of the complex are insensitive to the variation in the structure of the alcohols. Similar observations have been recorded earlier in the oxidation of mandelic acids[6] and alcohols[7] by ceric ammonium nitrate.

The rate of decomposition of the complex, however, shows large variation.

The rate was analysed in terms of Taft's polar and steric parameters separately.[8] The results are presented in equations (5) and (6).

$$\log k/k_0 = -2.06\,\sigma^* \qquad (5)$$
$$n = 9, r = 0.9017, \text{s.d.} = 0.47$$

$$\log k/k_0 = -1.43\,E_s \qquad (6)$$
$$n = 9, r = 0.7963, \text{s.d.} = 0.66$$

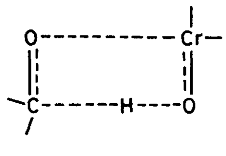
(k_0 is the rate of oxidation of the methyl compound, *i.e.* ethanol, E_s is Taft's steric substitute constant, r is the correlation coefficient, s.d. is the standard deviation, and n is the number of data points).

Since the single-substituent-parameter equations failed to give satisfactory correlations, the rates were analysed in terms of the Pavelich–Taft dual-substituent-parameter equation.[9] The substituent constants were obtained from the compilation by Wiberg.[10] The results presented in Table 5 indicated that the the reaction is susceptible to both polar and steric factors. The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the decomposition of the complex. The negative steric reaction constant indicates a steric acceleration of the reaction. This may be explained on the basis of the high ground-state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde as well as in the transition state leading to it, the transition state energy of the crowded and uncrowded alcohols do not differ much and steric acceleration, therefore, results.

There is no significant collinearity (r 0.4622) between σ^* and E_s of the nine substituents.

Mechanism.—The negative polar reaction constant suggests a hydride transfer in the rate-determining step. A similar conclusion was reached in the oxidation of PCC.[4] The hydride ion transfer may take place either *via* an ester intermediate or by an acyclic process.[4] Kwart and Nickle[11] have shown that a dependence of k_H/k_D on temperature can be gainfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic process.

The data for protio- and deuterio-ethanols, fitted to the familiar expression $k_H/k_D = A_HA_D \exp(-\Delta H^*/RT)$,[12,13] showed a direct correspondence with the properties of a symmetrical transition state in which the activation energy difference for k_H/k_D is equal to zero-point energy difference for the respective C–H and C–D bonds (*ca.* 4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are nearly equal. Bordwell[14] has given very cogent evidence against the occurrence of concerted one-step bimolecular processes of hydrogen transfer and it is clear that in the present study also, hydrogen transfer does not occur by an acyclic bimolecular process. The only truly symmetrical processes involving linear transfer of hydrogen are intrinsically concerted sigmatropic reactions characterized by transfer with cyclic transition state.[15] Littler[16] has also shown that a cyclic hydride transfer, in the oxidation of alcohols by Cr^{VI}, involves six electrons and, being a Hückel-type system, is an allowed process. Thus the transition state (A) can be envisaged for the oxidation of alcohols by PFC.



(A)

Experimental

Materials.—The alcohols were commercial products and were purified in the usual manner. PFC was prepared by the reported method[1] and its purity was checked by estimating Cr(VI) iodometrically. [1,1-$^2H_2$]Ethanol was prepared by Kaplan's method.[17] DMSO (E.Merck) was distilled under reduced pressure before use.

Product Analysis.—In a typical experiment a mixture of ethanol (4.6 g, 0.1 mol) and PFC (3.98 g, 0.02 mol) in DMSO (100 ml) was allowed to stand in the dark for *ca.* 8 h to ensure completion of the reaction. It was then treated with an excess

(250 ml) of a saturated solution of 2,4-dinitrophenylhydrazine in 2M-HCl and kept for *ca.* 12 h. Most of the solvents were removed under reduced pressure. The residue was diluted by water (250 ml) and kept in a refrigerator for *ca.* 6 h. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The DNP was found to be identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. The yields of DNP were 11.8 g (88%) and 10.6 g (79%) before and after recrystallization, respectively.

Kinetic Measurements.—The reactions were maintained under pseudo-first-order conditions by keeping a large excess of the alcohol with respect to PFC. The reactions were carried out at constant temperature (± 0.1 K). The reactions were followed both iodometrically and spectrophotometrically at 356 nm. It was found that the rate constant obtained by the two procedures agreed within $\pm 2\%$. The rate constants was evaluated from the linear ($r > 0.990$) plots of log[PFC] against time. The solvent was DMSO. The reaction mixture remained homogeneous in this solvent.

Multiple linear regression by the least-squares method was carried out using an Apple IIe microcomputer. The computer program enabled us to evaluate, in addition to the regression coefficients, the coefficient of multiple correlation (R) and the standard deviations (s.d.).

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