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Solvolysis of *p,p′*-Dichlorobenzhydryl Chloride in Ethanol–2,2,2-Trifluoroethanol Mixtures

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The solvolysis of *p,p′*-dichlorobenzhydryl chloride (1) in the nearly isodielectric EtOH–TFE mixtures gives a Grunwald–Winstein *m* value of 1.30. The solvolysis is subject to common ion rate depression and the mass law constants α increase with the increase in the mole fraction of TFE. A $k_{\mathrm{TFE}}/k_{\mathrm{EtOH}}$ ratio of ~0.025 was calculated from the product distribution by assuming reaction of the solvent components with a free cationic intermediate. Ionizing power parameters *Y* for EtOH–TFE mixtures were calculated from the solvolysis of 1 and from the solvatochromic shifts of the charge-transfer band of 1-(*p*-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine. It is suggested that the reaction proceeds via a selective free *p,p′*-dichlorobenzhydryl cation.

Solvent effects on solvolytic displacement reactions involve several solvent properties such as nucleophilicity, electrophilicity, and dielectric constant. A linear free energy relationship for describing these reactions (eq 1) was suggested by Winstein, Grunwald, and Jones,[1] where k and k_0 are the rate constants in a certain solvent and in 80% EtOH, and Y and N are the solvent ionizing power and nucleophilicity, respectively, m and l being the sensitivities to these parameters.

$$\log (k/k_0) = mY + lN \tag{1}$$

$$\log (k/k_0) = mY \tag{2}$$

However, in the absence of a scale of N values a more restricted form (eq 2)[2] is usually applied where the nucleophilicity is either assumed to be unimportant (k_c process[3]) or nearly constant in the solvents studied. Only recently have scales of N values become available.[4] Schleyer and co-workers who presented an extensive list of N values[4d] showed the superiority of eq 1 over eq 2 in analyzing solvent effects in solvolysis.[4d]

A useful way to gradually change the solvent properties is by studying binary solvent mixtures. Only one solvent property may be changed significantly as in aqueous EtOH mixtures where the change in N is small compared with the change in Y.[4d] On the other hand, in aqueous TFE mixtures both N[4,5] and Y[4b,6] (which are based on solvolytic data) increase with the increase of the water content.

The ionization power parameter Y involves contributions from two solvent properties: from the dielectric constant which is related to electrostatic solvation and from electrophilic solvation, mainly via hydrogen bonding to the leaving group. In aqueous EtOH the two effects are in the same direction since water has a higher dielectric constant and a higher electrophilicity than EtOH. In aqueous TFE the two properties operate in opposite directions since water has higher dielectric constant, but TFE is probably a better electrophilic solvator.[7] The nonlinear log k vs. Y plots found for solvolysis of α-arylvinyl derivatives in aqueous TFE were ascribed to this reason.[7]

The different bulk of the solvent components in a binary mixture was invoked for explaining the selectivity in the product-forming process in terms of different stabilities of solvent separated ion pairs.[8]

It is therefore surprising that more attention was not paid to the binary solvent mixtures EtOH–TFE. Mukherjee and Grunwald showed that these are nearly isodielectric mixtures, where the dielectric constants of TFE (26.14) and EtOH (24.32) are the extremes.[9] The bulk of the two solvents is also very similar. On the other hand, the nucleophilicity of TFE is much lower[4d] and its acidity[10] and probably its electrophilicity are higher than those of EtOH. Nevertheless, only three solvolytic studies in EtOH–TFE mixtures appeared so far.[11–13] da Roza, Andrews, and Keefer measured several Y and N values and studied the solvolyses of several benzyl halides.[11] They found that Y increases and N decreases on increasing the molar fraction of TFE in EtOH–TFE and that eq 2 gives nonlinear correlations, as expected since the lN term was neglected. From the dependence of the shape of these plots, of the product distribution, and of the $k_{\mathrm{Br}}/k_{\mathrm{Cl}}$ ratios on the substituent in the aryl ring, the extent of solvent involvement as a nucleophile and an electrophile in the transition state was probed.[11] Ando and Tsukamoto used the product distribution in the solvolysis of 1- and 2-adamantyl systems in 50% EtOH–TFE as a tool for evaluating various proposals concerning the product-forming selectivities in binary mixtures.[12] Kaspi and Rappoport[13] found a nearly linear N vs. Y correlation in the region of 20–90% TFE with a slope of −0.83.

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Table I. Kinetic Data for the Solvolysis of *p,p′*-Dichlorobenzhydryl Chloride in EtOH–TFE[a]

% TFE in EtOH–TFE	X_{TFE}[b]	10^5k_{obsd}, s^{-1} at 0 °C	at 25 °C	at 50 °C	$\Delta H^{\ddagger}$, kcal mol^{-1} [c]	$\Delta S^{\ddagger}$, eu[c]
0	0		0.81[d]			
10	0.083		2.68 ± 0.004	36.7 ± 0.1	19.4 ± 0.03	−14.2 ± 0.1
20	0.168		4.70 ± 0.003	69 ± 0.1	19.9 ± 0.03	−11.4 ± 0.1
30	0.257		11 ± 0.1[e]	145 ± 0.2	19.2 ± 0.2	−12.2 ± 0.6
40	0.349		29 ± 0.03	308 ± 6[e]	17.5 ± 0.3	−16.1 ± 1.0
50	0.447		68 ± 0.1	664 ± 23[e]	16.8 ± 0.5	−16.6 ± 1.9
60	0.548	11.6 ± 0.01	176 ± 0.3		17.0 ± 0.02	−14.1 ± 0.1
70	0.652	31 ± 0.06	478 ± 7[e]		17.1 ± 0.2	−11.8 ± 0.7
80	0.763	113 ± 0.1	1291 ± 42[e]		15.2 ± 0.4	−16.2 ± 1.5
90	0.880	349 ± 22[e]	3751 ± 71[e]		14.8 ± 0.8	−15.5 ± 2.8
95	0.940	567 ± 29[e]	6561 ± 792		15.2 ± 1.6	−12.8 ± 5.5

[a] $[\mathrm{Ar_2CHCl}]$ = 3.5–4.2 mM. [b] Mole fraction of trifluoroethanol. [c] The errors were calculated by the method of R. C. Peterson, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961). [d] S. Nishida, *J. Org. Chem.*, **32**, 2695 (1967). [e] Average of two experiments.

Since the solvolyses of most of the compounds studied so far involve either nucleophilic participation or product formation from ion pairs it was of interest to apply eq 1 and 2 and to determine the product distribution for a substrate more prone to react via a k_c route, where products are derived from a free cation. We therefore studied the solvolysis of *p,p′*-dichlorobenzhydryl chloride (**1**), a substrate likely to solvolyze via the k_c route, in EtOH–TFE mixtures. Several new *Y* values for EtOH–TFE mixtures were also derived by two independent methods.

$$(p\text{-}\mathrm{ClC_6H_4})_2\mathrm{CHCl}$$

1

Results

Solvolysis of 1 in EtOH–TFE Mixtures. Solvolysis of **1** in EtOH–TFE mixtures containing 5–90% EtOH was followed by the conventional conductometric technique. The solvolysis rate in pure TFE was higher than the dissolution rate of **1** and meaningful rate constants were not obtained. Several measurements were conducted in the fast solvents containing 5–30% EtOH and average values of the rate constants are given. In the other mixtures duplicate experiments were conducted whenever the correlation coefficient of the first-order plot was <0.999. Activation parameters were calculated from the data at 0 and 25 °C for the fast reactions and at 25 and 50 °C for the slow reactions. The first-order constants obtained at ca. 4 mM concentrations of **1** and the derived activation parameters are given in Table I.

Clean first-order constants were obtained at 4 mM concentrations of **1**. However, since benzhydryl chlorides show common ion rate depression in other solvents,[14] several experiments were conducted in which the concentration of the substrate was increased in some TFE-rich mixtures to 20 or 50 mM in order to detect a possible decrease in the rate constant during the run caused by the formed chloride ion. A slight decrease was detected in some cases but it was sufficiently small so that attempts to treat it with the usual computer programs which were successful in treating common ion rate depression in vinylic systems[7,15] gave meaningless results. However, by addition of a large excess of external chloride ion, as the tetraethylammonium salt, a rate decrease of 9–58%, which was larger in the TFE-rich mixtures, was observed. An appreciable error may be involved in these experiments since the conductivity could be measured only after 5 min which was the time required to attain equilibrium. By this time a significant part of the reaction (up to 30% for the fast reactions) took place.

In order to evaluate the part of the salt effect which is not due to common ion rate depression, parallel experiments were conducted in the presence of tetraethylammonium bromide. A small rate decrease was found in the fast solvents and this was ascribed to the difficulties mentioned above. A small rate increase was found in the slower solvent, 50% EtOH. The solvolysis data for high concentrations of **1** and for reactions in the presence of added salts are given in Table II.

Table II. Solvolysis of 1 in the Presence of Added Salts[a]

% TFE in EtOH–TFE	added salt	*T*, °C	10^5k_{obsd}, s^{-1}
100		0	319 ± 105
80		0	139 ± 1.2
	0.020 M $\mathrm{Et_4NCl}$	0	72.3 ± 3.4
	0.040 M $\mathrm{Et_4NCl}$	0	57.6 ± 2.8
	0.041 M $\mathrm{Et_4NBr}$	0	154.7 ± 14
70		25	460 ± 20[b]
	0.020 M $\mathrm{Et_4NCl}$	25	375 ± 2.2
	0.039 M $\mathrm{Et_4NCl}$	25	341 ± 1.6
	0.021 M $\mathrm{Et_4NBr}$	25	436 ± 3.5
	0.041 M $\mathrm{Et_4NBr}$	25	427 ± 3.1
50		25	70 ± 1.2[c]
	0.022 M $\mathrm{Et_4NCl}$	25	60.7 ± 0.2
	0.037 M $\mathrm{Et_4NCl}$	25	59.0 ± 0.2
	0.020 M $\mathrm{Et_4NBr}$	25	66.2 ± 0.1
	0.040 M $\mathrm{Et_4NBr}$	25	64.1 ± 0.3
30		25	12.0 ± 1.4[c]
	0.026 M $\mathrm{Et_4NCl}$	25	10.9 ± 0.02

[a] [1] = 0.02 M. [b] [1] = 0.06 M. [c] [1] = 0.02–0.05 M.

The extent of common ion rate depression was evaluated from the simplified solvolysis scheme (Scheme I)[16] which involves only one intermediate, the free carbonium ion **2**. The rate equation is eq 3, and the mass law constant $\alpha = k_{-1}/k_2$ was calculated from eq 4 where k_d is the depressed rate constant in the presence of added salt from Table II, and $k_{\mathrm{obsd'}}$ is the undepressed rate constant corrected for the expected rate increase by the "normal" salt effect according to eq 5.[17] The *b* value is taken to be identical for $\mathrm{Et_4NBr}$, a noncommon ion salt, and for $\mathrm{Et_4NCl}$, the common ion salt.

$$k_{\mathrm{obsd}} = k_1/(1 + (k_{-1}/k_2)[\mathrm{X}^-]) \tag{3}$$

$$\alpha = (k_{\mathrm{obsd'}}/k_{\mathrm{d}} - 1)/[\mathrm{X}^-] \tag{4}$$

$$k_{\mathrm{obsd'}} = k_{\mathrm{obsd}}(1 + b[\mathrm{Et_4NX}]) \tag{5}$$

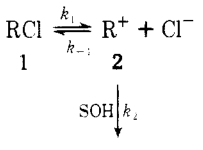
The extent of product formation from the free ion **2** is given by eq 6 and the values should be regarded as lower limits since no attempt was made to investigate whether the reaction shows a limit to the rate depression by added salt. The values are given in Table III.

Table III. α Values for $(p\text{-ClC}_6\text{H}_4)_2\text{CHCl}$ in EtOH–TFE

% TFE in EtOH–TFE (v/v)	T, °C	α, L mol^{-1}	% of product from the free R$^+$
80	0	40.8 ± 5.3[a]	≥58.5
70	25	10.0 ± 1.2[b]	≥26.0
50	25	5.9 ± 0.9[b]	≥15.7
30	25	4.0	≥9.2

[a] Average of four experiments. [b] Average of two experiments.

Scheme I

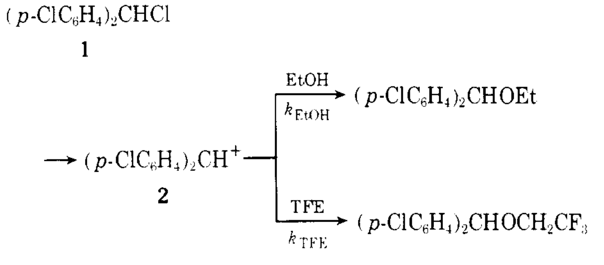


% of products formed from the free ion

$$= ((k_{\text{obsd}'} - k_{\text{d}})/k_{\text{obsd}'})\cdot 100 \quad (6)$$

It is obvious that the α values are highly sensitive to the $k_{\text{obsd}'}$ (or the k_{obsd}) value and this is demonstrated by the α values of 40.8 and 20.6 which are based on the k_{obsd} values at 20 and 4 mM, respectively, in 20% EtOH–80% TFE.

The solvolysis products are 4,4′-dichlorobenzhydryl ethyl ether (**3**) and 4,4′-dichlorobenzhydryl trifluoroethyl ether (**4**). The product distribution was obtained by gas chromatography, using an appropriate calibration curve. Relative rate constants for capture of the intermediate **2** were calculated by assuming that the competition for **2** depends on the molar concentrations of the nucleophilic solvent components (reaction 7).



(7)

The ratio of the rate constants was calculated from eq 8 where [TFE], [EtOH], [ROCH$_2$CH$_3$], and [ROCH$_2$CF$_3$] are the molar concentrations of the solvents and the products, respectively.

$$k_{\text{TFE}}/k_{\text{EtOH}} = ([\text{EtOH}]/[\text{TFE}])\cdot([\text{ROCH}_2\text{CF}_3]/[\text{ROCH}_2\text{CH}_3]) \quad (8)$$

The $k_{\text{TFE}}/k_{\text{EtOH}}$ ratios which are given in Table IV are low, being 0.017–0.032, and the trend is for a higher ratio in EtOH-rich medium. However, if the large experimental error in the ratio at 60% TFE is considered, the ratios are remarkably constant over an appreciable region of solvent composition.

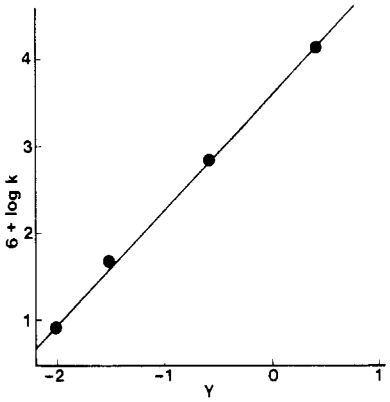
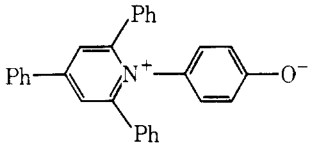


Figure 1. log k_{obsd} vs. Y plot for the solvolysis of **1** in EtOH–TFE at 25 °C.

E_{T} Values of EtOH–TFE Mixtures. An independent measure of the ionizing power of the medium was sought by measuring the position of the maximum of the internal charge transfer band of 1-(p-hydroxyphenyl)-2,4,6-triphenylpyridinium betaine (**5**) (Dimroth's Betaine 1[18]) as a function of



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the solvent composition. Triethylamine (0.1 M) was added to this mixture since otherwise protonation of the betaine oxygen resulted in the disappearance of the charge transfer band. The spectral data and the derived values of the transition energies, E_{T}, are given in Table V.

Other Benzhydryl Derivatives. Preliminary experiments showed that the solvolysis rate of benzhydryl chloride in solvent mixtures rich in TFE is too high to be measured accurately by conventional conductometric methods. For example, k_{obsd} is ca. 0.027 s^{-1} in pure TFE at 0 °C. On the other hand, the much less reactive benzhydryl 3,5-dinitrobenzoate was not sufficiently soluble in TFE-rich mixtures in order to enable kinetic measurements.

Discussion

The solvent effect, the common ion rate depression, and the products distribution are consistent with a k_{c} solvolysis mechanism for **1** which initiates by a C–Cl bond heterolysis.

The Solvent Effect. When k_{obsd} values at 25 °C for **1** were plotted against the Y values for 20, 50, and 80% EtOH–TFE from the work of da Roza, Andrews, and Keefer[11] and the value for pure EtOH,[2] a linear plot (Figure 1) was obtained with a slope m = 1.30 ± 0.02 (r = 0.99964). This is the first example of a linear Grunwald–Winstein plot in EtOH–TFE

Table IV. Solvolysis Products of p,p'-Dichlorobenzhydryl Chloride in EtOH–TFE at 25 °C

% TFE (v/v) in EtOH–TFE	[TFE]/[EtOH][a]	% ROCH$_2$CF$_3$	[ROCH$_2$CF$_3$]/[ROEt][a]	100$k_{\text{TFE}}/k_{\text{EtOH}}$[b]
60	1.21	3.7 ± 1	0.0384	3.18 ± 0.90
70	1.89	4.8 ± 1	0.0504	2.67 ± 0.58
80	3.23	7.6 ± 1	0.0823	2.55 ± 0.36
90	7.27	15.0 ± 1	0.176	2.43 ± 0.20
95	15.36	21.0 ± 1	0.266	1.73 ± 0.10

[a] Molar ratio. [b] From eq 8.

Table V. UV Spectra and $E_T(1)$ Values for 1-(p-Hydroxyphenyl)-2,4,6-triphenylpyridinium Betaine in EtOH-TFE[a]

% TFE (v/v) in EtOH-TFE	X_{TFE}[b]	Y[c]	λ_{max}, nm	ϵ	λ_{max}, nm	ϵ	E_T, kcal mol^{-1}
0	0	−2.033	305	28 200	468	1960	61.2
10	0.083		305	27 200	455	1740	62.8
20	0.168	−1.515	305	27 000	445	1690	64.3
30	0.257		305	27 300	436	1760	65.6
40	0.349		306	27 400	426	1830	67.1
50[d]	0.447	−0.588	306	27 500	419	1870	68.3
60	0.548		306	27 300	408	1780	70.0
70	0.652		306	27 600	405	2090	70.6
80	0.763	0.406	306	27 200	399	2120	71.7
90	0.880		305	27 700	393	2180	72.8
100	1.000	1.147	306	27 900	389[e]	2270	73.5

[a] Measurements in the presence of 0.1 M Et_3N; [5] = 5.6–6.0 × 10^{-4} M. [b] Mole fraction of TFE. [c] From ref 11. [d] Without Et_3N: λ_{max} 308 nm (ϵ 22 000). No absorption was observed at 419 nm. [e] Reported[7] 390 nm (ϵ 2900).

Table VI. Ionizing Power Parameters (Y) in EtOH-TFE Mixtures

% TFE (v/v) in TFE-EtOH	Y from log k_{obsd}	Y from $E_T(1)$	Y from t-BuCl[a]
100			1.147[b]
90	0.77	0.80	
80			0.406
70	0.07	0.06	
60	−0.27	−0.28 (−0.12)[c]	
50			−0.588
40	1−0.87	−0.90	
30	−1.22	−1.24	
20			−1.515
10	−1.69	−1.68	
0			−2.033[d]

[a] From ref 11. [b] From ref 6. [c] Value from Table V (see text). [d] From ref 2.

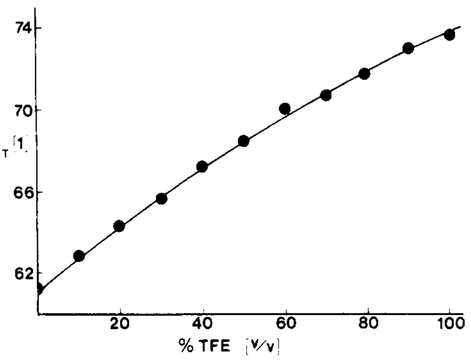

Figure 2. Change of $E_T(1)$ values with the percent volume of TFE in EtOH-TFE.

since the solvolyses of substituted benzyl halides in the same media gave curved relationships.[11] The m value is one of the highest known and points to the absence of a significant solvent participation in the solvolysis in the entire solvent range. Values of m higher than unity were found for other solvolyses which proceed via the k_c route, e.g., 1.20 for 1-adamantyl bromide[19] in aqueous EtOH and 1.20 for α-phenylethyl chloride[20] and 1.71 for benzhydryl chloride[1b] in AcOH-HCOOH mixtures.

The actual m value which measures the sensitivity to Y alone, when contribution from the solvent nucleophilicity is excluded (m of eq 1), may be even higher than 1.30. We recently showed that a linear relationship of N and Y (eq 9) holds for several binary solvent mixtures.[13] Combination of eq 1 and 9 gives eq 10.

$$N = aY + b \tag{9}$$

$$m(\text{eq } 1) = m \text{ (calcd by eq 2)} - al \tag{10}$$

The EtOH-TFE mixtures are unique among the mixtures investigated in that a of eq 9 is negative and appreciable, being $a = -0.83$, since increase in the TFE content increases Y but decreases N. Consequently, since $l \geqslant 0$ the m value of eq 1 is $\geqslant 1.30$.

By applying eq 1 we obtained $m = 1.41 \pm 0.14$, $l = 0.16 \pm 0.2$, and $r = 0.994$. The low value and the high error in l show that the addition of the nucleophilicity parameter does not improve significantly the correlation, i.e., the higher rates in TFE-rich media are due to the higher ionizing power.

High m values of eq 2 (1.65–2.08) were found recently for the solvolysis of several substituted benzhydryl bromides in TFE-C_6H_6 mixtures.[21] These values were interpreted as due to increased ion pair return with the increase in the molar fraction of the less ionizing solvent. The gap between the observed rate constant k_t and the ionization rate constant k_{ion} in benzene is therefore larger than in TFE. Consequently, the observed m from the log k_t vs. Y plot is higher than the expected value for a log k_{ion} vs. Y plot. A similar explanation does not apply to our high m value since if the ion pair return increases on decreasing the nucleophilicity it will be more pronounced in solvent mixtures richer in TFE. The m value of the log k_{ion} vs. Y plot would then be expected to be higher than the observed value of 1.30. While we have no independent evidence for ion pairs in our system, the linearity of the mY plot suggests that if ion pairing during the solvolysis of **1** is important, its extent is either proportional to that in the solvolysis of *tert*-butyl chloride or it is linear with Y in the EtOH-TFE mixtures studied.

Y Values in EtOH-TFE Mixtures. Only a few Y values in EtOH-TFE mixtures are available from the solvolysis of t-BuCl. The linearity of Figure 1 suggests that the solvolysis of 4,4′-dichlorobenzhydryl chloride can serve as a secondary source for additional Y values for TFE-EtOH mixtures. By using the data of Table I and Figure 1, the new Y values of Table VI were obtained.

An enormous difference between the Y values which are based on solvolytic data and those based on the solvatochromic changes of the betaine **5** were observed in TFE-H_2O mixtures.[7] It was therefore of interest to evaluate the polarity of EtOH-TFE mixtures by a nonkinetic approach which is based on the solvatochromic shift of the internal charge transfer band of the betaine **5**. Table V shows that by this approach TFE is much more polar than EtOH. Plots of $E_T(1)$ values vs. the percent volume of TFE in the mixture (Figure 2) or vs. Y (Figure 3) are nonlinear, but they can be used for evaluating unknown $E_T(1)$ and Y values. Comparison of the Y values which were obtained from Figures 1 and 3 (Table VI) shows a very good agreement between the two sets of values.

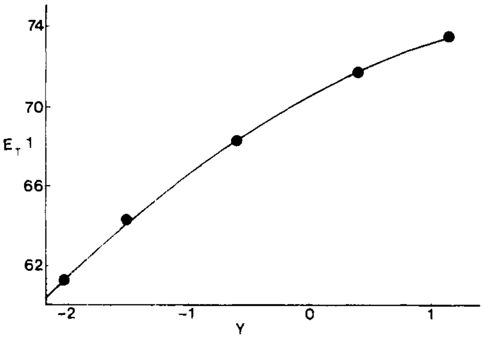

Figure 3. Change of $E_T(1)$ values with Y in EtOH–TFE.

The only discrepancy is in the Y value at 60% TFE–40% EtOH, but Figure 2 shows deviation of the measured E_T value at this composition. When the E_T value from the plot of Figure 2 is used for calculating the Y value from Figure 3, the value agrees with that based on the solvolysis data.

The correspondence between the two sets of Y values which are based on completely different model processes strengthens the case for their use for correlation purposes. Moreover, since the spectroscopic model does not distinguish implicitly between the several possible intermediates, we conclude that ion pair return is either unimportant in the solvolyses of **1** and *tert*-butyl chloride, or that its extent is proportional to Y.[22]

In view of the complex behavior showed in the solvolysis of 7-methyl-7-norbornyl-OTs[23] and several α-arylvinyl derivatives[7] in TFE–H_2O mixtures, it is gratifying that the behavior of all the compounds studied so far is accounted for by eq 1. Substrates solvolyzing via the k_c route, such as **1**, 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl tosylate,[24] and adamantyl bromide,[24] give linear log k vs. Y plots with m = 0.89–1.50. For benzyl halides which give curved log k vs. Y plots and interpolated low and even negative m values, eq 1 gives m (eq 1) values which are expected for benzyl substituted derivatives when the lN term is taken into account.[13] The apparent less complicated behavior in EtOH–TFE media is probably due to a lower number of variable solvent parameters than in TFE–H_2O, since the structures and the dielectric constants of the two pure components are very similar. These mixtures therefore seem suitable for studying solvent effects when N and Y change gradually at almost isodielectric conditions.

Comparison of the $E_T(1)$ values in EtOH–TFE and in TFE–H_2O[7] reveal an interesting behavior. The $E_T(1)$ value of pure TFE is the highest and addition of either EtOH or water decreases the $E_T(1)$ value, although this effect is more pronounced on addition of EtOH. Apparently, the higher acidity of TFE[10] which results in high hydrogen bonding donor ability is more important in solvatochromic changes of the betaine **5** than changes in the dielectric constant. It is impossible at present to evaluate the generality of this behavior since E_T values in acidic media are not available.

Selectivity of the 4,4′-Dichlorobenzhydryl Cation 2. The appearance of common ion rate depression is a compelling evidence for the intermediacy of a free ("dissociated") carbonium ion intermediate.[16b,c] The mass law constant α measures the selectivity of the cation toward Cl^- and the solvent. Within structurally related substrates α increases with the lifetime and the stability of the cationoid intermediate.[14,16a]

Common ion rate depression was amply demonstrated in the solvolysis of substituted benzhydryl chlorides in aqueous acetone. For example, α = 10 and 33 for benzhydryl chloride and *p*-methylbenzhydryl chloride in 80% acetone[14a] and 2.1 and 0.7 for benzhydryl chloride and *p*-nitrobenzhydryl chloride, respectively, in 70% acetone.[14b] Substituent and solvent effects showed that α increases with the electron donating ability of the substituents and decreases with the increase in the water content of the medium.[14]

Tables II and III show that the common ion depression in the solvolysis of **1** is appreciable. For example, addition of 40 mmol of Cl^- in 20% EtOH–80% TFE (Y = 0.41) at 0 °C reduces k_{obsd} by 58% while k_{obsd} for benzhydryl chloride decreases by only 13% on addition of 0.1 M of LiCl in 80% acetone (Y = 0.67) and extrapolation gives a 5.5% decrease in k_{obsd} by addition of 40 mmol of Cl^-.

In order to enable a closer comparison with previous data we applied the linear free energy relationship in substituent effects suggested by Mindl and Večeřa[25] for disubstituted benzhydryl bromides and estimated that the relative solvolysis rate ratio $k_{obsd}(1)/k_{obsd}(Ph_2CHCl)$ is 0.085 at 0 °C. From the semiquantitative relationship between k_{obsd} and α values in 70% acetone,[14b] **1** should have an α value of 1.5–2 in 70% acetone. Since the Y value of 70% acetone (0.13)[2] is close to that of 70% TFE–30% EtOH (0.06) while the α value for **1** in this solvent is 10 we conclude that the selectivity of **1** is higher in TFE–EtOH than in aqueous acetone of the same ionizing power. This is not surprising since the nucleophilicity of 70% TFE–30% EtOH[24] is much lower than that of 70% acetone[4d] and the lifetime of **2** before irreversible collapse with the solvent should be longer.

Table III shows that α decreases with the increase of the ethanol content of the media, and this is reminiscent of the decrease of α for 1-(*p*-methoxyphenyl)-2-methylpropen-1-yl bromide with the increase of the water content in aqueous TFE.[7] The effect of a binary nucleophilic solvent on the α values was discussed in this later case. It was suggested that α will increase on enhancing the cation solvation and decrease by enhanced anion solvation, by increasing the concentration of the more nucleophilic component and by increasing the dielectric constant. Since the dielectric constant does not change significantly in our media, and TFE is a better anion solvator than EtOH, the higher α values in the TFE-rich media are due to the reduced nucleophilicity of the medium which more than compensates for the reduced nucleophilicity of the better solvated Cl^- [26] and for the reduced cation solvation.[26]

Table III also gives the extent of product formation from the free ion **2**, as calculated by eq 6. The difficulty associated with measurement of a small conductivity change in the presence of a large amount of added salt prevented the use of higher salt concentrations so that the values of Table III are minimum values for the extent of product formation from the free ion. While we believe that the actual values are much higher, at present it can be concluded that a large fraction, e.g., 59% of the products in 80% TFE–20% EtOH, is derived from the free *p,p*′-dichlorobenzhydryl cation. Ion pairs can still be involved in an internal return process.[27]

Another measure of selectivity of the ion **2** are the product distributions given in Table IV. The lower nucleophilicity of TFE is expected to result in a k_{TFE}/k_{EtOH} ratio lower than unity, but the observed ratios of ca. 0.025 are much lower than the values of 0.8–2.6 obtained for the 1-adamantyl system[12,24] or the values of 0.8–1.4 for the 2-adamantyl system,[12] and lower than the values for the substituted benzyl halides.[11] This can be understood if products are formed in these systems from collapse of solvent separated ion pairs.[8,28] In this case the stability of the TFE and EtOH separated ion pairs will be at least as important as the nucleophilicities of the solvent components.

Our k_{TFE}/k_{EtOH} value can be tentatively taken as a ratio for capture of a free cation by the two solvents. Since N(EtOH) − N(TFE) = 2.87[4d] and log (k_{EtOH}/k_{TFE}) = 1.6, the selectivity of **2** toward EtOH and TFE is lower than the coresponding selectivity of methyl tosylate, but it is still appreciable. Consequently, by the product distribution criterion, as well as by the kinetics, the ion **2** is relatively long lived.

The selectivity of substituted benzhydryl chlorides in aqueous EtOH was determined from the product distribution. The $k_{\mathrm{EtOH}}/k_{\mathrm{H_2O}}$ ratios were found to increase on increasing the water content of the medium.[29] Three possible explanations for this effect were proposed: (a) a greater stabilization of the intermediates in the more polar solvent with a consequent increased selectivity; (b) an increased dissociation to more selective free ions; (c) enhanced nucleophilicity of ethanol in the more polar media. The $k_{\mathrm{TFE}}/k_{\mathrm{EtOH}}$ ratios for **2** are nearly constant at $X_{\mathrm{TFE}} = 0.65$–0.88. However, there is a trend for lower ratios in the TFE-rich media, i.e., for a relatively higher rate for the faster nucleophile (higher selectivity) in a medium of higher ionizing power. Explanation (b) can be excluded for our system where **2** is already a free ion, but either (a) or (c) can account for the trend in the $k_{\mathrm{TFE}}/k_{\mathrm{EtOH}}$ ratios. Further decision between these two alternatives is difficult. A more general question is to what extent the $k_{\mathrm{TFE}}/k_{\mathrm{EtOH}}$ ratios which were derived by assuming that eq 7 and 8 hold reflect the selectivities of the ion at different compositions of TFE–EtOH. TFE–EtOH mixtures show severe deviations from ideal solution behavior[9] and the presence of a mixed hydrogen bond species, probably $CF_3CH_2OH\cdots OHCH_2CH_3$, was shown by the infrared spectra. The stability of this species in CCl_4 is higher than either that of the TFE dimer or the EtOH dimer.[9] Consequently, the concentrations of the three hydrogen-bonded species and probably of the monomers and of higher aggregates and their respective nucleophilicities should be considered when discussing the product-forming step. Hence, caution should be exercised when small differences in the $k_{\mathrm{TFE}}/k_{\mathrm{EtOH}}$ ratios calculated only from the stoichiometric concentrations and nucleophilicities of EtOH and TFE are used as mechanistic probes.

Experimental Section

Melting points were determined with a Fisher instrument and are uncorrected. NMR spectra were recorded with Varian HA-100 or T-60 instruments, IR spectra were recorded with a Perkin-Elmer 337 instrument, and mass spectra were recorded with a MAT-311 instrument.

Materials. 4,4′-Dichlorobenzhydryl chloride, mp 61–63 °C (lit.[30a] mp 62.5–63.5 °C), was prepared from 4,4′-dichlorobenzhydrol and hydrogen chloride according to Nishida.[30b] Benzhydryl 3,5-dinitrobenzoate was prepared by refluxing benzhydrol (25 g, 0.135 M) and 3,5-dinitrobenzoyl chloride (27 g, 0.11 M) in a mixture of benzene (200 mL) and pyridine (21.5 g) for 2 h, extracting first with dilute aqueous hydrochloric acid and then with dilute aqueous sodium bicarbonate solution, drying ($MgSO_4$), and evaporating the solvent. The recrystallized material had mp 144–146 °C (lit.[31] mp 142 °C).

Solvents. β,β,β-Trifluoroethanol (Halocarbon) was refluxed for 2 h over a mixture of 8:1 of anhydrous $CaSO_4$ and anhydrous K_2CO_3. The fraction boiling at 70–74 °C was used for the kinetic experiments. Absolute ethanol (Frutarom) was purified according to Lund and Bjerrum,[32] 2,6-lutidine and triethylamine were distilled from solid potassium hydroxide, and 2,6-lutidinium hydrochloride was prepared by dissolving the base in HCl and evaporation of the water.

4,4′-Dichlorobenzhydryl Ethyl Ether (3). To a solution of 4,4′-dichlorobenzhydryl chloride (1.01 g, 3.72 mM) in absolute ethanol (40 mL), sodium (0.39 g, 17 mM) in absolute ethanol (5 mL) was added, and the mixture was refluxed for 4 days. The sodium chloride was filtered, the solvent was evaporated to dryness, and the remainder was separated by chromatography over alumina using petroleum ether (60–80 °C). The fraction which contained the ether was distilled and the material boiling at 165–172 °C (8 mm) was collected and repurified by gas chromatography. The purified ether has δ (CCl_4) 1.25 (3 H, t, Me), 3.45 (2 H, q, CH_2), 5.18 (1 H, s, CH), 7.18 (8 H, s, Ar); ν_{max} (KBr) 2990, 1600, 1090, 820, 795, 530 cm^{-1}; *m/e* 284, 282, 280 (M, 1, 6, 9), 254, 252, 250 (Ar_2CO^+, 3, 15, 22), 239, 237, 235 (Ar_2CH^+, 5, 25, 37), 171, 169 (ArCHOEt, 7, 17), 165 (Ph_2CH^+, 30), 141, 139 ($ArCO^+$, 38, 100), 113, 111 (C_6H_5Cl, 19, 42).

Anal. Calcd for $C_{15}H_{14}Cl_2O$: C, 64.07; H, 5.01; Cl, 25.2; OEt, 16.02. Found: C, 63.98; H, 5.04; Cl, 24.5; OEt, 15.1.

Another fraction from the distillate gave a solid, mp 146–148 °C, which was identified as 4,4′-dichlorobenzophenone by melting point, mixture melting point, IR (ν_{max} 1655 cm^{-1}, C=O), and NMR (CCl_4) δ 7.55 (AA′BB′ q)). 4,4′-Dichlorobenzophenone was also obtained from reaction mixtures which remained for a few days before workup, from recrystallized sample of 4,4′-dichlorobenzhydryl chloride, from the ether **3** after long standing, from several attempts to prepare **3** by reaction of 4,4′-dichlorobenzhydryl chloride in absolute ethanol containing sodium ethoxide or a catalytic amount of concentrated sulfuric acid, as well as from attempts to prepare the ether **4** from **1** in trifluoroethanol/sodium trifluoroethoxide.

4,4′-Dichlorobenzhydryl β,β,β-Trifluoroethyl Ether (4). 4,4′-Dichlorobenzhydryl chloride (0.47 g, 1.73 mM) was added to a suspension of potassium carbonate (0.26 g, 2.6 mM) in trifluoroethanol (20 mL) at room temperature. The mixture was warmed for a few minutes until a complete dissolution of the benzhydryl chloride took place, the inorganic salts were filtered, and the solvent was evaporated. The remaining oil was chromatographed over alumina using petroleum ether (40–60 °C) as the eluent. One fraction was identified as 4,4′-dichlorobenzhydryl β,β,β-trifluoroethyl ether (**4**) from its analysis and spectra: ($CDCl_3$) δ 3.78 (2 H, q, CH_2), 5.45 (1 H, s, CH), 7.21 (8 H, s, Ar); ν_{max} 2940, 1600, 1495, 1415, 1280, 1170, 1120, 1090, 1015 cm^{-1}; *m/e* 338, 336, 334 (M, 4.5, 27, 40), 301, 299 (M − Cl, 15, 41), 254, 252, 250 ((p-$ClC_6H_4)_2CO$, 0.6, 3, 5), 239, 237, 235 ((p-$ClC_6H_4)_2CH^+$, 11, 66, 100), 225, 223 (M − ClC_6H_4, 16, 44), 201, 199 (M − Cl − OCH_2CF_3, 11, 27), 165 (fluorenyl$^+$, 68), 141, 139 (p-$ClC_6H_4CO^+$, 33, 91), 113, 111 ($C_6H_4Cl^+$, 14, 39).

Anal. Calcd for $C_{15}H_{11}Cl_2F_3O$: C, 53.76; H, 3.31; F, 17.00; Cl, 21.15. Found: C, 53.75; H, 3.18; F, 16.71; Cl, 21.12.

Product Analysis. The product distribution was determined on a 5% SE-30 column on 60/80 Chromosorb W (5 ft × ⅛ in.) at 170 °C at 1.3 atm of He. The retention times under these conditions were 7 min for the trifluoroethyl ether and 10.5 min for the ethyl ether. The solutions were prepared from reaction mixtures which were kept for 10 half-lives at 25 °C. Calibration curves of the purified products were used to obtain the correct product analysis.

E_T Values. These values were calculated from the spectra of the betaine **5**, determined with a Gilford 2400-S spectrophotometer.

Kinetic Work. The substrate was dissolved in absolute ethanol which was kept for 15 min at the reaction temperature. The appropriate amount of TFE was added at the reaction temperature and the solution was introduced after mixing to a conductance cell at the reaction temperature. The resistance of the solution was measured with a Pye Conductance Bridge. When solutions of the tetraethylammonium salts were added, the salts were dried at low pressure for 1 day and dissolved in TFE before the beginning of the measurements. It was found that the conductance was linear with the concentration of either 2,6-lutidinium hydrochloride or of hydrochloric acid in 80% EtOH. The first-order rate constants were calculated from the logarithms of the conductivity difference at the beginning and at the end of the reaction, by using the KINDAT program.[33]

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Registry No.—**1**, 782-08-1; **3**, 57070-99-2; **4**, 66922-40-5; **5**, 17658-06-9; benzhydryl 3,5-dinitrobenzoate, 21573-83-1; benzhydrol, 91-01-0; 3,5-dinitrobenzoyl chloride, 99-33-2; β,β,β-trifluoroethanol, 75-89-8; ethanol, 64-17-5; 4,4′-dichlorobenzophenone, 90-98-2.

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Kinetics of the Acid-Catalyzed α-Bromination of Aliphatic Acids

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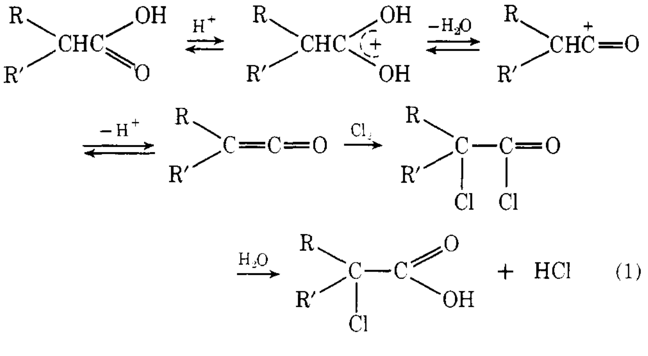
Aliphatic acids were found to be easily α-brominated in good yields (78–95%) by molecular bromine in the presence of chlorosulfonic acid as a catalyst in 1,2-dichloroethane as a solvent at 84 °C. Kinetic study shows that the rate is expressed as: $v = k_{\mathrm{obsd}}[\mathrm{RCO_2H}][\mathrm{Br_2}]$, where k_{obsd} is proportional to the initial concentration of chlorosulfonic acid at an early stage. The substituent effect fits Taft's equation with little steric effect, giving $\rho^* = -0.97$ at 60 °C, which suggests that the reaction is accelerated by electron-releasing groups, thus the reactivity increases as follows: $CH_3CO_2H < CH_3CH_2CO_2H < CH_3CH_2CH_2CO_2H < (CH_3)_2CHCH_2CO_2H < (CH_3)_2CHCO_2H < (CH_3CH_2)_2CHCO_2H$. The mechanism involving ketene intermediates is discussed.

Ketones and aldehydes are α-halogenated by molecular halogen in the presence of acid or base catalysts;[2] the reaction mechanism is said to involve the corresponding enol which is in equilibrium with the keto form. The rate-determining step in most cases is the enolization, hence the rate is independent of the concentration and nature of halogen, i.e., chlorination, bromination, and iodination under the same conditions proceed at the same rate irrespective of their concentration.[2b,3]

In the Hell–Volhard–Zelinsky reaction the aliphatic acids are α-halogenated by halogen in the presence of phosphorus halides.[4] Little et al. have proposed that this reaction proceeds via enol or ketene intermediate with little evidence,[5] but most workers prefer the intermediacy of enol.[4] Only one kinetic study for the Hell–Volhard–Zelinsky reaction was reported, in which the rate was said to depend on the concentration of bromine,[4c] in contrast to the behavior of ketones.

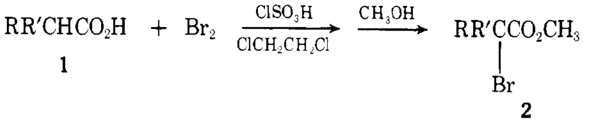
We have reported previously that aliphatic acids can be α-chlorinated by a Cl_2–O_2 mixture in the presence of a strong acid such as chlorosulfonic or fuming sulfuric acid,[6] and we suggested that the reaction intermediate may be ketene on the basis of NMR and laser-Raman spectral data, deuterium tracer study, and trapping by aniline forming acetanilide.[7] However, no kinetic study could yet be done because of the low solubility of chlorine.



The present paper reports the application of this chlorination method to bromination of aliphatic acids and also the kinetics of bromination which presents further support and detailed information for the mechanism of reaction.

Results and Discussion

α-Bromination. It was found that aliphatic acids could also be easily α-brominated by molecular bromine in 1,2-dichloroethane using a strong acid catalyst, chlorosulfonic acid, as in the case of chlorination, but the presence of a radical trapper such as molecular oxygen was unnecessary. The yields and physical properties for identification of esters of α-bromo acids are listed in Tables I and II, respectively. The yields are satisfactory (78–95%) under these conditions except for bromination of acetic acid.



$$\underset{\mathbf{1}}{\mathrm{RR'CHCO_2H}} + \mathrm{Br_2} \xrightarrow[\mathrm{ClCH_2CH_2Cl}]{\mathrm{ClSO_3H}} \xrightarrow{\mathrm{CH_3OH}} \underset{\mathbf{2}}{\mathrm{RR'}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}}\mathrm{CO_2CH_3}} \quad (2)$$

Kinetics of α-Bromination. The rate of α-bromination of isobutyric acid in 1,2-dichloroethane at 60 °C using 0.05 M chlorosulfonic acid as a catalyst fits eq 3.

$$v = k_{\mathrm{obsd}}[\mathrm{RR'CHCO_2H}][\mathrm{Br_2}] \quad (3)$$

The first-order dependence of rate on bromine concentration was confirmed at various concentrations of bromine (Table III). Equation 3, which depends on $[\mathrm{Br_2}]$, suggests that

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