involves a transition structure with long bonds and with energy close to that of the products of CO elimination.

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Registry No. CH_3CO^+, 15762-07-9; $CH_3CH_2CO^+$, 17158-30-4; $NH_2CH_2CO^+$, 113925-08-9; $HOCH_2CO^+$, 51583-45-0; FCH_2CO^+, 51583-46-1; $H_3CO^+{=}Si$, 113925-09-0; $H_3SiC^+{=}O$, 113925-10-3; $H_3SiO^+{=}C$, 113925-11-4; $H_3CSi^+{=}O$, 113925-12-5; CH_4, 74-82-8.

Oxidation of Substituted Benzyl Alcohols by Pyridinium Fluorochromate: A Kinetic Study

Kalyan K. Banerji

Department of Chemistry, University of Jodhpur, Jodhpur 342 001, India

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The kinetics of the oxidation of 30 monosubstituted benzyl alcohols to the corresponding benzaldehydes by pyridinium fluorochromate (PFC) have been studied. The reaction is first order with respect to PFC. A Michaelis–Menten type kinetics was observed with respect to the substrate, indicating the formation of a PFC–alcohol complex in the preequilibrium. The formation constants and the rates of disproportionation of the complexes were determined. The oxidation of [α,α-$^2H_2$]benzyl alcohol indicated the presence of a substantial primary kinetic isotope effect. The rates of the decomposition of the complexes of the meta- and para-substituted alcohols were analyzed in terms of Taft's and Swain's dual substituent parameter equations. The meta compounds showed an excellent correlation with Taft's σ_I and $\sigma_R{}^0$ values while the para-substituted compounds correlate with σ_I and $\sigma_R{}^{BA}$ constants. The rates of the ortho-substituted alcohols correlate with Charton's equation of inductive, resonance, and steric parameters. The reaction was studied in 19 solvents. The correlation analysis of the solvent effect indicated the greater importance of the cation-solvating power of the solvent. The reaction involves a hydride ion transfer in the rate-determining step.

Pyridinium fluorochromate (PFC), a complex of chromic oxide, pyridine, and hydrogen fluoride,[1] is reported to be a more versatile oxidant than pyridinium chlorochromate (PCC).[2] Preliminary reports about the kinetics of the oxidation of alcohols[3] by PFC indicated that oxidations by PFC and PCC[4] follow different mechanistic pathways. In continuation of our earlier reports about the mechanism of the oxidation by PCC,[4] we report now the kinetics of the oxidation of some meta-, para-, and ortho-monosubstituted benzyl alcohols by PFC. Attempts have been made to study the correlation of organic reactivity in this reaction.

Experimental Section

(Acetylamino)benzyl alcohols were prepared by the reported methods.[5-7] The other alcohols (Fluka or Aldrich) were purified by either recrystallization or distillation. [α,α-$^2H_2$]Benzyl alcohol was prepared by the reduction[8] of ethyl benzoate by lithium aluminum deuteride (Fluka). PFC was prepared by the reported procedure.[1] The solvents were purified by the usual methods.[9]

Product Analysis. Benzyl alcohol (4.9 g, 0.05 mol) and PFC (2.0 g, 0.01 mol) were made up to 100 mL in DMSO. The reaction mixture was allowed to stand for ca. 12 h to ensure completion of the reaction. Most of the solvent was removed by distillation 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 kept in a refrigerator for ca. 8 h. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The product was identical (mp and mixture mp) with an authentic sample of the DNP of benzaldehyde. The yields of DNP before and after recrystallization were 2.75 g (96%) and 2.57 g (90%) respectively. In similar experiments, with the other alcohols, the yields of DNP after recrystallization were 83–95%.

Table I. Rate Constants for the Oxidation of Benzyl Alcohol by PFC at 298 K in DMSO

10^3[PFC], M	[BA], M	10^5k_1, s^{-1}	10^3[PFC], M	[BA], M	10^5k_1, s^{-1}
0.5	0.02	5.10	2.0	0.08	17.3
1.0	0.02	5.00	2.0	0.10	20.7
2.0	0.02	5.07	2.0	0.15	27.8
3.0	0.02	5.03	2.0	0.20	33.6
4.0	0.02	5.13	2.0	0.40	48.8
5.0	0.02	5.02	0.20	0.60	57.5
2.0	0.04	9.06	0.20	1.00	67.7
2.0	0.06	13.6			

Kinetic Measurements. The pseudo-first-order conditions were attained by keeping a large excess of the alcohol over PFC. The temperature was kept constant to ±0.1 K. The reactions were followed both iodometrically and spectrophotometrically at 356 nm. Duplicate kinetic runs showed that the rate constants obtained by the two procedures agreed within ±2%. The reactions of the alcohols containing methoxy and acetylamino groups were very fast, and they were studied on a stopped-flow spectrophotometer (Hi-Tech, U.K.). The pseudo-first-order rate constant, k_1, was obtained from the linear plots of log [PFC] vs time. The kinetics were studied in dimethyl sulfoxide (DMSO), unless mentioned otherwise.

Results and Discussion

The rates and other data were obtained for all the alcohols investigated. Since results are similar, only repre-

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Table II. Formation Constants for the Complex between PFC and Substituted Benzyl Alcohols

subst	K				
	293 K	298 K	303 K	308 K	313 K
H	3.10	3.00	3.00	2.97	2.90
p-Me	3.15	3.07	3.00	2.95	2.83
p-OMe	3.14	3.00	2.97	2.82	2.78
p-NHCOMe	3.23	3.12	3.00	2.73	2.85
p-SMe	3.10	3.02	2.97	2.90	2.86
p-F	2.93	2.87	2.80	2.74	2.70
p-COOMe	2.95	2.86	2.81	2.77	2.72
p-Cl	2.83	2.79	2.74	2.68	2.62
p-CF_3	2.93	2.80	2.74	2.68	2.60
p-NO_2	2.83	2.75	2.63	2.5	2.52
m-Me	3.00	2.93	2.88	2.80	2.73
m-F	2.97	2.90	2.80	2.72	2.65
m-Br	3.03	2.97	2.89	2.80	2.72
m-OMe	3.21	3.13	3.01	2.92	2.85
m-OPh	3.00	2.91	2.83	2.71	2.68
m-CN	2.91	2.83	2.74	2.67	2.60
m-SMe	2.97	2.90	2.84	2.75	2.70
m-CF_3	2.85	2.79	2.73	2.63	2.58
m-NO_2	2.82	2.78	2.71	2.65	2.59
m-NHCOMe	3.20	3.11	3.02	2.95	2.87
o-Me	3.32	3.18	3.03	2.92	2.85
o-F	3.00	2.91	2.87	2.81	2.79
o-Cl	3.05	2.97	2.86	2.80	2.73
o-Br	2.87	2.80	2.70	2.63	2.58
o-NO_2	2.77	2.70	2.63	2.59	2.55
o-NHCOMe	3.05	2.97	2.91	2.82	2.73
o-I	3.13	2.98	2.90	2.80	2.71
o-CF_3	3.00	2.93	2.85	2.73	2.65
o-SMe	2.97	2.90	2.85	2.74	2.67
o-OMe	3.24	3.12	3.01	2.92	2.84
[α,α-$^2H_2$]benzyl alcohol	3.04	2.95	2.90	2.86	2.80

sentative data are reproduced here.

The oxidation of substituted benzyl alcohols by PFC results in the formation of the corresponding benzaldehydes (eq 1).

$$3ArCH_2OH + 2Cr(VI) \rightarrow 3ArCHO + 2Cr(III) + 6H^+ \tag{1}$$

The oxidation of benzyl alcohols by PFC is first order with respect to PFC. Further, the pseudo-first-order rate coefficients are independent of the initial concentration of PFC. The variation in the concentration of the alcohol showed that the rate increases with an increase in the concentration of the alcohol but the order is less than 1 (Table I). A plot of $1/k_1$ against 1/[alcohol] is linear (r = 0.9986) with an intercept on the rate ordinate (Figure 1). This shows that a Michaelis–Menten type kinetics is followed with respect to the alcohol, and the broad mechanism may be postulated as follows.

$$\text{PFC} + \text{alcohol} \overset{K}{\rightleftharpoons} \text{complex} \tag{2}$$

$$\text{complex} \xrightarrow[\text{slow}]{k_2} \text{products} \tag{3}$$

The above mechanism leads to the following rate equation.

$$\text{rate} = \frac{k_2K[\text{PFC}][\text{alcohol}]}{1 + K[\text{alcohol}]} \tag{4}$$

The variation of the concentration of the alcohol was studied at different temperatures between 293 and 313 K, and values of the formation constant of the complex, K, and the rate of its disproportionation, k_2, were evaluated from the double reciprocal plots. The activation parameters for its decomposition were also calculated (Tables II and III).

A linear correlation (r = 0.9978, slope = 0.8017) between the log k_2 at 293 and 313 K for the 30 aromatic alcohols suggests that all the alcohols are oxidized by the same

Table III. Rate Constants and the Activation Parameters for the Oxidation of Substituted Benzyl Alcohols by PFC

subst	10^5k_2, s^{-1}					ΔH^*,[a] kJ mol^{-1}	ΔS^*,[a] J mol^{-1} K^{-1}
	293 K	298 K	303 K	308 K	313 K		
H	692	895	1120	1710	2520	46.5 ± 1.7	−128 ± 1.0
p-Me	1750	2150	2680	3570	5100	37.6 ± 1.2	−151 ± 3.0
p-OMe	5620	7130	9400	11000	14700	33.3 ± 0.6	−158 ± 1.8
p-NHCOMe	1440	1860	2350	3160	4980	43.1 ± 0.8	−133 ± 1.5
p-SMe	1250	1730	2260	3180	4520	45.7 ± 0.7	−125 ± 1.0
p-F	636	900	1300	1640	2860	52.2 ± 1.3	−109 ± 1.3
p-COOMe	52.3	89.0	142	210	353	68.9 ± 1.1	−73 ± 0.9
p-Cl	219	315	446	795	1130	61.3 ± 1.5	−87 ± 1.0
p-CF_3	38.3	58.0	84.5	174	280	74.4 ± 2.0	−56 ± 0.7
p-NO_2	7.90	12.6	21.3	50.0	83.3	89.8 ± 1.8	−17 ± 0.5
m-Me	1350	1770	2120	3000	4410	41.4 ± 1.8	−140 ± 1.1
m-F	108	136	179	280	410	48.3 ± 1.0	−136 ± 0.7
m-Br	80.0	118	160	281	400	59.5 ± 1.6	−101 ± 1.0
m-OMe	710	810	1070	1390	2150	39.2 ± 0.6	−153 ± 1.5
m-OPh	200	312	416	530	892	50.9 ± 0.5	−123 ± 0.5
m-CN	10.0	16.0	30.7	54.1	82.2	80.0 ± 2.0	−48 ± 0.5
m-SMe	341	560	646	895	1270	44.6 ± 1.1	−139 ± 1.6
m-CF_3	25.0	39.6	70.8	100	185	72.3 ± 1.3	−67 ± 1.0
m-NO_2	5.64	8.93	14.7	27.1	49.7	80.3 ± 1.7	−52 ± 1.0
m-NHCOMe	330	468	585	832	1260	46.8 ± 1.2	−133 ± 0.8
o-Me	14800	16700	18200	22400	28900	22.2 ± 0.3	−186 ± 2.0
o-F	417	550	790	1200	1780	53.4 ± 0.9	−109 ± 1.4
o-Cl	742	912	1210	1730	2500	44.0 ± 1.5	−136 ± 1.8
o-Br	1170	1390	1770	2490	3810	42.0 ± 1.9	−145 ± 1.1
o-NO_2	17.9	32.0	57.4	89.1	160	79.6 ± 1.9	−44 ± 0.2
i-NHCOMe	8000	10000	11500	14900	20000	31.3 ± 0.5	−159 ± 2.3
o-I	2010	2480	3200	4180	6080	38.9 ± 0.8	−145 ± 1.1
o-CF_3	637	840	1360	1780	2530	50.8 ± 1.6	−114 ± 0.8
o-SMe	6260	7000	8400	11200	15600	32.2 ± 0.5	−159 ± 1.5
o-OMe	7130	8030	10000	12700	16000	28.9 ± 0.7	−169 ± 1.7
[α,α-$^2H_2$]benzyl alcohol	100	144	201	287	418	51.4 ± 1.0	−127 ± 0.3

[a] At 298 K.

Table IV. Correlation of the Rates of Oxidation of Para- and Meta-Substituted Benzyl Alcohols by PFC with Dual Substituent Parameters[a]

	para-substituted					meta-substituted				
subst constants	ρ_I	ρ_R	R	SD	f	ρ_I	ρ_R	R	SD	f
σ_I, σ_R^0	−2.19	−3.12	0.9941	0.104	0.036	−2.75	−1.64	0.995	0.03	0.01
σ_I, σ_R^{BA}	−2.74	−1.64	0.9995	0.03	0.005	−2.83	−1.18	0.9974	0.06	0.03
σ_I, $\sigma_I^{-\,b}$	−1.86	−2.03	0.9721	0.24	0.09	−2.58	−1.08	0.9946	0.10	0.04
σ_I, $\sigma_R^{+\,c}$	−2.13	−1.50	0.9805	0.20	0.07	−2.79	−0.74	0.9914	0.12	0.05
Swain et al.[d]	−1.00	−0.81	0.9935	0.11	0.04	−1.50	−0.53	0.9958	0.08	0.04

[a] Temperature 298 K, SD = standard deviation, f = SD/root mean square of log k/k_0; σ_I and σ_R values are from ref 13. [b] Data for NHCOMe and OPh not considered; no σ_R^- values are available. [c] Data for SMe not considered; no reliable σ_R^+ value is available. [d] Field and resonance substituted constants are from ref 14.

Table V. Temperature Dependence of the Reaction Constants for Decomposition of Substituted Alcohol–PFC Complexes[a]

temp, K	ρ_I	ρ_R[b]	λ	R	SD	f
			Para-Substituted			
293	−2.39	−2.59	1.08	0.9996	0.030	0.011
298	−2.26	−2.49	1.10	0.9999	0.012	0.005
303	−2.13	−2.39	1.12	0.9990	0.014	0.005
308	−1.87	−2.15	1.15	0.9989	0.037	0.012
313	−1.78	−2.09	1.17	0.9996	0.021	0.006
			Meta-Substituted			
293	−2.83	−1.73	0.61	0.9947	0.022	0.010
298	−2.74	−1.64	0.60	0.9995	0.026	0.011
303	−2.59	−1.40	0.54	0.9993	0.030	0.012
308	−2.45	−1.29	0.53	0.9987	0.032	0.014
313	−2.36	−1.22	0.52	0.9996	0.020	0.007

[a] $\lambda = \rho_R/\rho_I$, f = SD/root mean square of log k/k_0. [b] ρ_R is ρ_R^{BA} and ρ_R^0 for para- and meta-substituted compounds respectively.

mechanism.[10] The value of the isokinetic temperature is 432 K.

The substantial kinetic isotope effect (k_H/k_D = 6.22 at 298 K) confirms that the rate-determining step involves a C–H bond cleavage from the carbon bearing the hydroxy group.

The oxidation of alcohols by PCC[4] and PFC differs in the observation of a Michaelis–Menten kinetics in the latter. 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 kinetically detectable complexes in the oxidation by PFC.

Correlation Analysis of Reactivity. The formation constants of the alcohol–PFC complexes are almost insensitive to substitution in the benzene ring. Similar observations have been recorded earlier in the oxidations of benzyl alcohols[11] and mandelic acids[12] by ceric ammonium nitrate. The rate of disproportionation of the complex is, however, strongly dependent on the substituent. The rates of decomposition of the complex were, therefore, subjected to correlation analysis.

(i) Para- and Meta-Substituted Benzyl Alcohols. Since the decomposition rates failed to show a significant correlation with any single-parameter substituent constants, the rates were analyzed in terms of the dual substituent parameter (DSP) equations of Taft[13] and Swain et al.[14] The rates of disproportionation of para and meta compounds were separately correlated with σ_I and four different σ_R values in Taft's equation[13] and with the field and resonance substituent constants of Swain et al.[14] The results are summarized in Table IV. Both the para and meta series of substituted benzyl alcohols meet the requirement of minimum number of substituents for analysis by DSP equations.[15]

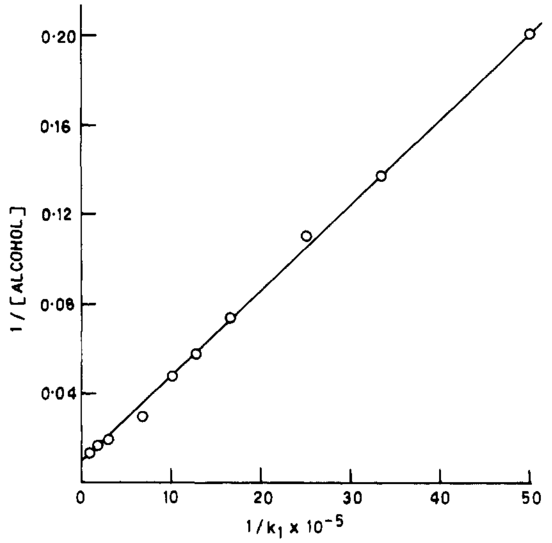

Figure 1. Michaelis–Menten plot for the oxidation of benzyl alcohol by PFC; [PFC] 2 × 10^{-3} M, temperature 298 K, solvent DMSO.

The rates of para-substituted benzyl alcohols show excellent correlation with σ_I and σ_R^{BA} values. The correlations with the other σ_R values and in Swain's equation[14] are relatively poor. We have used the coefficient of multiple correlation (R), the standard deviation (SD), and f as the criteria of goodness of fit. f has been defined[16] as f = SD/RMS, where RMS is the root mean square of the data points (here log k/k_0). The comparison of the f values shows that f is smaller for the σ_R^{BA} scale than those of other

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Table VI. Temperature Dependence of the Reaction Constants for the Oxidation of Ortho-Substituted Benzyl Alcohols by PFC[a]

temp, K	α	β	ϕ	R	SD	P_R	P_S
293	−3.30	−2.33	1.75	0.9995	0.030	41.6	23.7
298	−3.09	−2.16	1.66	0.9994	0.031	41.1	24.0
303	−2.86	−1.97	1.55	0.9992	0.023	40.8	24.3
308	−2.72	−1.93	1.48	0.9998	0.013	41.5	24.1
313	−2.57	−1.81	1.41	0.9995	0.025	41.5	24.3

[a] σ_I, σ_R, and V values are from ref 18.

scales by factors of ~7 to ~18. Therefore, it is apparent that the rates of the oxidation of para-substituted benzyl alcohols by PFC correlate best with σ_I and $\sigma_R{}^{BA}$ values.

The rates of the oxidation of meta-substituted compounds show excellent correlation with σ_I and $\sigma_R{}^0$ substituent constants, though the discriminating factor for the precision of fit with the other scales is not as sharp as in the case of para-substituted compounds. In fact, correlation with $\sigma_R{}^{BA}$ and $\sigma_R{}^-$ and in Swain's equation meets the requirement[16] for a satisfactory fit ($f < 0.1$). Even the correlation with $\sigma_R{}^+$ is not very poor. This agrees with the observation of Ehrenson, Brownlee, and Taft[16] that correlation of meta-substituted compounds is generally best with $\sigma_R{}^0$ constants and meta-substituted compounds are less discriminating.

The reaction constants and statistical data at different temperatures are given in Table V.

The values of λ^p (1.08–1.17) show that the oxidation is slightly more susceptible to the delocalized effect than to localized effects. The oxidation of the meta-substituted compounds is, however, more susceptible to localized effects (λ^m = 0.52–0.61), as is expected. The selectivity of the reaction decreases at higher temperature. For the para compounds, the decrease is more pronounced in the localized effect, resulting in a gradual increase in the value of λ^p. The reverse is the case in the oxidation of the meta-substituted benzyl alcohols, reflected in the gradual decrease in the value of λ^m.

(ii) Ortho-Substituted Benzyl Alcohols. It was observed that the rates of oxidation of ortho-substituted benzyl alcohols did not give any significant correlations with either Taft's steric or polar substituent constants. Thus the observed reactivity is not compatible with either the size of substituents or their Taft polar substituent constants. In view of this, the rates were analyzed by using Charton's method.[17] The rate constants were correlated with equations 5 and 6, where σ_I, σ_R, and V are inductive, resonance, and steric substituent constants, respectively, and the values were those compiled by Aslam et al.[18]

$$\log k_{\text{ortho}} = \alpha\sigma_I + \beta\sigma_R + h \tag{5}$$

$$\log k_{\text{ortho}} = \alpha\sigma_I + \beta\sigma_R + \phi V + h \tag{6}$$

In multiple linear regression analysis using eq 5, the coefficient of correlation is poor and SD is high (eq 7).

$$\log k_2 = -2.62\sigma_I - 1.83\sigma_R - 1.26 \tag{7}$$

$$R = 0.8367,\ \text{SD} = 0.47,\ n = 11$$

The absence of a significant correlation with eq 5 leads to the conclusion that the electric effects alone are not sufficient to account for the ortho-substituent effects in this reaction.

The correlation with eq 6 was performed with the rate data obtained at different temperatures, and the results are summarized in Table VI. The effect of an o-NO_2 group is consistent with its orthogonal conformation.

The significance of the correlation was tested by means of an F test.[19] The confidence levels of the F test are >99.9%. The confidence level for the significance of α, β, and ϕ terms was evaluated by means of a Student's t test.[19] The confidence level of the t test is >99.9%, indicating the operation of significant inductive, resonance, and steric effects.

To test the significance of σ_I and σ_R when V is included, multiple linear regression analyses were carried out with σ_I and V and with σ_R and V. The absence of significant correlations (eq 8 and 9) showed that both σ_I and σ_R are significant.

$$\log k_2 = -2.84\sigma_I + 1.36V - 1.49 \tag{8}$$

$$R = 0.8096,\ \text{SD} = 0.50,\ n = 11$$

$$\log k_2 = -1.83\sigma_R + 1.09V - 2.74 \tag{9}$$

$$R = 0.5808,\ \text{SD} = 0.70,\ n = 11$$

These results show that this reaction belongs to case 1 of the classification given by Charton. There is no significant collinearity between σ_I and σ_R, σ_I and V, and σ_R and V (r = 0.0744, 0.2150, and 0.1467, respectively) for the 10 substituents. The contribution of the resonance effect[17] to the polar effect is given by eq 10.

$$P_R = \frac{100 \times |\beta|}{|\alpha| + |\beta|} \tag{10}$$

The contribution of the steric parameter[17] to the total effect of the substituent, P_S, was determined by using eq 11.

$$P_S = \frac{100 \times |\phi|}{|\alpha| + |\beta| + |\phi|} \tag{11}$$

The values of P_R and P_S are also recorded in Table VI. The values of P_R show that the inductive effect is more dominant than the resonance effect. The P_R for the para position is 50% by definition.[20] The observed value of P_R (ca. 41%) in the case of ortho substituents shows that the balance of the inductive and resonance effects is different for the ortho and para positions, the resonance effects being less pronounced in the former case. This may be due to the twisting away of the primary alcohol group from the benzene ring. The value of P_S shows that there is considerable steric effect in this reaction.

(iii) Solvent Effect. The rates of the oxidation of benzyl alcohol by PFC were determined at 298 K in 19 different solvents. The kinetics are similar to those observed in DMSO. The rates are recorded in Table VII. The choice of solvents was limited by the solubility of PFC and the reaction of PFC with primary and secondary al-

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Table VII. Formation Constants and the Rates of Decomposition of PFC–Benzyl Alcohol Complexes in Different Solvents at 298 K[a]

solvent	K	10^5k_2, s^{-1}
chloroform	3.72	142
carbon disulfide	3.47	10.1
1,2-dichloroethane	3.28	160
dichloromethane	3.42	223
DMSO	3.00	895
acetone	2.90	133
dimethylformamide	4.03	345
butanone	3.27	99.7
nitrobenzene	3.82	177
benzene	3.56	39.5
cyclohexane	2.83	1.43
toluene	3.48	24.0
acetophenone	3.52	314
tetrahydrofuran	3.02	54.0
tert-butyl alcohol	2.25	41.5
dioxane	3.17	64.2
1,2-dimethoxyethane	3.42	31.7
acetic acid	2.85	8.60
ethyl acetate	2.76	50.0

[a] Solvent parameters are from ref 22.

cohols. There was no noticeable reaction of PFC with the solvents used. The rates in different solvents were analyzed by using the linear solvation energy relationship (LSER) of Kamlet and Taft[21] and by the anion-solvating and cation-solvating concept of Swain et al.[22]

The Kamlet–Taft LSER is a triparametric equation with the form

$$\log k_2 = A_0 + p\pi^* + a\alpha + b\beta \qquad (12)$$

where π^* represents "solvent polarity" for the solvent–solute interaction of nonspecific kind, α is the solvent hydrogen bond donor acidity, and β is the solvent hydrogen bond acceptor basicity. The values of π^*, α, and β were taken from the compilation by Kamlet et al.[21] Out of the 18 solvents analyzed by LSER (CS_2 was not considered, as the solvent parameters were not available), 12 have a value of 0 for α; only acetic acid, *tert*-butyl alcohol, dichloromethane, and chloroform have any appreciable value of α. The rates were analyzed in the terms of the triparametric equation (12), a biparametric equation involving π^* and β (eq 13), and also individually with π^* and β. The results are given in eq 14–17.

$$\log k_2 = A_0 + p\pi^* + b\beta \qquad (13)$$

$$\log k_2 = -4.47 + 0.42\pi^* + 1.55\beta + 0.72\alpha \qquad (14)$$

$$R = 0.7985,\ \mathrm{SD} = 0.43,\ n = 18$$

$$\log k_2 = -4.07 + 1.11\pi^* + 0.77\beta \qquad (15)$$

$$R = 0.6678,\ \mathrm{SD} = 0.51,\ n = 18$$

$$\log k_2 = -4.69 + 2.38\pi^* \qquad (16)$$

$$r = 0.8787,\ \mathrm{SD} = 0.32,\ n = 18$$

$$\log k_2 = -3.44 + 0.85\alpha \qquad (17)$$

$$r = 0.4002,\ \mathrm{SD} = 0.61,\ n = 18$$

The results indicate that Kamlet–Taft treatment failed to explain the effect of solvents on the oxidation of benzyl alcohol by PFC.

The rates were then analyzed in terms of the Swain equation[22] of solvent acity and basity (eq 18), where A is

$$\log k_2 = aA + bB + \mathrm{C} \qquad (18)$$

the anion-solvating and B is the cation-solvating tendency of the solvent and C is the intercept term. The result of multiple linear regression in the terms of Swain's equation is given in eq 19.

$$\log k_2 = 0.69A + 2.51B - 4.96 \qquad (19)$$

$$R = 0.9952,\ \mathrm{SD} = 0.07,\ n = 19$$

The rates showed no significant correlation with A and B individually or with $A + B$ (r = 0.0977, 0.9601, and 0.8895, respectively).

The result presented in eq (19) indicates that the cation-solvating power of the solvent is more important; the anion-solvating capacity plays a relatively small role. The absence of a significant correlation with (A + B) showed the failure of solvent polarity to explain the effect of solvents on this reaction.

Mechanism. The negative polar reaction constants indicate an electron-deficient carbon center in the transition state and suggest a hydride ion transfer in the rate-determining step. This is supported by the fact that the cation-solvating capacity of the solvent is much more dominant than the anion-solvating capacity. A similar conclusion was reached in the oxidation by PCC also.[4] The hydride transfer may take place either via an ester intermediate or by an acyclic process. Kwart and Nickle[23] 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 acylic process.

The data for protio and deuterio benzyl alcohols, fitted to the familiar expression $k_H/k_D = A_H/A_D \exp(-\Delta H^*/RT)$, 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 the zero-point energy difference for the respective C–H and C–Dbonds (ca. 4.5 kJ mol^{-1}) and the entropies of activation of the respective reactions are nearly equal.[23,24] Bordwell[25] has given very cogent evidence against the occurrence of concerted one-step bimolecular processes of hydrogen transfer, and it is evident that in the 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 transferby cyclic transition states.[26] Littler[27] 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. The correlation of the oxidation rates of para-substituted benzyl alcohols with σ_R^{BA} values, with negative reaction constants, also indicates a weak resonance interaction of the substituents with a developing positive charge. Thus the transition state I can be envisaged for the oxidation of benzyl alcohol by PFC.

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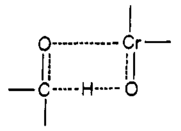

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Registry No. PhCH$_2$OH, 100-51-6; 4-HOCH$_2$C$_6$H$_4$Me, 589-18-4; 4-HOCH$_2$C$_6$H$_4$OMe, 105-13-5; 4-HOCH$_2$C$_6$H$_4$NHCOMe, 16375-88-5; 4-HOCH$_2$C$_6$H$_4$SMe, 3446-90-0; 4-HOCH$_2$C$_6$H$_4$F, 459-56-3; 4-HOCH$_2$C$_6$H$_4$CO$_2$Me, 6908-41-4; 4-HOCH$_2$C$_6$H$_4$Cl, 873-76-7; 4-HOCH$_2$C$_6$H$_4$CF$_3$, 349-95-1; 4-HOCH$_2$C$_6$H$_4$NO$_2$, 619-73-8; 3-HOCH$_2$C$_6$H$_4$Me, 587-03-1; 3-HOCH$_2$C$_6$H$_4$F, 456-47-3; 3-HOCH$_2$C$_6$H$_4$Br, 15852-73-0; 3-HOCH$_2$C$_6$H$_4$OMe, 6971-51-3; 3-HOCH$_2$C$_6$H$_4$OPh, 13826-35-2; 3-HOCH$_2$C$_6$H$_4$CN, 874-97-5; 3-HOCH$_2$C$_6$H$_4$SMe, 59083-33-9; 3-HOCH$_2$C$_6$H$_4$CF$_3$, 349-75-7; 3-HOCH$_2$C$_6$H$_4$NO$_2$, 619-25-0; 3-HOCH$_2$C$_6$H$_4$NHCOMe, 16375-94-3; 2-HOCH$_2$C$_6$H$_4$Me, 89-95-2; 2-HOCH$_2$C$_6$H$_4$F, 446-51-5; 2-HOCH$_2$C$_6$H$_4$Cl, 17849-38-6; 2-HOCH$_2$C$_6$H$_4$Br, 18982-54-2; 2-HOCH$_2$C$_6$H$_4$NO$_2$, 612-25-9; 2-HOCH$_2$C$_6$H$_4$NHCOMe, 20939-77-9; 2-HOCH$_2$C$_6$H$_4$I, 5159-41-1; 2-HOCH$_2$C$_6$H$_4$CF$_3$, 346-06-5; 2-HOCH$_2$C$_6$H$_4$SMe, 33384-77-9; 2-HOCH$_2$C$_6$H$_4$OMe, 612-16-8; D$_2$, 7782-39-0; pyridinium fluorochromate, 83042-08-4.

β-Cyclodextrin as a Molecular Reaction Vessel: Reactions of Included Phenylmethyldiazirine

Christopher J. Abelt* and Jennifer M. Pleier

Department of Chemistry, The College of William and Mary in Virginia, Williamsburg, Virginia 23185

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Phenylmethyldiazirine forms a stable, solid complex with β-cyclodextrin. The diazirine was decomposed by pyrolysis or irradiation of the complex, and the reaction products were analyzed. The major volatile products consist of the isomeric 1,2-diphenyl-1-methylcyclopropanes. Under photolytic conditions a significant amount of styrene also is formed. The selectivity for trans isomer formation is 10 times greater from the CD complex than from the neat state. Carbene insertion products with β-cyclodextrin are formed under both reaction conditions. The product distributions are explained by cage and shape-selective effects exerted by β-cyclodextrin.

The cyclodextrins (CD's) are a series of cyclic oligosaccharides which possess a hydrophobic pocket.[1] Their inclusion complexes with lipophilic molecules, especially aromatic compounds, have been studied thoroughly. The interest in CD's derives in part from their similarity to enzymes, and recent effort has been put into modifying cyclodextrins to enhance their catalytic powers.[2] Cyclodextrins also have been used to control photoreactions of bound guests.[3] However, few studies report the chemistry of thermally generated reactive intermediates inside the cyclodextrin cavity.

Ramamurthy, Turro, and co-workers have found that cyclodextrins exert "super cage" effects and conformational effects in certain ketone photoreactions.[3] Cage effects result in the preference for direct coupling products over escape products from radical pairs. They are typically demonstrated by using a precursor to an unsymmetrical radical pair (A$^\bullet$ $^\bullet$B). Symmetrical products (A–A and B–B) are produced from coupling of escaped radicals, whereas unsymmetrical products (A–B) result from both direct coupling and from coupling of escaped radicals. The cage effect exerted by cyclodextrins on ketone cleavage photoreactions was shown by using unsymmetrical dibenzyl ketones and benzyl phenylacetates; both predominantly produce unsymmetrical 1,2-diphenylethanes by direct coupling of the benzyl–benzyl radical pair produced via loss of CO and CO$_2$, respectively.[4] Conformational effects can result in selectivity for one reaction pathway over another, especially when at least one pathway is conformationally dependent. For instance, type I and type II reactions are often competing pathways in the photochemistry of ketones. Cyclodextrin complexation has altered the reactivity to favor either pathway. Benzoin alkyl ethers, which react via α-cleavage in solution, selectively undergo type II reactions in the cyclodextrin complex.[5] On the other hand, α-alkyl dibenzyl ketones undergo type I reactions while included into cyclodextrin, whereas both reactions occur in solution.[3] These disparate results can be understood based on the geometry of the inclusion complex. In the benzoin alkyl ether complex the ether chain is not bound by the cavity, so it can participate in the type II process. In the α-alkyl dibenzyl ketone complex, however, the alkyl chain is buried inside the cavity and therefore not accessible to the carbonyl oxygen.

Cyclodextrins have been used to influence many thermal reactions. However, they have rarely been used as a medium for thermally generating very reactive intermediates. The pyrolysis of azobisisobutyronitrile (AIBN) as the solid complex with β-cyclodextrin is an example of thermal generation of a radical pair. The radical pair produced after nitrogen extrusion undergoes recombination; it behaves like the radical pairs generated from ketone photolysis.[3] Again, the cyclodextrin appears to enhance the cage effect, although in this case the escape products and the coupling products would be identical. Only one example of carbene generation inside a CD has been found.[6]

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