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Kinetics and mechanism of the oxidation of some hydroxyacids by pyridinium fluorochromate

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Abstract. Oxidation of glycolic, lactic and mandelic acids by pyridinium fluorochromate (PFC) leads to the formation of the corresponding oxoacids. The reaction is first order with respect to PFC. Michaelis–Menten type kinetics were observed with respect to the hydroxy acid. The values of the formation constants of the hydroxy acid-PFC complexes and the rates of their decomposition, at different temperatures, have been evaluated. Thermodynamic parameters of the complex formation and activation parameters for the decomposition of the complexes have been calculated. The oxidation of mandelic acid has been studied in 19 different organic solvents. Analysis of the solvent effect indicates that the cation-solvating power of the solvents plays the major role in reaction rate. Oxidation of α-deuteriomandelic acid indicates the presence of a primary kinetic isotope effect. The analysis of the dependence of kinetic isotope effect on temperature indicates that the reaction involves a symmetrical cyclic transition state. A suitable mechanism has been proposed.

Keywords. Hydroxy acid; pyridinium fluorochromate; oxidation mechanism; kinetics; correlation analysis; solvent effect.

1. Introduction

Pyridinium fluorochromate (PFC), a complex of chromium trioxide, pyridine and hydrofluoric acid, converts hydroxy compounds to carbonyl products in $\approx 80\%$ yields (Bhattacharjee *et al* 1982). Kinetics of the oxidation of alcohols, sulphides and aldehydes have been reported from this laboratory (Banerji 1988; Agarwal *et al* 1990). Hydroxy acids can be oxidised either like alcohols (Banerji 1978) or may undergo oxidative decarboxylation (Levesley and Waters 1955). There seems to be no report on the oxidation of α-hydroxy acids by PFC. In this paper, we report the oxidation of glycolic acid (GA), lactic acid (LA) and mandelic acid (MA) in dimethylsulphoxide (DMSO) as a solvent.

2. Experimental

2.1 *Material*

All the hydroxy acids were commercial products of the highest purity available and were used as such. Their solutions were standardized by alkalimetry. PFC was

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prepared by the reported method (Bhattacharjee *et al* 1982) and its purity was checked by iodometric determination. α-Deuteriomandelic acid (PhCD(OH)COOH or DMA) was prepared by the method of Kemp and Waters (1963); its isotopic purity, ascertained by NMR spectra, was $93 \pm 4\%$. Solvents were purified by the usual methods (Perrin *et al* 1966).

2.2 *Product analysis*

In a typical experiment, mandelic acid (7·6 g, 0·05 mol) and PFC (2·0 g, 0·01 mol) were dissolved in 100 ml of DMSO and allowed to stand in the dark for ≈ 24 h to ensure completion of the reaction. Most of the solvent was then removed by distillation under reduced pressure. The residue was treated with a saturated solution (250 ml) of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept in a refrigerator for ≈ 8 h. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The product was identical (m.p. and mixed m.p.) to an authentic sample of DNP of phenylglyoxylic acid. The yields of DNP, before and after recrystallization, were 2·25 g (92%) and 1·96 (80%) respectively. Similar experiments with the other hydroxy acids yielded the DNP of the corresponding oxoacids in 76–87% yields after recrystallization. The oxidation state of chromium in the spent reaction mixture, determined by iodometric titrations, was $3{\cdot}87 \pm 0{\cdot}21$.

2.3 *Kinetic measurements*

The reactions were carried out under pseudo-first order conditions by keeping a large excess of the hydroxy acid over PFC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperature ($\pm 0{\cdot}1$ K), by monitoring the decrease in [PFC] spectrophotometrically at 356 nm. The pseudo-first order rate constant, k_{obs}, was evaluated from the linear ($r = 0{\cdot}990 - 0{\cdot}999$) plots of log [PFC] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. Simple and multivariate linear regression analyses were carried out by the least-squares method on a personal computer.

3. Results

The oxidation of the hydroxy acids by PFC led to the formation of the corresponding oxoacids

$$\begin{aligned} &RCH(OH)COOH + CrO_2FOPyH \\ &\rightarrow RCOCOOH + H_2O + CrOFOPyH. \end{aligned} \quad (1)$$

PFC undergoes a two-electron change. This agrees with the earlier observations with both PFC (Bhattacharjee *et al* 1987) and pyridinium chlorochromate (Brown *et al* 1979).

3.1 *Rate laws*

The reaction is first order with respect to PFC and k_{obs} did not depend on the initial concentration of PFC. The reaction exhibited Michaelis–Menten type kinetics with

Table 1. Rate constants of oxidation of α-hydroxy acids by PFC at 298 K.

[Hydroxy acid] (mol dm^{-3})	10^3[PFC] (mol dm^{-3})	$10^5 k_{obs}$		
		GA	LA	MA
0·016	1·0	2·00	9·70	20·0
0·033	1·0	3·25	15·8	32·3
0·048	1·0	4·06	19·2	40·1
0·064	1·0	4·61	22·1	45·7
0·080	1·0	5·10	23·6	50·4
0·133	1·0	6·00	28·1	58·6
0·133*	1·0	6·15	27·7	58·6
0·166	1·0	6·22	30·0	62·5
0·247	1·0	6·84	31·5	67·0
0·329	1·0	7·15	33·0	70·0
0·133	2·0	6·10	28·1	58·8
0·133	4·0	5·87	28·9	57·2
0·133	8·0	6·03	28·4	59·3
0·133	10·0	6·21	27·5	58·3

*Contained 10^{-3} mol dm^{-3} acrylonitrile

respect to the substrate (table 1). A plot of 1/[hydroxy acid] against $1/k_{obs}$ is linear with an intercept on the rate ordinate. This indicates the following overall mechanism and leads to the rate law (4),

$$\text{hydroxy acid} + \text{PFC} \overset{K}{\rightleftarrows} [\text{complex}], \tag{2}$$

$$[\text{complex}] \overset{k_2}{\rightarrow} \text{products}, \tag{3}$$

$$-\text{d[PFC]}/\text{d}t = k_2 K[\text{PFC}][\text{hydroxy acid}]/(1 + K[\text{hydroxy acid}]). \tag{4}$$

The dependence of the reaction rate on substrate concentration was determined at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic and activation parameters were calculated from the values of K and k_2 respectively at different temperatures (tables 2 and 3). Addition of a radical scavenger, acrylonitrile, has no effect on the reaction. Thus a one-electron oxidation, giving rise to free radicals, is highly unlikely.

3.2 *Kinetic isotope effect*

To ascertain the important of the cleavage of the C–H bond in the rate-determining step, the oxidation of α-deuteriomandelic acid (DMA) was studied. The results recorded in tables 2 and 3 showed that formation constants of the complex of ordinary and deuteriated mandelic acids have similar values but the rate of decomposition of the complex showed considerable primary kinetic isotope effect ($k_H/k_D = 6{\cdot}31$ at 298 K). The rate of oxidation of the deuteriated acid was corrected for the ordinary acid present.

Table 2. Formation constants and thermodynamic parameters of hydroxy acid-PFC complexes.

Acid	K (dm^3 mol^{-1}) 288 K	298 K	308 K	318 K	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
GA	25·5 ± 1·2	20·0 ± 1·0	15·7 ± 1·1	10·2 ± 0·8	− 25 ± 2	− 52 ± 6	− 9·8 ± 1·5
LA	27·2 ± 1·5	21·5 ± 1·3	17·0 ± 1·0	11·3 ± 1·0	− 24 ± 2	− 48 ± 6	− 10·0 ± 1·4
MA	26·0 ± 1·7	20·7 ± 0·5	16·3 ± 0·9	10·5 ± 0·8	− 25 ± 2	− 51 ± 7	− 9·9 ± 1·7
DMA	27·5 ± 1·6	21·0 ± 1·2	16·5 ± 1·0	10·7 ± 1·0	− 26 ± 2	− 54 ± 6	− 10·0 ± 1·4

Table 3. Rates of decomposition of hydroxy acid-PFC complexes and activation parameters.

Acid	$10^5 k_2$(s^{-1}) 288 K	298 K	308 K	318 K	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}	ΔG^* kJ mol^{-1}
GA	4·37 ± 0·25	8·22 ± 0·20	16·4 ± 1·0	33·3 ± 1·5	49·1 ± 1·3	− 159 ± 4	96·2 ± 1·1
LA	20·5 ± 0·8	37·9 ± 1·1	79·5 ± 1·8	116 ± 11	42·8 ± 2·2	− 167 ± 7	92·5 ± 1·7
MA	41·0 ± 2·0	80·2 ± 3·5	161 ± 8	337 ± 14	50·8 ± 1·3	− 134 ± 4	90·6 ± 1·0
DMA	5·60 ± 0·4	12·7 ± 1·0	26·0 ± 1·1	55·4 ± 2·1	55·3 ± 0·6	− 135 ± 2	95·3 ± 0·5

3.3 *Solvent effect*

The rate of oxidation of mandelic acid was determined in 19 different organic solvents. The choice of solvents was limited by the solubility of PFC and its reaction with primary and secondary alcohols. There was no noticeable reaction with the solvents chosen. The kinetics were similar in all the solvents. The values of K and k_2 are recorded in table 4.

4. Discussion

The presence of a substantial primary kinetic isotope effect confirms the cleavage of the α-C–H bond in the rate-determining step.

It is observed that the formation constant, K, of the MA-PFC complex does not depend much on the nature of the solvent but the rates of decomposition, k_2, show considerable variation.

The rate constants for decomposition of the complex, k_2, in 17 solvents (CS_2 and acetic acid were not considered as the complete range of the solvent parameters were not available) were correlated in terms of the linear solvation energy relationship (LSER) of Kamlet *et al* (1983).

$$\log k_2 = A_0 + p\pi^* + a\alpha + b\beta. \tag{5}$$

π^* represents the solvent polarity for the solvent–solute interaction of non-specific type, β is a scale of solvent hydrogen-bond acceptor basicity while α represents the solvent hydrogen-bond donor acidity of the solvent. A_0 is the intercept term. It may be mentioned here that out of the 17 solvents, α for 12 solvents has the value zero.

Table 4. Effect of solvents on the oxidation of mandelic acid by PFC at 298 K.

Solvent	K (dm^3 mol^{-1})	$10^6 k_2$(s^{-1})
Chloroform	17·6 ± 1·0	217 ± 8
Carbon disulphide	18·3 ± 0·9	36·0 ± 1·2
1,2-Dichloroethane	21·0 ± 1·3	263 ± 7
Dichloromethane	15·6 ± 0·8	249 ± 9
Dimethyl sulphoxide	20·7 ± 0·5	802 ± 35
Acetone	20·0 ± 0·5	252 ± 10
Dimethyl formamide	23·0 ± 1·3	403 ± 21
Butanone	21·3 ± 1·1	184 ± 12
Nitrobenzene	19·3 ± 0·9	303 ± 22
Benzene	25·1 ± 1·5	86·2 ± 2·7
Cyclohexane	18·7 ± 0·9	9·45 ± 0·6
Toluene	23·9 ± 1·4	70·5 ± 3·1
Acetophenone	25·7 ± 1·6	308 ± 25
Tetrahydrofuran	15·6 ± 0·6	125 ± 7
t-Butyl alcohol	18·3 ± 0·7	92·0 ± 4
Dioxane	24·3 ± 1·7	134 ± 8
1,2-Dimethoxyethane	22·5 ± 1·2	63·8 ± 3·5
Acetic acid	23·6 ± 1·4	38·3 ± 2·1
Ethyl acetate	18·3 ± 1·3	100 ± 6

The analyses in terms of the triparametric LSER, (5), a biparametric equation involving π^* and β, and separately with π^* and β gave the following results.

$$\log k_2 = -4{\cdot}99 + 1{\cdot}70\,\pi^* + 0{\cdot}44\,\alpha + 0{\cdot}07\,\beta, \tag{6}$$

$$R^2 = 0{\cdot}9241; sd = 0{\cdot}13; n = 17; \psi = 0{\cdot}30;$$

$$\log k = -4{\cdot}92 + 1{\cdot}58\,\pi^* + 0{\cdot}18\,\beta, \tag{7}$$

$$R^2 = 0{\cdot}8939; sd = 0{\cdot}15; n = 17; \psi = 0{\cdot}35;$$

$$\log k_2 = -4{\cdot}89 + 1{\cdot}63\,\pi^*, \tag{8}$$

$$r^2 = 0{\cdot}8792; sd = 0{\cdot}15; n = 17; \psi = 0{\cdot}36$$

$$\log k_2 = -4{\cdot}00 + 0{\cdot}47\,\beta, \tag{9}$$

$$r^2 = 0{\cdot}1091; sd = 0{\cdot}42; n = 17; \psi = 0{\cdot}97.$$

Here n is the number of data points and ψ is Exner's statistical parameter (Exner 1966).

The results show that $\approx 92\%$ of the data on solvent effect is explained by Kamlet *et al*'s (1983) triparametric equation (*cf.* (6)). By Exner's criterion (Exner 1966) however, the correlation is poor. The major contribution is by the solvent polarity term π^* (*cf.* (8)), both α and β play relatively insignificant roles.

The data on the solvent effect were also analysed in terms of Swain's equation (Swain *et al* 1983) of cation-solvating and anion-solvating concepts,

$$\log k_2 = aA + bB + C. \tag{10}$$

A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. $(A + B)$ is postulated to represent the solvent polarity.

The results of correlation analysis in terms of (10), individually with A and B, and with $(A + B)$ are given below.

$$\log k_2 = 0{\cdot}54\,A + 1{\cdot}7\,B - 3{\cdot}14, \tag{11}$$

$$R^2 = 0{\cdot}9990; sd = 0{\cdot}02; n = 19; \psi = 0{\cdot}03,$$

$$\log k_2 = 1{\cdot}32(A + B) - 3{\cdot}10, \tag{12}$$

$$r^2 = 0{\cdot}8197; sd = 0{\cdot}19; n = 19; \psi = 0{\cdot}44;$$

$$\log k_2 = 0{\cdot}29\,A - 1{\cdot}97, \tag{13}$$

$$r^2 = 0{\cdot}0157; sd = 0{\cdot}46; n = 19; \psi = 1{\cdot}02;$$

$$\log k^2 = 1{\cdot}67\,B - 2{\cdot}96, \tag{14}$$

$$r^2 = 0{\cdot}9470; sd = 0{\cdot}11; n = 19; \psi = 0{\cdot}24.$$

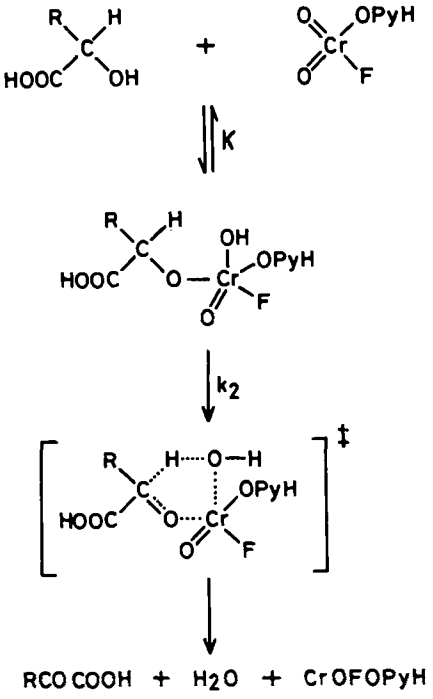
The rates of decomposition of the complex show an excellent correlation in Swain's equation (*cf.* (11)) with both cation- and anion-solvating powers contributing towards the observed effect of the solvents though the contribution of the cation-solvation is relatively greater. The solvent polarity, represented by $(A + B)$ also accounts for $\approx 82\%$ of the data, (12). A comparison (11) and (14) indicates that the cation-solvating power of the solvents plays the major role. B alone accounts for $\approx 95\%$ of the data. The value of Exner's ψ points to an excellent correlation in (11) and a satisfactory correlation in (12).

The non-specfic solvent polarity, π^*, as defined by Kamlet *et al* (1983) is able to account for 88% of the data (*cf.* (8)) whereas the solvent polarity, $(A + B)$, of Swain's treatment accounts for $\approx 82\%$ of the data (*cf.* (12)). Thus it seems that π^* and $(A + B)$ represent more or less the same solvent property, and there is some collinearity between $(A + B)$ and π^* for the 17 solvents ($r^2 = 0{\cdot}8050$).

4.1 *Mechanism*

The greater importance of the cation-solvating power of the solvents indicates a hydride ion transfer from the hydroxy acid to PFC. This agrees with the observation that the introduction of electron-releasing methyl groups enhances the rate substantially. The higher rate of oxidation of mandelic acid can be attributed to the capacity of the phenyl group to stabilize the carbocation intermediate by resonance.

The hydride transfer may take place either via a chromate ester or by an acyclic process. Kwart and Nickle (1973) have shown that a dependence of k_H/k_D on temperature can be successfully used to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic one. The data for protio and deuterio mandelic acids, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(-H^*/RT)$ show a direct correspondence with the properties of a symmetrical transition state in which activation energy differences for protio and deuterio compounds are equal to the differences in the zero-point energy for the respective C–H and C–D bonds ($\approx 4{\cdot}5\,\text{kJ mol}^{-1}$) and the entropies of activation of the respective reactions are almost equal (Kwart and Latimer 1971; Kwart and Nickle 1973). Bordwell (1972) has given very cogent evidence against the occurrence of concerted one-step bimolecular processes of hydrogen transfer, and it is evident that in the



Scheme 1.

present reaction also, the 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 by cyclic transition states (Woodward and Hoffmann 1969). Littler (1971) has also shown that a cyclic hydride transfer, in the oxidation of hydroxy compounds by Cr(VI), involves six electrons and being a Huckel-type system, is an allowed process. Hence, the mechanism shown in scheme 1 may be proposed for this reaction.

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