Solvolyses of *para*-Substituted Benzoyl Chlorides in Trifluoroethanol and in Highly Aqueous Media

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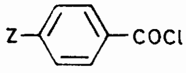
Rates of solvolyses of *para*-Z-substituted benzoyl chlorides (Z = OMe, Me, Cl, or NO_2) are reported for aqueous trifluoroethanol mixtures. Additional kinetic data for highly aqueous binary mixtures (with acetone and methanol cosolvents) were obtained from an improved rapid-mixing (0.4 s) conductimetric technique. These data and additional literature data (including those for carboxylic acids) are interpreted using the equation $\log(k/k_0)_{RCl} = mY_{Cl}$, where m is the sensitivity of the substrates (RCl) to solvent ionizing power (Y_{Cl}). A satisfactory Hammett–Brown correlation with σ^+ for solvolyses in trifluoroethanol–water shows the rate-enhancing effects of electron donation. These results support previous evidence that solvolyses of acid chlorides (possibily including *p*-nitrobenzoyl chloride) can proceed by an S_N2 process in which positive charge develops on the carbonyl group. An independent nucleophilically assisted process is carbonyl addition, in which negative charge develops on the carbonyl group; this process appears to be particularly favourable in methanol and in high percentage methanol–water mixtures, and has a lower sensitivity to solvent ionizing power (m) than the S_N2 process. Competition between the two processes leads to curved mY_{Cl} plots for a wide range of alcohol–water mixtures, the extent and position (solvent composition) of curvature changing in the expected order: OMe, Me, H, Cl, NO_2. The results are not consistent with a solvation effect as the cause of the curved mY_{Cl} plots.

Kinetic studies in fluorinated alcohols have provided new insights into the heterolytic reactivity of organic compounds in aqueous solutions, particularly into the role of water as nucleophile.[1–3] Our previous work on primary,[1a] secondary,[2b] and tertiary[2b,3] alkyl substrates is interpreted in terms of a spectrum of mechanisms from S_N2 to S_N1. Interpretation of kinetic data for solvent effects is aided by equation (1),[3a] in which m is the

$$\log(k/k_0)_{RX} = mY_X \qquad (1)$$

sensitivity of the substrate (RX, with X being the leaving group) to changes in solvent ionizing power (Y_X is based on solvolyses of adamantyl substrates and for this work we require Y_{Cl}[3a]) and k is the solvolysis rate relative to 80% v/v ethanol–water (k_0). As the reaction mechanism changes towards S_N1, m increases and data for trifluoroethanol approach the correlation line for binary mixtures of water and the more nucleophilic alcohols.[1,2] Application of these mechanistic criteria to solvolyses of benzoyl chloride showed deviations for trifluroroethanol, but also more complex behaviour which led to the proposal that there were two distinct, competing, nucleophilically assisted mechanistic pathways:[4] (i) carbonyl addition, having a low value for m and separate correlation lines for different binary mixtures; (ii) S_N2, having a much greater m value [equation (1)], but virtually identical correlation lines for different binary mixtures.

Independent evidence for nucleophilically assisted solvolyses, obtained from rate–product correlations in the presence of added *o*-nitroaniline,[4b] support our proposal[4a] that even solvolyses in relatively polar solvents (*e.g.* 50% w/w acetone–water) are not S_N1 processes. We have now investigated the mechanistic change from carbonyl addition to S_N2 by studying solvolyses of *para*-substituted benzoyl chlorides (1; Z = OMe, Me, Cl, or NO_2) in relatively polar solvents (highly aqueous) and/or weakly nucleophilic solvents (trifluoroethanol–water). This has required studies of solvents in which the substrates are very sparingly soluble, including some relatively rapid processes. Our interpretation of solvent effects on reactivity, including data obtained by previous workers,[5] provide quantitative information on the change of mechanism with variations in both solvent and substituent Z.



(1)

Results

Kinetic data for 97 and 70% w/w trifluoroethanol–water are shown in Table 1. Additional kinetic data for relatively rapid solvolyses in highly aqueous methanol–water and acetone–water mixtures are shown in Table 2. Two of the higher rate constants for (1; Z = OMe) were obtained by extrapolations from data at lower temperatures. Other data for aqueous media are summarized in Table 3, which includes data already published.[4b,5b,5c]

The experimental difficulties associated with this type of project have already been discussed.[4b,6] We have further reduced times for mixing and dissolving substrates by working with a smaller conductivity cell. Unfortunately it appears that rapid mixing of aqueous solutions can be achieved more easily than formation of truly homogeneous dilute solutions of sparingly soluble organic substrates. We employed the mixing of water and dilute HCl to monitor mixing rates, which have been reduced from 0.8 s in our previous work[4b] to 0.4 s in the smaller cell (this work) and further to only 0.20 s using a cylindrical slice-shaped cell and a spring-loaded syringe.[7] To our initial surprise and disappointment the cylindrical cell gave increased problems due to aggregation of substrate, and further work is needed to translate all the benefits of improved mixing to credible studies of even faster reactions of sparingly soluble solutes. It now appears that very rapid mixing may give rise to problems due to local supersaturation of substrate.

Discussion

Substituent Effects on Reactivity.—A Hammett–Brown σ^+ plot for solvolyses of *para*-substituted benzoyl chlorides in 97% w/w trifluoroethanol–water is shown in Figure 1. The reaction is strongly favoured by electron donation in marked contrast to

Table 1. Solvolysis rate constants (k) for *para*-Z-substituted benzoyl chlorides (**1**) in trifluoroethanol–water[a]

Solvent[b]	Z	Temp./°C	k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
97T	OMe	10.0	$(1.33 \pm 0.04) \times 10^{-1}$		
		25.0	$(5.66 \pm 0.06) \times 10^{-1}$	15.6	−7.3
	Me	10.0	$(7.84 \pm 0.09) \times 10^{-3}$		
		25.0	$(3.49 \pm 0.02) \times 10^{-2}$	16.1	−11.1
	H	9.8	$(7.45 \pm 0.03) \times 10^{-4}$		
		25.0[d]	$(3.63 \pm 0.03) \times 10^{-3}$	16.9	−13.1
	Cl	25.0	$(4.46 \pm 0.06) \times 10^{-4}$	17.5	−15.2
		40.0	$(1.93 \pm 0.05) \times 10^{-3}$		
	NO_2	70.0	$(3.42 \pm 0.08) \times 10^{-4}$		
		60.0	$(1.59 \pm 0.01) \times 10^{-4}$		
		50.0	$(7.54 \pm 0.01) \times 10^{-5}$		
		40.0	$(3.67 \pm 0.15) \times 10^{-5}$	15.2	−30.4
		25.0[c]	9.9×10^{-6}		
70T	OMe	−5.0	$(6.89 \pm 0.02) \times 10^{-2}$		
		10.0	$(3.82 \pm 0.06) \times 10^{-1}$	16.7	−1.4
		25.0[c]	1.8		
	Me	10.0	$(2.72 \pm 0.05) \times 10^{-2}$		
		25.0	$(1.41 \pm 0.01) \times 10^{-1}$	17.9	−2.4
	H	10.0	$(3.59 \pm 0.01) \times 10^{-3}$		
		25.0	$(1.95 \pm 0.01) \times 10^{-2}$	18.4	−4.8
	Cl	25.0	$(2.85 \pm 0.01) \times 10^{-3}$	18.4	−8.6
		40.0	$(1.32 \pm 0.01) \times 10^{-2}$		

[a] Determined conductimetrically in duplicate in a small-volume (2—3 ml), rapidly stirred conductivity cell; errors shown are average deviations. [b] Solvent code: T = % w/w trifluoroethanol–water. [c] Calculated from data at other temperatures. [d] In agreement with our published value (ref. 4*b*).

Table 2. Solvolysis rate constants (k) for *para*-Z-substituted benzoyl chlorides (**1**) in aqueous acetone and aqueous methanol[a]

Solvent[b]	Z	Temp./°C	k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
40A	OMe	10.0	$(2.22 \pm 0.01) \times 10^{-1}$		
		25.0	$(9.79 \pm 0.18) \times 10^{-1}$	16.0	−4.9
	Cl	25.0	$(9.08 \pm 0.08) \times 10^{-3}$	15.1	−17.3
		40.0	$(3.22 \pm 0.03) \times 10^{-2}$		
30A	Cl	10.0	$(4.26 \pm 0.01) \times 10^{-3}$		
		25.0	$(2.01 \pm 0.02) \times 10^{-2}$	16.8	−10.1
20A	Me	9.9[d]	$(2.75 \pm 0.06) \times 10^{-1}$		
		25.0	1.42 ± 0.01	17.7	1.4
	Cl	9.9	$(9.11 \pm 0.12) \times 10^{-3}$		
		25.0	$(4.79 \pm 0.03) \times 10^{-2}$	17.3	−6.7
		40.0	$(1.93 \pm 0.06) \times 10^{-1}$		
	NO_2	25.0	$(5.49 \pm 0.12) \times 10^{-2}$	12.7	−21.8
		40.0	$(1.60 \pm 0.03) \times 10^{-1}$		
10A	Cl	10.0	$(1.94 \pm 0.01) \times 10^{-2}$		
		25.0	$(1.10 \pm 0.01) \times 10^{-1}$	18.8	0.1
50M	OMe	−10.1	$(5.51 \pm 0.03) \times 10^{-2}$		
		0.0	$(1.81 \pm 0.01) \times 10^{-1}$	16.1	−2.8
		10.0	$(5.29 \pm 0.01) \times 10^{-1}$		
		25.0[c]	2.4		
40M	OMe	−20.0	$(3.52 \pm 0.01) \times 10^{-2}$		
		−10.1	$(1.30 \pm 0.05) \times 10^{-1}$	16.5	0.2
		0.0	$(4.16 \pm 0.08) \times 10^{-1}$		
		25.0[c]	6		

[a] As Table 1 (substrate concentrations typically 5×10^{-5} to 2×10^{-4}M). [b] Solvent codes: A = % v/v acetone–water; M = % v/v methanol–water. [c] Calculated from data at other temperatures. [d] Triplicate measurements with substrate concentrations 5×10^{-6} to 5×10^{-5}M in CO_2-free stock solution.

methanolysis (see Figure 1 and ref. 5*c*). We assume that only S_N2–S_N1 (not carbonyl addition) processes will be favoured by electron donation, because only this mechanism permits development (and stabilization) of positive charge on the carbonyl carbon atom.[4b] Solvolyses in 40% methanol–water also show a good σ^+ plot (Figure 1), except for Z = NO_2 where carbonyl addition may become dominant. Hence it appears that most of the solvolyses in weakly nucleophilic media and many in highly aqueous media are S_N2–S_N1 processes.

Two independent but indirect arguments suggest to us that the ρ^+ value for solvolyses in 97% trifluoroethanol (-3.1, Figure 1) is not due to a purely S_N1 reaction. Firstly, this ρ^+ value is less negative than for the S_N1 solvolyses of *para*-substituted cumyl chlorides [$\rho^+ = -4.5$ (ref. 8)] on which σ^+ values are based. The second argument is based on the following gas-phase data. We have recently employed enthalpies of reaction (ΔH) for gas-phase equilibria to provide useful insights into relative S_N1 reactivities.[3a,4] For solvolyses of acid chlorides

Table 3. Additional solvolysis rate constants (k) at 25 °C for *para*-Z-substituted benzoyl chlorides (**1**) in binary aqueous mixtures[a]

Solvent[b]	Z	k/s^{-1}	Z	k/s^{-1}
MeOH	Me	$(3.60 \pm 0.04) \times 10^{-3}$	Cl	$(6.05 \pm 0.07) \times 10^{-3}$
90M	Me[c]	$(8.18 \pm 0.24) \times 10^{-3}$		
80M	Me	$(1.54 \pm 0.02) \times 10^{-2}$	Cl	$(1.64 \pm 0.01) \times 10^{-2}$
70M	Me	$(4.15 \pm 0.02) \times 10^{-2}$		
60M	Me	$(8.44 \pm 0.03) \times 10^{-2}$	Cl	$(2.54 \pm 0.01) \times 10^{-2}$
50M	Me[d]	$(2.42 \pm 0.09) \times 10^{-1}$		
40M	Me[e]	5.54×10^{-1}	Cl	$(4.28 \pm 0.01) \times 10^{-2}$
20M	Me[e]	3.1	Cl	$(9.94 \pm 0.01) \times 10^{-2}$
50E	Me	$(5.84 \pm 0.03) \times 10^{-2}$	Cl	$(9.74 \pm 0.02) \times 10^{-3}$
80A	Me[f]	4.37×10^{-4}	Cl	$(1.24 \pm 0.01) \times 10^{-3}$
70A	Me	$(1.74 \pm 0.02) \times 10^{-3}$	Cl	$(2.02 \pm 0.01) \times 10^{-3}$
60A	Me	$(6.57 \pm 0.04) \times 10^{-3}$	Cl	$(3.11 \pm 0.01) \times 10^{-3}$
50A	Me[f]	2.45×10^{-2}	Cl	$(4.96 \pm 0.01) \times 10^{-3}$
40A	Me	$(1.03 \pm 0.02) \times 10^{-1}$	Cl[g]	9.08×10^{-3}
MeOH	NO_2	$(4.08 \pm 0.01) \times 10^{-2}$	OMe[c]	$(1.07 \pm 0.01) \times 10^{-2}$
90M			OMe	$(3.57 \pm 0.01) \times 10^{-2}$
80M	NO_2	$(1.25 \pm 0.01) \times 10^{-1}$	OMe	$(1.11 \pm 0.01) \times 10^{-1}$
70M			OMe[c]	$(3.16 \pm 0.04) \times 10^{-1}$
60M	NO_2[e]	1.51×10^{-1}	OMe[h]	$(8.63 \pm 0.08) \times 10^{-1}$
40M	NO_2	$(1.35 \pm 0.01) \times 10^{-1}$	OMe[g]	6
80E	NO_2[f]	4.90×10^{-2}	OMe[c]	$(2.17 \pm 0.01) \times 10^{-2}$
50E	NO_2	$(7.49 \pm 0.03) \times 10^{-2}$	OMe[e]	5.41×10^{-1}
80A	NO_2[f]	1.48×10^{-2}	OMe	$(2.24 \pm 0.02) \times 10^{-3}$
70A	NO_2[f]	2.19×10^{-2}	OMe	$(1.23 \pm 0.01) \times 10^{-2}$
60A	NO_2	$(3.18 \pm 0.01) \times 10^{-2}$	OMe[c]	$(5.35 \pm 0.08) \times 10^{-2}$
50A	NO_2[f]	3.72×10^{-2}	OMe[e]	2.29×10^{-1}
40A	NO_2	$(4.77 \pm 0.01) \times 10^{-2}$	OMe[g]	9.79×10^{-1}

[a] Determined conductimetrically in duplicate except where noted otherwise; errors shown are average deviations. [b] As Table 2; also E = % v/v ethanol–water. [c] Triplicate measurement of rate constant. [d] Four measurements of rate constant. [e] Ref. 4*b*. [f] Ref. 5*b*. [g] Table 2. [h] In agreement with our previous value of k, $(8.7 \pm 0.2) \times 10^{-1}$; see ref. 4*b*.

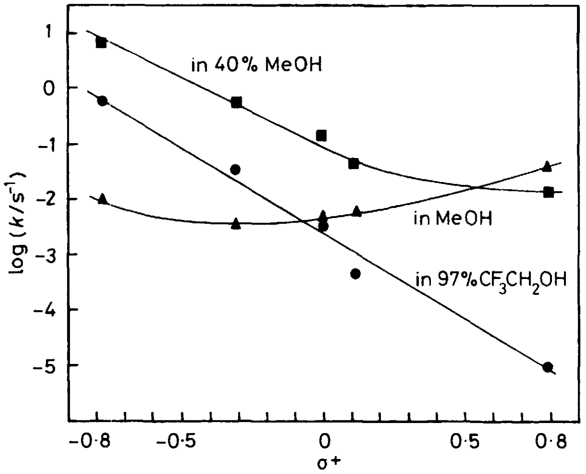


Figure 1. Correlation of logarithms of rate constants for *para*-Z-substituted benzoyl chlorides (**1**) *versus* σ^+ (ref. 8); kinetic data for Tables 1 and 3 (for MeOH) and from ref. 4*b*

$$Ar^1COR + Ar^2CO^+ \rightleftharpoons Ar^1CO^+ + Ar^2COR \quad (2)$$

$$Ar^1COR \longrightarrow Ar^1CO^+ + R^\cdot + \varepsilon \quad (3)$$

$$Ar^2COR \longrightarrow Ar^2CO^+ + R^\cdot + \varepsilon \quad (4)$$

$$\Delta H(2) = P(3) - P(4) \quad (5)$$

the required equilibrium is equation (2), and $\Delta H(2)$ is given by equation (5); *i.e.* by the differences in mass spectrometric appearance potentials (P) between reactions (3) and (4).[9a] Data for R = Me [equations (2)—(4)] will be used to estimate the relative stabilities of arylcarbonyl cations.

The differences in appearance potentials for a series of acetophenones [R = Me, equation (2)] should be more reliable than absolute values; they range up to 0.63 eV,[10] but each value has considerable experimental uncertainty.[9b,10] At the temperature of the mass spectrometer source (200 °C), 0.63 eV corresponds to a rate factor of $10^{6.7}$ and hence to a ρ^+ value of -4.3; systematic errors (*e.g.* the effects of variation in ionization probabilities[9c]) would make the predicted ρ^+ value even more negative. A slightly less negative ρ^+ value (-3.8) has been found for neutral and for acid-catalysed solvolyses of 4-substituted 2,6-dimethylbenzoyl chlorides in 99% acetonitrile–water at 25 °C.[11a] Much more negative ρ^+ values (*ca.* -7) have been observed for the more electron-demanding α-CF_3-substituted benzylic systems.[11b,c]

Solvent Effects on Reactivity.—Correlations of rate data for the four substrates (**1**; Z = OMe, Me, Cl, or NO_2) *versus* Y_{Cl} [equation (1), X = Cl] are shown in Figures 2—5. Deviations for the weakly nucleophilic solvents (carboxylic acids and fluorinated alcohol) from the correlation lines for aqueous media increase in the order: NO_2 > Cl > H[4b] > Me > OMe, and show the increasing contributions of nucleophilic solvent assistance. The foregoing trend can be explained either by S_N2 or by carbonyl addition pathways. The ethanol–water and methanol–water plots are non-linear, with upward curvature except for Z = NO_2. Following previous work,[4b] we attribute such changes in the slope of correlation lines to changes in mechanism from S_N2–S_N1 in highly aqueous media to carbonyl addition in nucleophilic solvents of lower ionizing power. As the S_N2–S_N1 process will be favoured by electron-donating substituents (see before), the solvent composition over which the mechanistic change occurs will depend on the substituent Z.

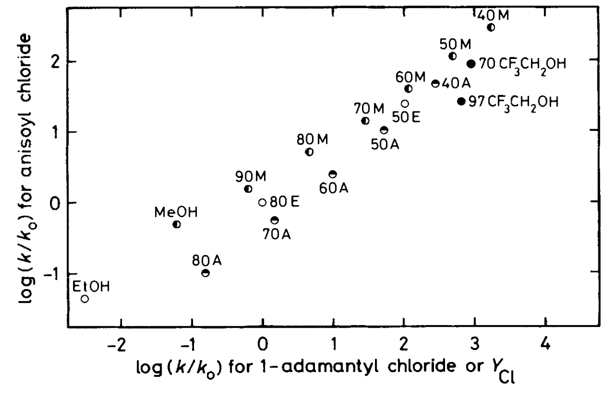


Figure 2. Correlation of logarithms of solvolysis rates for anisoyl chloride (**1**; Z = OMe), relative to rates in 80% v/v ethanol–water (k_0) at 25 °C *versus* Y_{Cl} (kinetic data and solvent codes given in Tables 1—3 and ref. 5; Y_{Cl} data from ref. 3*a*)

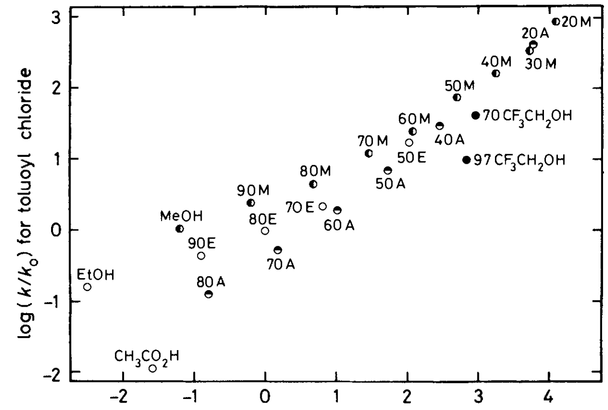


Figure 3. As for Figure 2, except the substrate is toluoyl chloride (**1**; Z = Me)

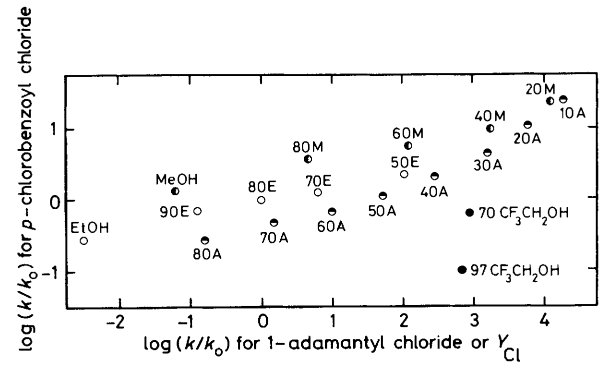


Figure 4. As for Figure 2, except the substrate is *para*-chlorobenzoyl chloride (**1**; Z = Cl)

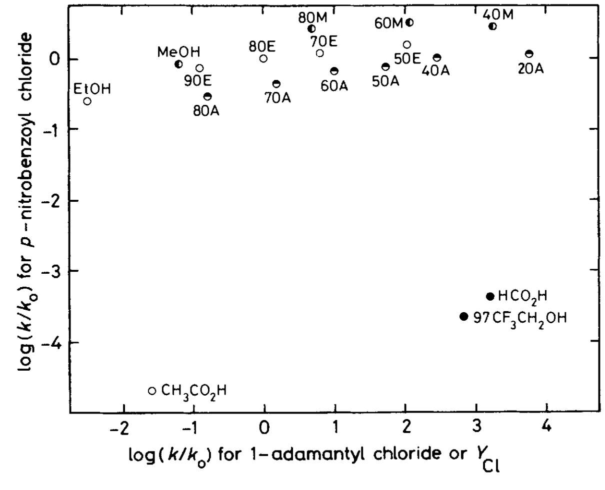


Figure 5. As for Figure 2, except the substrate is *para*-nitrobenzoyl chloride (**1**; Z = NO_2)

From the intersection of correlation lines for methanol–water mixtures, it appears that the *mechanistic change* occurs at compositions corresponding to the following *Y* values: when Z = OMe, $Y_{Cl} = 1.5$; Z = Me, $Y_{Cl} = 2.0$; Z = H, $Y_{Cl} = 2.7$;[4b] Z = Cl, $Y_{Cl} = 3.5$; Z = NO_2, $Y_{Cl} > 4$. The change in position of curvature with change in Z is strong evidence against a solvation effect as the cause of the curved mY_{Cl} plots, although such effects are known to occur when comparisons are not restricted to the same leaving group.[6-12]

On the right hand side of the graphs (Figures 2—4), the region of curvature of the plots for acetone–water, ethanol–water and methanol–water mixtures is followed by a linear region with very little dispersion between data for the three binary solvents, *i.e.* for a given Y_{Cl} value the rates for acetone–water, ethanol–water, and methanol–water are very similar. In contrast, the data for (**1**; Z = NO_2) show substantial dispersion throughout the range of solvents with no sign of the upward curvature and of the subsequent linear region. If the carbonyl addition process were of a higher kinetic order in protic solvent than the S_N2–S_N1 process, we could explain the dispersion between data for binary mixtures, *i.e.* the greater curvature of the methanol–water plots than the ethanol–water plots, which in turn are more curved than the acetone–water plots. This can be illustrated for 100% MeOH ($Y_{Cl} = -1.2$),[3a] 90% ethanol–water ($Y_{Cl} = -0.9$)[3a] and 80% acetone–water ($Y_{Cl} = -0.8$);[3a] for these three solvents of approximately the same Y_{Cl} value the molar concentration of protic solvent (or the combined molar concentrations of protic solvents) decreases in the order: 100% MeOH (24.7) > 90% ethanol–water (21) > 80% acetone–water (11). If we divided the observed first-order rate constants by the concentration of protic solvent, there would be less dispersion between data for binary mixtures. In support of the foregoing argument, it has been shown that methanolysis of (**1**; Z = NO_2) in acetonitrile is second-order in methanol (there is also a first-order term).[13] Another factor contributing to the dispersion is the lower nucleophilicity of acetone–water mixtures compared with ethanol– and methanol–water.[3b]

The *m* values for the two competing processes (Table 4) show that the results for benzoyl chloride are fairly typical of the whole series, although the *m* values for the carbonyl addition process vary from 0.16 to at least 0.55 (and possibly higher depending on how the slight curvature of the data for toluoyl and anisoyl chlorides (**1**; Z = Me or OMe) is interpreted). The change in *m* value with change in mechanism is shown clearly for Z = Cl and H, but is less clear for Z = Me and OMe. However, even for Z = OMe there is a marked dispersion between correlation lines for acetone–water and methanol–water mixtures having low Y_{Cl} values.

Another indication of mechanistic change is the entropy of activation ($\Delta S^{\ddagger}$), but we caution that this mechanistic probe must be applied in a restricted manner. S_N1 Solvolyses of tosylates in hexafluoropropan-2-ol have $\Delta S^{\ddagger} \approx -20$ cal K^{-1} mol^{-1},[2b] although such low values were thought to be indicative

Table 4. Slopes of mY_{Cl} correlations [equation (1)] for solvolyses of *para*-Z-substituted benzoyl chlorides (**1**)

	Carbonyl addition		S_N2–S_N1	
Z	Solvents[a]	m	Solvents[a]	m
NO_2	80A→40A	0.16 ± 0.01		
Cl	80A→50A	0.24 ± 0.01	30A→10A	0.69 ± 0.01
H[b]	80A→60A	0.39 ± 0.02	30A→H_2O	0.92 ± 0.12
H[b]	EtOH→70E	0.22 ± 0.01	40E→H_2O	0.81 ± 0.08
H[b]	MeOH→70M	0.25 ± 0.01	40M→H_2O	0.81 ± 0.07
Me	80A→60A	0.65 ± 0.02	50A→20A	0.87 ± 0.01
Me	EtOH→70E	0.35 ± 0.03		
Me	MeOH→80M	0.34 ± 0.01	50M→20M	0.77 ± 0.07
OMe[c]	80A→60A	0.77 ± 0.01	60A→40A	0.87 ± 0.01
OMe	EtOH→80E	0.54[d]		
OMe	MeOH→70M	0.55 ± 0.01	70M→40M	0.71 ± 0.07

[a] Solvent codes as Table 3, footnote *b*. [b] Data from ref. 4*b* except for H_2O (see Experimental section of this work). [c] For 80A→40A, m = 0.81 ± 0.02. [d] Two data points.

of S_N2 reactions.[14] We will apply this mechanistic probe to solvolyses of structurally similar compounds in identical or at least very similar solvents. For all solvolyses of (**1**; Z = NO_2) $\Delta S^{\ddagger}$ is highly negative (range −32 to −20 cal K^{-1} mol^{-1}; see refs. 4*b* and 5*c* and Tables 1 and 2). In 60% methanol–water, $\Delta S^{\ddagger}$ is 20 cal K^{-1} mol^{-1} more negative for (**1**) when Z = NO_2 than when Z = OMe.[4b] The change in $\Delta S^{\ddagger}$ with change in mechanism can be seen very clearly for (**1**; Z = Cl) over the curved region of acetone–water data; $\Delta S^{\ddagger}$ changes from −17.3 in 40% acetone–water to −10.1 in 30% acetone–water to −6.7 in 20% acetone–water and to +0.1 in 10% acetone–water. The highly negative $\Delta S^{\ddagger}$ value for solvolysis of Z = NO_2 in 97% trifluoroethanol–water (−30 cal K^{-1} mol^{-1}, Table 1) is unexpected because the linear σ^+ plot (Figure 1) is consistent with an S_N2–S_N1 process. Interestingly, the carbonyl addition process shows high bromide/chloride rate ratios for these leaving groups.[15]

Conclusion

The effect of *para*-substituents (Z) on the solvolytic reactivity of benzoyl chlorides is consistent with the mechanism discussed previously.[4b] The shapes of the curves (Figures 2—5) are explained as follows. A weakly nucleophilically assisted S_N2 process occurs in 97% trifluoroethanol and an S_N2 process is also dominant in highly aqueous media (except when Z = NO_2). This process has a higher m value [equation (1)] than the competing process, which is dominant when Z = NO_2 and is significant even when Z = OMe in less aqueous solvents (*e.g.* 80% methanol–water). This competing process is presumably a carbonyl addition; it has a more negative $\Delta S^{\ddagger}$ value and appears to be of a higher kinetic order in protic solvent than the S_N2–S_N1 process.

Experimental

Materials.—The acid chlorides (**1**; Z = OMe, Me, Cl, or NO_2) were commercial samples, checked for purity by h.p.l.c. analysis of methanolysis products,[4b] and shown to contain <0.3% of acid as the only detectable impurity. Some results were obtained for (**1**; Z = NO_2) containing >10% acid and the same rate constants were obtained. As the acid would be a major product of most of the solvolyses reported here, traces were not removed prior to kinetic studies.

Solvents for kinetic studies were acetone and methanol (Fisons, dried and distilled), water (distilled and stored in glass apparatus), and trifluoroethanol (distilled through a triple pass Widmer column), b.p. 74 °C. Solvent batches were usually prepared using calibrated pipettes except for trifluoroethanol–water solutions which were made in bulk stock (rate constants for 1-adamantyl bromide were checked[3a,16]). For highly aqueous media, some stock solutions were prepared nominally CO_2-free by heating the pure solvents under N_2 followed by making the binary mixtures under protection of septa and/or Carbosorb. Weights of solvents were measured to give appropriate % v/v stock solutions and compositions were then checked by carrying out a suitable kinetic study.

Kinetic Methods.—These were as described previously[4b] with the following modifications. To economize in the use of trifluoroethanol and to try to improve mixing times, a smaller conductivity cell was designed; electrodes 0.5 × 0.5 cm were 0.5 cm apart towards the bottom of a short test-tube-shaped cell (diameter 1.4 cm, height 3 cm, volume 2—3 ml), fitted with a long stem topped by a B10 joint. The cell constant was 1.1 cm^{-1}. An air-driven turbo-stirrer (Corning MU8/0) with a propeller-shaped blade located 1.5 cm above the electrodes provided rapid stirring (6 rev s^{-1}, measured using a strobe lamp) without formation of significant bubbles of air between the electrodes. Hence a steady conductance reading (variation ±0.7% or less) could be obtained during kinetic studies of rapidly stirred solutions. Samples were injected rapidly by syringe through a short side arm; injection of dilute HCl into water established a mixing time of 0.4 s. In a reinvestigation of the solvolysis of benzoyl chloride in water, we injected 3 µl of a 0.1% solution of the chloride in acetone into CO_2-free water at 25 °C and obtained a slightly higher rate constant (k = 1.8 ± 0.1 s^{-1}) than previously (lit.,[4b] 1.54 ± 0.14 s^{-1}). Lower mixing times (0.20 s) were achieved with a cylindrical slice-shaped conductivity cell, adapted from previous spectrophotometric studies.[7b] With a Hamilton CR700-200 spring-loaded syringe, samples were injected and simultaneously mixed by placing the needle very close to the bottom of the cell (but not between the electrodes). Unfortunately this system gave low rate constants (5—7 × 10^{-1} s^{-1}) for the solvolysis of (**1**; Z = OMe) in 60% methanol–water at 25 °C (see Table 3, footnote *h*).

As the resistance of the solution for a few of these experiments was in the megohm region, additional steps were taken to stabilize the output from the conductivity amplifer. Noise levels of ±0.2% (down from 3—4% for megohms) were achieved by replacing the 741 operational amplifer by one of higher input impedance (M.O.S./F.E.T. 3140E), shortening and individually shielding the connecting leads to the cell, and removing the mains neon indicator lamp. The data collection and processing system was as described previously;[4b] up to 30 precision readings per second were obtained using the microcomputer-controlled Solartron 7066 storage voltmeter (integration times down to 2.5 ms) operating at 9 600 baud.

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References

1 (*a*) F. L. Schadt, T. W. Bentley, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1976, **98**, 7667; (*b*) D. N. Kevill and G. M. L. Lin, *ibid.*, 1979, **101**, 3916; (*c*) B. Allard, A. Casadevall, E. Casadevall, and C. Largeau, *Nouv. J. Chim.*, 1979, **3**, 335; (*d*) see also S. A. I. Al-Shali, C. Eaborn, F. A. Fattah, and S. T. Najim, *J. Chem. Soc., Chem. Commun.*, 1984, 318.

2 (*a*) D. J. Raber, W. C. Neal, Jr., M. D. Dukes, J. M. Harris, and D. L. Mount, *J. Am. Chem. Soc.*, 1978, **100**, 8137; (*b*) T. W. Bentley, C. T. Bowen, D. H. Morten, and P. von R. Schleyer, *ibid.*, 1981, **103**, 5466.

3 T. W. Bentley and G. E. Carter, (*a*) *J. Am. Chem. Soc.*, 1982, **104**, 5741; (*b*) *J. Org. Chem.*, 1983, **48**, 579; (*c*) D. N. Kevill, W. A. Kamil, and S. W. Anderson, *Tetrahedron Lett.*, 1982, **23**, 4635.

4 T. W. Bentley, G. E. Carter, and H. C. Harris, (*a*) *J. Chem. Soc., Chem. Commun.*, 1984, 387; (*b*) *J. Chem. Soc., Perkin Trans. 2*, 1985, 983.

5 (*a*) E. W. Crunden and R. F. Hudson, *J. Chem. Soc.*, 1956, 501; (*b*) C. G. Swain, R. B. Mosely, and D. E. Brown, *J. Am. Chem. Soc.*, 1955, **77**, 373; (*c*) I. Lee, I. S. Koo, S. C. Sohn, and H. H. Lee, *Bull. Korean Chem. Soc.*, 1982, **3**, 92; (*d*) A. Kivinen, in 'The Chemistry of Acyl Halides,' ed. S. Patai, Wiley, New York, p. 188.

6 (*a*) T. W. Bentley and K. Roberts, *J. Org. Chem.*, 1985, **50**, 4821; (*b*) T. W. Bentley, C. T. Bowen, H. C. Brown, and F. J. Chloupek, *ibid.*, 1981, **46**, 38.

7 (*a*) B. Perlmutter-Hayman and M. A. Wolff, *Isr. J. Chem.*, 1965, **3**, 155; (*b*) S. V. Hill, S. Thea, and A. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1983, 437.

8 H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 1958, **80**, 4979.

9 T. W. Bentley and R. A. W. Johnstone, *Adv. Phys. Org. Chem.*, 1970, **8**, (*a*) p. 181; (*b*) p. 183; (*c*) p. 177.

10 (*a*) M. S. Chin and A. G. Harrison, *Org. Mass Spectrom.*, 1969, **2**, 1073; (*b*) A. Buchs, G. P. Rossetti, and B. P. Susz, *Helv. Chim. Acta*, 1964, **47**, 1563; see also A. I. Helal and N. F. Zahran, *Org. Mass Spectrum.*, 1978, **13**, 549.

11 (*a*) M. L. Bender and M. C. Chen, *J. Am. Chem. Soc.*, 1963, **85**, 30; (*b*) K.-T. Liu, M.-Y. Kuo, and C.-F Shu, *ibid.*, 1982, **104**, 211; (*c*) A. D. Allen, I. C. Ambidge, C. Che, H. Micheal, R. J. Muir, and T. T. Tidwell, *ibid.*, 1983, **105**, 2343.

12 D. N. Kevill, M. S. Bahari, and S. W. Anderson, *J. Am. Chem. Soc.*, 1984, **106**, 2895.

13 D. N. Kevill and F. D. Foss, *J. Am. Chem. Soc.*, 1969, **91**, 5054, and references there cited.

14 R. W. Alder, R. Baker, and J. M. Brown, 'Mechanism in Organic Chemistry,' Wiley, New York, 1971, p. 5.

15 J. Miller and O.-L. Ying, *J. Chem. Soc., Perkin Trans. 2*, 1985, 323.

16 D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1970, **92**, 5977.

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