Kinetics and Mechanism of the Oxidation of Aromatic Aldehydes by Pyridinium Fluorochromate

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Kinetics of oxidation of a number of ortho-, meta-, and para-substituted benzaldehydes by pyridinium fluorochromate (PFC), in dimethyl sulfoxide, were studied. The main product of oxidation is the corresponding benzoic acid. The reaction is first order with respect to PFC. Michaelis–Menten-type kinetics were observed with respect to the aldehyde. The formation constants of the intermediate PFC–aldehyde complexes and the rates of their decomposition were determined at different temperatures. The thermodynamic and activation parameters were also determined. The oxidation of [^{2}H]benzaldehyde (PhCDO) exhibited a substantial primary kinetic isotope effect. The rates of oxidation of para- and meta-substituted benzaldehydes were correlated with Taft's and Swain's dual substituent-parameter equations. For the para-substituted compounds, the best correlation is obtained with Taft's σ_I and σ_{R^+}; the meta-substituted benzaldehydes correlated best with σ_I and σ_{R^0}. The rates of oxidation of the ortho compounds correlated best with a triparametric equation involving Taft's σ_I and σ_{R^+} and Charton's steric parameter, *V*. An analysis of the rate of oxidation of benzaldehyde in 19 organic solvents indicated the greater importance of cation-solvating power of the solvents. A mechanism involving transfer of a hydride ion from the aldehyde to PFC has been proposed.

Pyridinium fluorochromate (PFC) is a versatile oxidant.[1] Kinetics of oxidation of aliphatic aldehydes by PFC have been reported previously from this laboratory.[2] However, aromatic and aliphatic aldehydes are reported to follow different mechanistic pathways in reactions with many oxidants, e.g., chromic acid,[3] permanganate ion,[4] and *N*-bromoacetamide.[5] In this paper, we report the kinetics of oxidation of a number of monosubstituted benzaldehydes by PFC in dimethyl sulfoxide (DMSO). The reactivity of substituted benzaldehydes has been subjected to correlation analysis, and the mechanistic aspects are discussed.

Results

Oxidation of the aromatic aldehydes by PFC results in the formation of the corresponding benzoic acid (reaction 1).

$$\mathrm{ArCHO + CrO_2FOPyH \rightarrow ArCOOH + CrOFOPyH} \quad (1)$$

The reaction is first order with respect to PFC. Further, the pseudo-first-order rate constants, k_{obs}, do not depend on the initial concentration of PFC. The rate increases with an increase in the concentration of aldehyde but the order is less than 1 (Table I). A plot of $1/k_{obs}$ against 1/[aldehyde] is linear with an intercept on the rate ordinate. This showed that Michaelis–Menten type kinetics are operative with respect to the aldehyde. This indicates the following overall mechanism (reactions 2 and 3) and rate law (4).

$$\text{aldehyde + PFC} \overset{K}{\rightleftharpoons} \text{[complex]} \quad (2)$$

$$\text{[complex]} \xrightarrow{k_2} \text{products} \quad (3)$$

$$-\mathrm{d[PFC]}/\mathrm{d}t = k_2K\mathrm{[PFC][aldehyde]}/(1 + K\mathrm{[aldehyde]}) \quad (4)$$

The variation in the concentration of aldehydes was studied at different temperatures, and the values of k_2 and K were evaluated from the double reciprocal plots. The thermodynamic parameters for reaction 2 and activation parameters for reaction 3 were also calculated (see the supplementary material). Addition of acrylonitrile had no effect on the reaction rate.

Kinetic Isotope Effect. The oxidation of [^{2}H]benzaldehyde (PhCDO) indicated the presence of a substantial primary kinetic isotope effect (k_H/k_D = 5.33 at 298 K).

Solvent Effect. The oxidation of benzaldehyde was studied in 19 different organic solvents. The choice of solvents was limited due to 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 II.

Discussion

The reaction is isoentropic, i.e., the entropies of activation of the oxidation of substituted benzaldehydes do not differ much.

The formation constants of the complexes of substituted benzaldehydes and PFC do not exhibit any appreciable variation. Similar observations have been recorded in the oxidation of benzyl alcohols by PFC[6] and by ceric ammonium nitrate.[7] The rate of decomposition of the complexes, however, showed a marked variation with the nature and position of the substituent.

Correlation Analysis of Reactivity. The rates of decomposition of the aldehyde–PFC complexes and the effect of solvents on them were subjected to correlation analysis. The analysis was carried out by the least-squares multivariate linear regression method.

(i) Para- and Meta-Substituted Benzaldehydes. Since the rate constants, k_2, of para- and meta-substituted benzaldehydes failed to show a satisfactory correlation with any single substituent-parameter equation, the rates were correlated with Taft's[8] and Swain's[9] dual substituent-pa-

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[1] Bhattacharjee, M. N.; Chaudhuri, M. K.; Dasgupta, H.; Roy, N.; Kathing, D. *Synthesis* 1982, 588.

[2] Agarwal, A.; Chowdhury, K.; Banerji, K. K. *J. Chem. Res., Synop.* 1990, 86.

[3] Freeman, F.; Lin, D. K.; Moore, G. R. *J. Org. Chem.* 1982, *47*, 56 and references cited therein.

[4] Sharma, V.; Banerji, K. K. *J. Chem. Res., Synop.* 1985, 340; *J. Chem. Res., Miniprint* 1985, 3551.

[5] Gupta, A.; Mathur, S.; Banerji, K. K. *J. Chem. Res., Synop.* 1988, 6; *J. Chem. Res., Miniprint* 1988, 0201.

[6] Banerji, K. K. *J. Org. Chem.* 1988, *53*, 2154.

[7] Young, L. B.; Trahanovsky, W. S. *J. Am. Chem. Soc.* 1969, *91*, 5060.

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Table I. Rate Constants of the Oxidation of Benzaldehyde by PFC at 298 K

[PhCHO], M	10^3 [PFC], M	$10^5 k_{obs}$, s^{-1}	[PhCHO], M	10^3 [PFC], M	$10^5 k_{obs}$, s^{-1}
0.1	1.0	3.75	0.5	2.0	9.35
0.2	1.0	5.93	0.5	4.0	9.27
0.3	1.0	7.40	0.5	5.0	9.12
0.5	1.0	9.20	0.5	7.0	9.10
0.9	1.0	10.9	0.5	9.0	9.31
1.2	1.0	11.7	0.5	15.0	9.20
1.5	1.0	12.1	0.5	5.0	9.24[a]
2.0	1.0	12.5			

[a] Contained 10^{-2} M acrylonitrile.

Table II. Effect of Solvents on Oxidation of Benzaldehyde by PFC at 298 K

solvent	K, L mol^{-1}	$10^6 k_2$, s^{-1}
dimethyl formamide	3.73	77.3
chloroform	3.31	36.5
carbon disulfide	3.54	6.80
1,2-dichloroethane	3.78	55.3
dichloromethane	4.01	50.5
DMSO	3.53	144
acetone	3.82	39.5
butanone	3.11	35.6
nitrobenzene	3.69	59.3
benzene	4.01	21.3
cyclohexane	3.95	2.17
toluene	3.64	14.5
acetophenone	3.70	76.2
tetrahydrofuran	3.87	27.1
tert-butyl alcohol	3.28	16.7
dioxane	3.36	24.2
1,2-dimethoxyethane	3.91	13.9
acetic acid	4.10	4.56
ethyl acetate	3.33	221.1

rameter (DSP) equations. The values of substituent constants were taken from the compilation by Swain et al.[9] and Taft et al.,[8] except that of σ_{R^+} for *p*-SMe group, which was obtained from our previous report.[5] We have used the coefficient of multiple correlation (R^2), standard deviation (sd), and parameter f as measures of goodness of fit. f has been defined[10] as sd/(root mean square) of the data (here log k/k_0). In the case of para compounds the best correlation is obtained with Taft's σ_I and σ_{R^+} values (Table III). Comparison showed that f is smaller for the σ_{R^+} scale than for the other scales by factors of ca. 4–26. Thus, it is apparent that the rates of oxidation of para-substituted benzaldehydes by PFC correlate best with σ_I and σ_{R^+}.

The rates of meta compounds show an excellent correlation with σ_I and σ_{R^0}, although the discriminating factor for the precision of fit with the other σ scales or with Swain's equation is not as sharp as in the case of para compounds. This agrees with the observation of Ehrenson et al.[10] that the correlation of meta-substituted compounds is generally best with σ_{R^0} and meta compounds are less discriminating.

The reaction constants and statistical data were determined at different temperatures (see the supplementary material). The value of λ^p (ca. 1.9) showed that the oxidation of para-substituted benzaldehydes is more susceptible to the resonance effect than to the field effect. In the oxidation of meta compounds, however, the value of λ^m is ca. 0.55, indicating the greater importance of the field effect.

(ii) Ortho-Substituted Benzaldehydes. The rate constants of the oxidation of ortho-substituted benzaldehydes failed to yield any significant correlation with Taft's polar or steric substituent constants.[11] The rates were, therefore, analyzed by Charton's method.[12] It was found that the correlations with Charton's equations are also not significant (see the supplementary material).

Since the rates of the oxidation of meta- and para-substituted benzaldehydes showed excellent correlation in Taft's DSP equation with σ_{R^0} and σ_{R^+}, respectively, the rates of the oxidation of ortho-substituted benzaldehydes were correlated with triparametric equations using Taft's

Table III. Correlation of Rates of Oxidation of Para- and Meta-Substituted Benzaldehydes with Dual Substituent-Parameter Equations (Temperature 298 K)

subst. constants[a]	ρ_I	ρ_R	R^2	sd	f	n[b]
		Para Substituted				
σ_I, σ_{R^0}	−1.11 (±0.44)	−6.42 (±0.65)	0.8820	0.58	0.14	13
σ_I, σ_R^{BA}	−1.23 (±0.27)	−4.80 (±0.29)	0.9564	0.35	0.08	13
σ_I, σ_{R^-}	−2.14 (±0.85)	−4.16 (±1.07)	0.5595	1.14	0.26	12[c]
σ_I, σ_{R^+}	−1.33 (±0.04)	−2.59 (±0.02)	0.9989	0.06	0.01	13
Swain et al.[d]	−0.02 (±0.08)	−1.22 (±0.04)	0.9883	0.18	0.04	13
		Meta Substituted				
σ_I, σ_{R^0}	−1.83 (±0.03)	−0.99 (±0.05)	0.9956	0.03	0.03	11
σ_I, σ_R^{BA}	−1.85 (±0.04)	−0.77 (±0.05)	0.9914	0.05	0.06	11
σ_I, σ_{R^-}	−1.65 (±0.05)	−0.66 (±0.08)	0.9826	0.07	0.10	10[c]
σ_I, σ_{R^+}	−1.87 (±0.06)	−0.45 (±0.04)	0.9840	0.07	0.08	11
Swain et al.[d]	−0.99 (±0.03)	−0.34 (±0.02)	0.9823	0.07	0.08	11

[a] σ_I and σ_R values are from ref 8. [b] Number of data points including that of PhCHO. [c] Data for NHCOMe-substituted compound not considered; no σ_{R^-} value is available. [d] Field and resonance substituent constants are from ref 9.

σ_I and $\sigma_{R^+}/\sigma_{R^0}$ and Charton's steric parameter, V. Excellent correlations were obtained with Taft's σ_I, σ_{R^+}, and Charton's V parameters (eq 5). The behavior of NO_2 and COOMe groups are consistent with their orthogonal conformations where ψ is Exner's statistical parameter[13] and n is the number of data points.

$$\log k_2 = -1.91\sigma_I - 1.56\sigma_{R^+} - 1.14V - 3.15 \qquad (5)$$

$$R^2 = 0.9980;\ \text{sd} = 0.04;\ \psi = 0.05;\ n = 13;\ T = 298\ \text{K}$$

To test the significance of the three substituent constants, multivariate linear regressions were carried out with Taft's σ_I and σ_{R^+}, Taft's σ_I and V, and σ_{R^+} and V. The absence of significant correlations (see supplementary material) showed that all the three substituent constants are significant.

There is no significant collinearity between Taft's σ_I and V, σ_{R^+} and V, and Taft's σ_I and σ_{R^+} (r^2 = 0.0352, 0.0952, and 0.0546, respectively).

(iii) Solvent Effect. The data recorded in Table II indicate that the equilibrium constant, K, is fairly insensitive to the change in solvent, but that k_2 varies considerably with the solvents. The correlation analysis of the rate constants of 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 was not available) in terms of linear solvation energy relationship of Kamlet and Taft[14] is not significant (see the supplementary material). Therefore, the data on solvent effect was analyzed in terms of Swain's equation[15] of cation-solvating and anion-solvating concept also (eq 6).

$$\log k_2 = aA + bB + C \qquad (6)$$

A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. The results of correlation analysis in terms of eq 6 are given in eq 7.

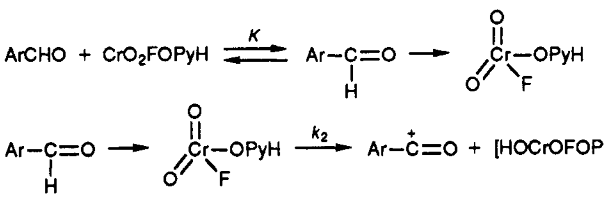
$$\log k_2 = 0.24(\pm 0.01)A + 1.73(\pm 0.04)B - 5.79 \qquad (7)$$

$$R^2 = 0.9932;\ \text{sd} = 0.04;\ n = 19;\ \psi = 0.09$$

The rates of decomposition of the complex show an excellent correlation in Swain's equation (cf. eq 7) and both cation- and anion-solvating power contributing toward the observed effect of the solvents. The contribution of the cation solvation is relatively greater.

Mechanism

The presence of a substantial primary kinetic isotope effect confirms the cleavage of aldehyde C–H bond in the rate-determining step. A one-electron oxidation, giving rise to free radicals, is unlikely in view of no effect of acrylonitrile on the reaction rate. The large negative polar reaction constants point to an electron-deficient carbon center in the transition state of the rate-determining step. Correlation of reaction rates of the oxidation of para- and ortho-substituted compounds with σ_{R^+} suggests a strong resonance interaction between the substituents and a developing positive charge in the transition state. Thus, the transition state of the decomposition of the PFC–aldehyde complex approaches a carbocation in character. This postulate is supported by the analysis of the solvent effect also. The following mechanism may then be proposed.



(8)

(9)

$$\text{Ar—}\overset{+}{\text{C}}\text{=O} + [\text{HOCrOFOPyH}]^- \xrightarrow{\text{fast}} \underset{\text{Cr(IV)}}{\text{ArCOOH} + \text{CrOFOPyH}} \qquad (10)$$

PFC is known to act as 2-electron oxidant and is reduced to a Cr(IV) species.[16]

A similar mechanism has been proposed for the oxidation of aliphatic aldehydes by PFC.[2] In the oxidation of substituted benzyl alcohols also, the rate-determining step is postulated to involve an intramolecular hydride transfer via a chromate ester.[6]

Experimental Section

Materials. The preparation and specifications of the aldehydes have been reported earlier.[5] PFC was prepared and purified by the reported method.[1] [^{2}H]Benzaldehyde (PhCDO) was prepared by the reported method.[17] Solvents were purified by the usual methods.[18]

Product Analysis. Freshly distilled benzaldehyde (3.15 g, 0.03 mol) and PFC (2.05 g, 0.01 mol) were made up to 100 mL in DMSO. The reaction mixture was allowed to stand for ca. 15 h to ensure completion of the reaction. Most of the solvent was removed by distillation under reduced pressure. The residue was extracted with a saturated aqueous solution of $NaHCO_3$ (200 mL). The bicarbonate extract was concentrated by evaporating the solvent at 80 °C. The concentrated solution was acidified with concd HCl and cooled in ice to furnish crude acid (1.4 g), which was recrystallized from hot water to produce pure benzoic acid (1.1 g, 97%; mp 121 °C).

Kinetic Measurements. Pseudo-first-order conditions were maintained by keeping an excess of the aldehyde over PFC. The solvent was DMSO, unless mentioned otherwise. Reactions were followed by monitoring the decrease in [PFC] at 356 nm for at least 2 half-lives. There were 12–15 experimental points in each kinetic run. Reactions too fast to be followed by the conventional method were studied by a stopped-flow technique using a Hi-Tech SFL-44 stopped-flow spectrophotometer. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear plots ($r > 0.990$) of log [PFC] against time by a least-squares method. Duplicate kinetic runs showed that the rates were reproducible to within ±3%.

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Supplementary Material Available: Tables of formation constants and thermodynamic parameters of PFC–aldehyde complexes, rate of decomposition of the complexes and their activation parameters, reaction constants and statistical parameters at different temperatures, and details of correlation analysis with various parameters (6 pages). Ordering information is given on any current masthead page.

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(8) Dayal, S. K.; Ehrenson, S.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 9113.

(9) Swain, C. G.; Unger, S. H.; Rosenquest, N. R.; Swain, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 492.

(10) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

(11) Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*; Cambridge University Press: Cambridge, 1979; p 57.

(12) Charton, M. *J. Org. Chem.* **1975**, *40*, 407.

(13) Exner, O. *Collect. Czech. Chem. Commun.* **1966**, *31*, 3222.

(14) Kamlet, M. J.; Abboud, J. L. H.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877 and references cited therein.

(15) Swain, C. G.; Swain, M. S.; Powell, A. L.; Alunni, S. *J. Am. Chem. Soc.* **1983**, *105*, 502.

(16) Bhattacharjee, M. N.; Chaudhuri, M. K.; Purakayastha, S. *Tetrahedron* **1987**, *43*, 5389.

(17) Wiberg, K. B. *J. Am. Chem. Soc.* **1954**, *76*, 5371.

(18) Perrin, D. D.; Armstrong, W. L.; Perrin, D. R. *Purification of Organic Compounds*; Pergamon Press: Oxford, 1966.