

Correlation analysis of reactivity in the oxidation of substituted mandelic acids by pyridinium fluorochromate

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Kinetics of oxidation of nine substituted mandelic acids by pyridinium fluorochromate (PFC) have been studied. The main product is the corresponding arylglyoxylic acid. The reaction is first order in [PFC] and Michaelis-Menten type kinetics has been observed with respect to the reductant. The formation constants of the complexes and the rates of their decomposition have been calculated. The formation constants are not sensitive to substitution in the benzene ring. The rates of decomposition of the complexes showed an excellent correlation with Brown's σ^+ values with negative reaction constants. The effect of solvent has been analysed using multiparametric equations and mechanistic aspects are discussed.

Hydroxy acids may either be oxidised as alcohols, yielding corresponding oxoacids¹ or undergo oxidative decarboxylation to yield a ketone². Pyridinium fluorochromate (PFC) is a highly versatile oxidant³. Several reports concerning the kinetics and mechanism of oxidation of organic compounds including that of mandelic acid have emanated from our laboratory⁴⁻⁸. Herein we report the effect of substituents and solvents on the oxidation of mandelic acid by PFC.

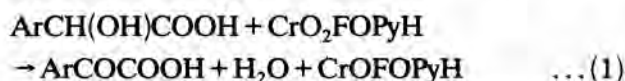
Experimental

The preparation and specification of the substituted mandelic acids have been described earlier⁹. PFC was prepared by the reported method³ and its purity checked by iodometric determination. Solvents were purified by the usual methods¹⁰.

Kinetic measurements were carried out in DMSO as a solvent spectrophotometrically at 356 nm as described earlier⁸. Reactions too fast to be studied by the conventional method were studied by a stopped-flow technique using a Hi-Tech SFL-44 stopped-flow spectrophotometer coupled to an MCS-1 data processing system. All other experimental procedures have been described earlier⁸.

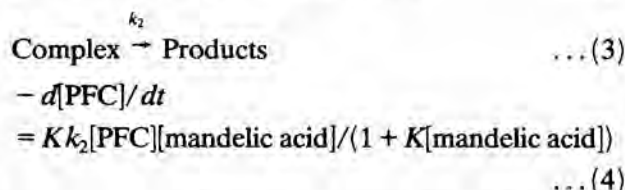
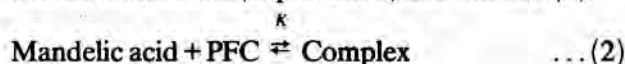
Results and discussion

The main product of oxidation is the corresponding arylglyoxylic acid. The overall reaction can be represented as Eq. (1).



PFC undergoes a 2-electron change. This accords with the earlier observations^{11,12}.

The reaction is first order in [PFC] and Michaelis-Menten type kinetics are observed with respect to the reductant (Table 1). This points to the following overall mechanism (Eqs 2 and 3) and rate law (4).



The dependence on [reductant] was studied at different temperatures and values of K and k_2 were calculated from the linear plots of $1/k_{\text{obs}}$ versus $1/[\text{mandelic acid}]$. The thermodynamic parameters of the complex formation and the activation parameters of its decomposition were evaluated from

Table 1—Rate constants for the oxidation of *p*-methylmandelic acid by PFC at 288 K

[Hydroxy acid] (mol dm ⁻³)	10 ³ [PFC] (mol dm ⁻³)	10 ⁴ k_{obs} (s ⁻¹)
0.010	1.0	4.17
0.015	1.0	5.63
0.020	1.0	7.90
0.030	1.0	8.83
0.040	1.0	10.0
0.060	1.0	12.1
0.080	1.0	13.5
0.110	1.0	15.0
0.170	1.0	16.0
0.080	2.0	13.2
0.080	4.0	13.7
0.080	8.0	13.5
0.080	10.0	13.4
0.080†	2.0	13.6

† contained 10⁻³ mol dm⁻³ acrylonitrile

the values of K and k_2 at different temperatures respectively (Tables 2 and 3).

The oxidation of *p*-methylmandelic acid was studied 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 solvent chosen. The kinetics were similar in all the solvents. The values of K and k_2 were determined (Table 4).

The entropy and enthalpy of activation of the oxidation of the ten compounds are linearly related ($r=0.9818$) and the value of isokinetic temperature, evaluated from the slope of this plot, is 416 ± 28 K. The validity of the isokinetic relationship was checked and found genuine by using Exner's criterion¹³. A linear isokinetic relationship is a necessary

condition for the validity of linear free energy relationships¹⁴.

A perusal of values in Tables 2 and 3 showed that the formation constants of the substituted mandelic acids-PFC complexes are not much sensitive to substitution in the aromatic ring. Similar observations have earlier been made in the oxidation of substituted benzyl alcohols by PFC⁵ and by ceric ammonium nitrate¹⁵, and in the oxidation of mandelic acids by ceric ammonium nitrate¹⁶. But the rates of decomposition of the complexes showed considerable variation with the substitution.

The rate of decomposition is increased by the introduction of electron-releasing groups; electron-withdrawing groups have an opposite effect. The rates did not yield a significant correlation with

Table 2—Formation constants and thermodynamic parameters of the substituted mandelic acid-PFC complexes

Subst.	K (dm ³ mol ⁻¹)				ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔG^0 (kJ mol ⁻¹)
	288	298	308	318 K			
H ^a	26.0	20.7	17.3	10.5	-25.0	-51	-9.9
<i>p</i> -F	30.3	25.0	19.5	14.1	-21.8	-39	-10.4
<i>p</i> -Cl	28.5	23.0	17.7	12.3	-23.6	-46	-10.2
<i>p</i> -Br	24.5	18.0	14.3	9.0	-27.0	-59	-9.6
<i>p</i> -Me	26.7	21.0	15.8	10.3	-26.3	-55	-9.9
<i>p</i> -Pr ⁱ	28.0	23.0	16.3	11.0	-26.3	-55	-9.9
<i>p</i> -OMe	30.7	26.0	19.7	14.2	-22.0	-40	-10.4
<i>m</i> -Cl	27.5	21.3	16.5	10.7	-25.9	-54	-10.0
<i>m</i> -NO ₂	24.7	17.5	13.8	9.0	-27.3	-60	-9.6
<i>p</i> -NO ₂	25.6	20.1	15.8	10.2	-25.2	-52	-9.9

Average errors: K , ± 1.3 dm³mol⁻¹; ΔH^0 , ± 1.8 kJ mol⁻¹; ΔS^0 , ± 6 J mol⁻¹K⁻¹; ΔG^0 , ± 1.4 kJ mol⁻¹

^aData from ref. 8

Table 3—Rates of decomposition of the complexes and the activation parameters

Subst.	$10^6 k_2$ (s ⁻¹)				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ K ⁻¹)	ΔG^* (kJ mol ⁻¹)
	288	298	308	318 K			
H ^a	41.0	80.2	161	337	50.8	-134	90.6
<i>p</i> -F	60.4	110	208	462	48.7	-138	89.7
<i>p</i> -Cl	22.8	46.0	108	225	56.2	-120	91.9
<i>p</i> -Br	20.1	40.4	88.1	185	50.1	-129	92.2
<i>p</i> -Me	198	318	636	1140	42.7	-149	87.0
<i>p</i> -Pr ⁱ	165	282	473	960	41.5	-155	87.5
<i>p</i> -OMe	2150	3020	3960	6360	24.2	-193	81.6
<i>m</i> -Cl	6.24	14.0	35.7	90.6	65.6	-98	94.8
<i>m</i> -NO ₂	1.21	3.07	10.0	28.3	78.3	-68	98.5
<i>p</i> -NO ₂	0.79	2.10	6.64	19.0	78.7	-70	99.5

Average errors: ΔH^* 1.7 kJ mol⁻¹; ΔS^* 7 J mol⁻¹K⁻¹; ΔG^* 1.4 kJ mol⁻¹

^aData from ref. 8

Table 4—Effect of solvents on the oxidation of *p*-methylmandelic acid by PFC at 298 K

Solvent	<i>K</i> (dm ³ mol ⁻¹)	10 ⁶ <i>k</i> ₂ (s ⁻¹)
Chloroform	24.1	93.7
Carbon disulphide	22.5	15.8
1,2-Dichloroethane	18.5	113
Dichloromethane	20.7	108
Dimethylsulphoxide	21.0	318
Acetone	24.3	110
Dimethylformamide	23.9	170
Butanone	22.5	78.3
Nitrobenzene	21.4	134
Benzene	25.3	37.7
Cyclohexane	19.7	4.25
Toluene	18.8	31.0
Acetophenone	23.0	140
Tetrahydrofuran	22.7	52.0
<i>t</i> -Butyl alcohol	19.6	38.7
Dioxane	20.7	54.5
1,2-Dimethoxyethane	23.5	28.0
Acetic acid	24.6	17.3
Ethyl acetate	22.2	42.0

Hammett's σ substituent constants ($r=0.9419$). However, an excellent correlation ($r>0.9980$) is obtained when the rates are correlated with Brown's σ^+ values¹⁷; the reaction constants being negative ($-2.18, -2.00, -1.76$ and -1.59 at 288, 298, 308 and 318 K respectively).

The formation constant, *K*, of *p*-methylmandelic acid-PFC complex is not much sensitive to the nature of medium but the rate of decomposition showed considerable variation.

The rate constants for the decomposition, *k*₂, in 17 solvents (CS₂ and acetic acid were not considered as the complete range of the solvent parameters were not available) were correlated in terms of linear solvation energy relationship of Kamlet *et al.*¹⁸.

$$\log k_2 = A_0 + p\pi^* + a\alpha + b\beta \quad \dots(5)$$

In Eq. (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 a value of zero. The analyses in terms of the triparametric LSER (Eq. 5), a biparametric equation involving π^* and β , and separately

with π^* and β gave the following results (Eqs 6-9).

$$\log k_2 = (1.70 \pm 0.13)\pi^* + (0.05 \pm 0.11)\beta + (0.45 \pm 0.18)\alpha - 0.65 \quad \dots(6)$$

$$R^2 = 0.9344; \text{sd} = 0.12; n = 17; \psi = 0.26$$

$$\log k_2 = (1.58 \pm 0.25)\pi^* + (0.16 \pm 0.12)\beta - 0.72 \quad \dots(7)$$

$$R^2 = 0.9025; \text{sd} = 0.14; n = 17; \psi = 0.31$$

$$\log k_2 = (1.62 \pm 0.15)\pi^* - 0.75 \quad \dots(8)$$

$$r^2 = 0.8904; \text{sd} = 0.15; n = 17; \psi = 0.36$$

$$\log k_2 = (0.45 \pm 0.34)\beta - 1.64 \quad \dots(9)$$

$$r^2 = 0.1030; \text{sd} = 0.41; n = 17; \psi = 0.84$$

Here *n* is the number of data points and ψ is Exner's statistical parameter¹⁹. The results show that about 93% of the data on the solvent effect are explained by Kamlet and Taft's triparametric equation (*cf.* Eq. 6). By Exner's criterion¹⁹ however, the correlation is poor. The major contribution is by the solvent polarity term, π^* (*cf.* Eq. 8), both α and β play relatively insignificant roles.

The data on the solvent effect were also analysed in terms of Swain's equation²⁰ of cation-solvating and anion-solvating concept (Eq. 10).

$$\log k_2 = aA + bB + C \quad \dots(10)$$

In this equation, *A* represents the anion-solvating power of the solvent and *B* the cation-solvating power, *C* is the intercept term and (*A* + *B*) is postulated to represent the solvent polarity. The results of correlation analysis in terms of Eq. (10), individually with *A* and *B*, and with (*A* + *B*) are given in Eqs (11)-(14).

$$\log k_2 = (0.55 \pm 0.02)A + (1.68 \pm 0.01)B - 0.51 \quad \dots(11)$$

$$R^2 = 0.9993; \text{sd} = 0.01; n = 19; \psi = 0.02$$

$$\log k_2 = 1.31 \pm 0.15 (A+B) - 0.54 \quad \dots(12)$$

$$r^2 = 0.8260; \text{sd} = 0.19; n = 19; \psi = 0.24$$

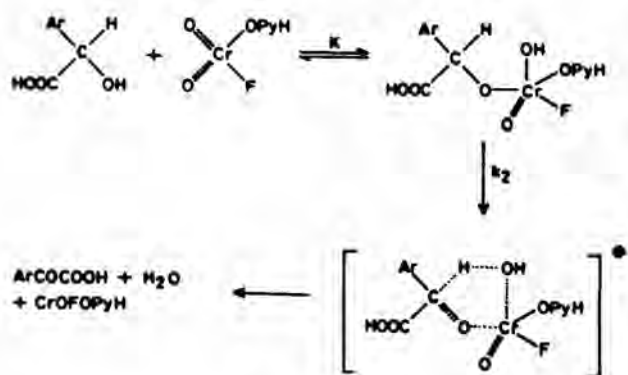
$$\log k_2 = (0.31 \pm 0.55)A - 1.67 \quad \dots(13)$$

$$r^2 = 0.0178; \text{sd} = 0.46; n = 19; \psi = 1.02$$

$$\log k_2 = (1.64 \pm 0.10)B - 0.69 \quad \dots(14)$$

$$r^2 = 0.9437; \text{sd} = 0.11; n = 19; \psi = 0.14$$

The rates of decomposition of the complex show an excellent correlation in Swain's equation (*cf.* Eq. 11) with both cation- and anion-solvating powers contributing towards the observed effect of the solvents, though the contribution of the cation-solvating power is more. In fact the cation-solvating power



Scheme 1

alone accounts for about 94% of the data (Eq. 14). The value of Exner's statistical parameter points to an excellent correlation in Eq. (11) and a satisfactory correlation in Eq. (14).

Mechanisms

Absence of any effect of acrylonitrile on the reaction discounts the possibility of a one-electron oxidation, leading to the formation of free radicals. The presence of a substantial kinetic isotope effect in the oxidation of mandelic acid⁸ confirms the cleavage of the α -C-H bond in the rate-determining step. The large negative reaction constants together with the excellent correlation with Brown's σ^+ values point to a highly electron-deficient carbon centre in the transition state. The transition state thus approaches a carbocation in character. This is supported by the solvent effect also. Greater role played by the cation-solvating power of the solvents supports the postulation of a carbocationic transition state.

Therefore, the correlation analysis of substituent and solvent effects on the oxidation of mandelic acid supports a mechanism involving a hydride-ion transfer via a chromate ester (Scheme 1).

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