Competing S_N2 and Carbonyl Addition Pathways for Solvolyses of Benzoyl Chloride in Aqueous Media

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The further development of a convenient, conductimetric method for studying the rates of relatively fast solvolytic reactions in highly aqueous media is described. Rate and product data are reported for solvolyses of benzoyl chloride at 25 °C in water and in binary aqueous mixtures with acetone, ethanol, methanol, trifluoroethanol, and hexafluoropropan-2-ol. Comparison of these kinetic data with rate data for the S_N1 model, 1-adamantyl chloride, reveals sensitivity to solvent nucleophilicity even for highly aqueous media. In contrast with other nucleophilically solvent-assisted processes, the solvent effects are not satisfactorily correlated by one linear free energy relationship. Gas-phase thermochemical data show the feasibility of a direct heterolytic cleavage of the C–Cl bond in benzoyl chloride. Rate–product correlations for hydrolysis and aminolysis in 50% w/w acetone–water are observed, providing that allowance is made for the medium effect of the added *o*-nitroaniline. These results are consistent with an S_N2 mechanism, not S_N1 and/or ion-pair mechanisms previously discussed. Another pathway, dominant in less aqueous media, is much less sensitive to changes in solvent ionizing power, consistent with earlier proposals for a carbonyl addition–elimination mechanism.

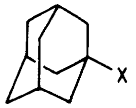
Solvent effects on reactivity provide useful insights into the mechanisms of a wide range of reactions.[1] Such studies are particularly helpful when alternative mechanistic probes are not applicable, *e.g.*, for solvolytic reactions of aromatic acid chlorides, α- and β-deuterium kinetic isotope effects cannot be obtained. Reactions of acid chlorides have usually been studied in relatively non-polar solvents and the effects of solvent, aromatic ring substituents, and added amines have been examined.[2] We now report kinetic data for solvolyses of benzoyl chloride in relatively polar solvents, with an analysis of the data based on the Winstein–Grunwald equation (1).[3a] In equation

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

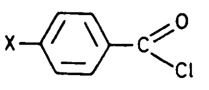
(1), k is the rate of reaction in any solvent relative to 80% v/v ethanol–water (k_0). The solvent ionizing power Y (defined by $m = 1.000$ for solvolyses of t-butyl chloride at 25 °C[3a]) includes contributions from solvent nucleophilicity, and so a new Y scale (Y_{Cl}) has recently been defined by $m = 1.00$ for solvolyses of 1-adamantyl chloride (**1**; X = Cl) at 25 °C.[3b]

Curved plots based on equation (1) have been observed for correlations of solvolyses in which the leaving group of the substrate differs from chloride.[4] When recently published[5] rates of hydrolysis of benzoyl chloride (**2**; X = H) in water and aqueous alcohol mixtures were plotted against Y or Y_{Cl}, we obtained markedly curved graphs. A preliminary re-investigation showed that the rate of reaction was determined by dissolution, and that homogeneous hydrolysis was very rapid. Having already studied some relatively fast solvolytic reactions,[6] we decided to obtain accurate kinetic data for hydrolysis of benzoyl chloride.

As an initial approach we examined solvolyses of t-butyl bromide, which dissolved more rapidly than benzoyl chloride. Eventually this work developed into a separate project,[7a] and we later studied relatively fast solvolytic reactions of 1-adamantyl mesylate (**1**; X = OMs).[7b] We now report the current state of development of our techniques for determining the rates of relatively fast solvolytic reactions ($t_{\frac{1}{2}}$ *ca.* 1 s). A preliminary account of a correlation of rate data for solvolyses of benzoyl chloride with Y [equation (1)] has been published.[8] The correlation is curved in the opposite direction to that obtained from previously published data.[5] We also show that the lack of rate–product correlation previously obtained[9,10] for reactions of benzoyl chloride in 50% w/w acetone–water with added *o*-nitroaniline is due to medium effects; this work provides independent support for our previous prediction[8] that hydrolysis of benzoyl chloride is significantly assisted by solvent participating as nucleophile; *i.e.*, it is not an S_N1 process.



(**1**)



(**2**)

Results

Kinetic data for several relatively fast solvolytic reactions, examined by a variety of conductimetric experimental techniques, are shown in Table 1. To separate the experimental problems posed by high substrate reactivity and by low solubility of substrate, we initially examined solvolyses of triphenylmethyl chloride in 90% v/v acetone–water (we established a linear relationship between conductance and HCl concentrations up to at least 1.5×10^{-5}M at −20 °C). Most of our results were obtained in continuously stirred solutions but, for solvolyses of sparingly soluble substrates, superior agitation of the solution was achieved using a laboratory shaker.[7b] This procedure gave satisfactory results even for benzoyl chloride in water at 25 °C (Table 1); the rate constant obtained by extrapolation is slightly higher, but the discrepancy may be due at least in part to heat capacity effects.[7a] Conductance data can be collected on an X–t chart recorder,[7b] but we have now implemented a more precise data collection system based on a high-precision storage voltmeter. The high precision of the data for many of these relatively fast solvolytic reactions ($t_{\frac{1}{2}} > 3$ s) now equals that observed for conventional conductimetric measurements. Steady conductance readings could be obtained even in very vigorously stirred solutions, providing that there was plenty of solution above the electrodes. Rate constants up to 0.8 s^{-1} have now been obtained in this manner [data for (**2**), X = OMe, NO$_2$, Table 1].

Table 1. Rate constants (k) for relatively fast solvolytic reactions[a]

Substrate	Solvent[b]	T/°C	k/s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} k^{-1}
Ph_3CCl	90% Me_2CO	−20.1	0.052 ± 0.001		
		0.1	0.347 ± 0.007		
		10.0	0.94 ± 0.04		
		25.0[c]	3.0	13.0	−12.7
		25.0[c,d]	2.83	13.7	
		25.0[c,e]	3.4	14.3	−8.2
		25.0	1.9 ± 0.1	11.7	−17.6
		25.0[f]	1.83		
Me_3CBr	H_2O	29.9	1.4 ± 0.2	22.4[g]	15.9[g]
		30.0[c]	1.3	22.1[g]	14.7[g]
		30.0[c,h]	1.6	22.9	17.9
(2) X = H	H_2O	5.0	0.151 ± 0.006		
		14.9	0.517 ± 0.007		
		25.0[c]	1.67	19	+7
		25.0[i]	1.4 ± 0.1	18	+2
(2) X = H	50% MeOH	35.0	0.150 ± 0.003		
		25.0	0.063 ± 0.001	15	−13
	40% Me_2CO	50.1	0.240 ± 0.007		
		35.0	0.064 ± 0.001		
		25.0	0.025 ± 0.001	16.7	−9.8
(2) X = Me	40% MeOH	13.9	0.186 ± 0.001		
		25.0	0.554 ± 0.005	16.1	−5.9
(2) X = Me	30% MeOH	−5.2	0.049 ± 0.001		
		4.4	0.133 ± 0.001		
		13.9	0.408 ± 0.004		
		25.0[c]	1.2	16.5	−3.0
(2) X = Me	20% MeOH	−5.1	0.087 ± 0.001		
		−0.1	0.157 ± 0.004		
		4.4	0.265 ± 0.016		
		9.9	0.596 ± 0.021		
		25.0[c]	3.1	18.6	6.1
(2) X = OMe	50% EtOH	0.0	0.032 ± 0.001		
		10.0	0.106 ± 0.001		
		25.0	0.541 ± 0.002	17.7	−0.3
(2) X = OMe	60% MeOH	−0.1	0.063 ± 0.002		
		10.0	0.193 ± 0.002		
		25.0[c]	0.89	16.6	−3.1
		25.0	0.844 ± 0.008	16.2	−4.5
(2) X = OMe	50% Me_2CO	0.0	0.017 ± 0.001		
		10.0	0.052 ± 0.001		
		25.0	0.229 ± 0.005	16.2	−7.0
(2) X = NO_2	60% MeOH	0.0	0.023 ± 0.001		
		10.0	0.050 ± 0.001		
		25.0	0.151 ± 0.001	11.7	−23.1

[a] Determined conductimetrically at least in duplicate in a continuously stirred solution, except where noted otherwise; errors shown are average deviations. Data for the first four substrates were collected on the *X–t* chart recorder; other data were obtained with a storage voltmeter. [b] Percent Me_2CO refers to acetone–water (%v/v), % MeOH refers to methanol–water (%v/v), and % EtOH refers to ethanol–water (%v/v); H_2O contained <0.1% cosolvent (acetone or dioxane) to help to disperse the substrate. [c] Calculated from rate data at other temperatures. [d] Values quoted from ref. 11*a*. [e] Our estimates based on extrapolation of the same rate data at −40 to −20 °C as footnote *d*. [f] Direct measurement in a flow system, ref. 11*a*. [g] Additional data at 0, 15, and 25 °C from previous work (ref. 7*a*). [h] Reference 11*b*. [i] Ten measurements of rate constant using the laboratory shaker technique for dissolution of substrate (ref. 7*b*).

Rate and product data for solvolyses of benzoyl chloride are shown in Table 2. Reaction rates were monitored conductimetrically as previously described.[7] Product ratios were obtained by reversed-phase high-performance liquid chromatography (h.p.l.c.).[13a] Analyses were performed directly on 10^{-2}—10^{-3}M solutions, and in some cases the same solutions were used to obtain rate then product data. It was established that the esters formed by reaction of solvent alcohols with benzoyl chloride were stable under the acidic reaction conditions. Potentiometric titrations of 10^{-2}M solutions did not give sufficiently sharp end points for accurate analyses of HCl in the presence of benzoic acid.[13b] The data in Table 3 are relevant to the discussion of rate–product correlations.[9,10,13a]

Discussion

Accuracy of Kinetic Data.—Our results for Ph_3CCl at 25 °C (Table 1) are in satisfactory agreement with those already published from studies using a flow system.[11a] However, judging from extrapolations of rate data from lower temperatures, the direct measurements at 25 °C may be slightly too low. Our results at 35 °C gave k *ca.* 3 s^{-1}, much lower than values obtained by extrapolation from data at lower temperatures. Satisfactory results for hydrolyses of t-butyl bromide were obtained at 30 °C but not at 35 °C; again the results obtained by extrapolation from rate data at lower temperatures were significantly higher than those obtained by direct measurement. It appears that rate constants of 2 s^{-1} ($t_{\frac{1}{2}}$ < 0.4 s) are close to the

Table 2. Rate constants, product ratios, and product selectivities for solvolyses of benzoyl chloride at 25 °C

	Rate constants (s^{-1})		Products[c]	
Solvent[a]	This work[b]	Literature (10^3k)	$\frac{[\text{ester}]}{[\text{acid}]}$	S[d]
EtOH		0.748,[e] 0.776[f]		
90% EtOH	$(1.70 \pm 0.02) \times 10^{-3}$		5.8	2.1
80% EtOH		1.70[e]	2.8	2.3
70% EtOH	$(4.20 \pm 0.03) \times 10^{-3}$	2.57,[f] 2.77[e]		
60% EtOH		3.98[e]		
50% EtOH	$(1.71 \pm 0.01) \times 10^{-2}$	7.76[f]	0.45	1.5
40% EtOH	$(4.82 \pm 0.05) \times 10^{-2}$	17.8[f]		
30% EtOH	$(1.8 \pm 0.1) \times 10^{-1}$	51.3[f]	0.14	1.0
20% EtOH	$(3.7 \pm 0.1) \times 10^{-1}$			
10% EtOH[g]	$(9.1 \pm 0.8) \times 10^{-1}$			
H_2O[h]	1.54 ± 0.14			
MeOH	$(4.3 \pm 0.1) \times 10^{-3}$			
90% MeOH	$(8.07 \pm 0.08) \times 10^{-3}$	4.27,[f] 4.29[i]		
80% MeOH	$(1.31 \pm 0.02) \times 10^{-2}$		8.3	4.7
70% MeOH	$(1.97 \pm 0.03) \times 10^{-2}$			
60% MeOH	$(3.46 \pm 0.03) \times 10^{-2}$	1.91[f,j]	2.0	3.0
50% MeOH[h]	$(6.3 \pm 0.1) \times 10^{-2}$			
40% MeOH[k]	$(1.34 \pm 0.04) \times 10^{-1}$		0.55	1.9
30% MeOH	$(2.9 \pm 0.1) \times 10^{-1}$			
20% MeOH	$(5.4 \pm 0.1) \times 10^{-1}$		0.15	1.4
10% MeOH	$(8.9 \pm 0.4) \times 10^{-1}$			
90% Me_2CO				
80% Me_2CO		0.17[f]		
		0.49[f]		
70% Me_2CO		1.1[f]		
60% Me_2CO		2.52[l]		
50% Me_2CO	$(7.3 \pm 0.1) \times 10^{-3}$	8.13[f]		
40% Me_2CO[h]	$(2.5 \pm 0.1) \times 10^{-2}$			
30% Me_2CO	$(8.3 \pm 0.3) \times 10^{-2}$			
20% Me_2CO	$(2.5 \pm 0.1) \times 10^{-1}$			
10% Me_2CO	$(5.5 \pm 0.2) \times 10^{-1}$			
97% CF_3CH_2OH	$(3.64 \pm 0.04) \times 10^{-3}$		0.7	0.1
70% CF_3CH_2OH	$(2.10 \pm 0.02) \times 10^{-2}$		0.09	0.2
50% CF_3CH_2OH	$(5.44 \pm 0.05) \times 10^{-2}$		0.04	0.2
97% $(CF_3)_2CHOH$	$(6.28 \pm 0.07) \times 10^{-2}$		0.01	0.003
CH_3CO_2H		0.0105[f]		
HCO_2H		*ca.* 20[m]		

[a] Percent EtOH refers to ethanol–water (% v/v); % MeOH refers to methanol–water (% v/v); % Me_2CO refers to acetone–water (% v/v); % fluorinated alcohol refers to fluorinated alcohol–water (% w/w). [b] Determined conductimetrically in duplicate, except where otherwise noted; errors shown are average deviations. [c] Determined by reversed-phase high-performance liquid chromatography by duplicate analyses of products from at least two independent measurements (10^{-3} or 10^{-2}M-benzoyl chloride initially). [d] S = Selectivity, calculated from [ester][water]/[acid][alcohol]. [e] Ref. 12*a*. [f] Ref. 12*b*. [g] Determined conductimetrically in quadruplicate. [h] Data from Table 1. [i] Ref. 12*c*; solvent contained 2.6% dioxane. [j] For 69.5% MeOH. [k] Ref. 13*b*, triplicate measurement. [l] Ref. 12*d*. [m] Estimated from data at 9 °C, ref. 12*e*.

achievable limits of this relatively uncomplicated procedure. If the substrate dissolved *during* the kinetic run, the rate constants obtained were usually too low. Low rate constants were also obtained when carbon dioxide concentrations were appreciable compared with substrate concentrations (see also reference 7*a*).

Our kinetic data for benzoyl chloride are in satisfactory agreement with previous independent workers for solvent compositions of 70% or more organic cosolvent (Table 2). However, we obtained a *ca.* 80-fold *increase* in rate from 70% methanol–water to pure water whereas other workers[5] have reported a 40-fold *decrease*. There is a 3 000-fold discrepancy between our value (Table 1) and the previously published[5] rate constant for hydrolysis of benzoyl chloride in water at 25 °C. We were unable to obtain homogeneous 10^{-1} or 10^{-2}M solutions of benzoyl chloride in water at 25 °C (the previously reported conditions[5]). Our results were obtained by rapid injection of a 0.25% solution of benzoyl chloride in acetone into thermostatted water to obtain a *ca.* 10^{-5}M solution containing <0.25% acetone. Our values obtained by direct measurement at 25 °C are in satisfactory agreement with the rate constant predicted by extrapolation from data at lower temperatures (Table 1) and from data in other solvents (Figure 1). A recent independent estimate[14] ($k = 8.6 \times 10^{-1}$ s^{-1}) is much closer to our value, (1.5 ± 0.14), but is still significantly different.

These results emphasise the experimental difficulties associated with kinetic studies of sparingly soluble solutes, which we have discussed previously.[4a] It is not possible to ensure by visual inspection whether a solute has dissolved to give a truly homogeneous solution. This experimental difficulty is not resolved by filtration, even in cases where there is sufficient time for this extra step. However, visual inspection is very useful because one can often observe even minute amounts of undissolved solid or liquid.

Solvent Effects on Reactivity.—The remaining discussion in this paper will be concerned exclusively with solvolyses of benzoyl chloride. In this section, material presented in our previous communication[8] is supplemented; the previously published[8] Figure, showing a plot of logarithm of rate constants for solvolyses of benzoyl chloride *versus* Winstein–Grunwald *Y*

Table 3. Rate constants (k)[a] for hydrolysis and aminolysis (o-nitroaniline, RNH_2) of benzoyl chloride in aqueous acetone containing added nitrobenzene

Reaction medium				
Solvent (acetone–water)	$[RNH_2]$/M	$[PhNO_2]$/M	T/°C	k/s^{-1}
50% w/w	0	0	25.0[b]	$(4.11 \pm 0.03) \times 10^{-3}$
50% w/w	0.1	0	25.0	$(4.70 \pm 0.01) \times 10^{-3}$
50% w/w	0.2	0	25.0	$(4.59 \pm 0.06) \times 10^{-3}$
50% w/w	0	0.1	25.0	$(3.97 \pm 0.03) \times 10^{-3}$
50% w/w	0	0.2	25.0	$(3.26 \pm 0.01) \times 10^{-3}$
50% w/w	0	0	−0.1[c,d]	$(2.93 \pm 0.06) \times 10^{-4}$
50% w/w	0.1	0	−0.1	$(3.75 \pm 0.01) \times 10^{-4}$
50% w/w	0.2	0	−0.1	$(4.31 \pm 0.03) \times 10^{-4}$
50% w/w	0	0.1	−0.1	$(2.53 \pm 0.01) \times 10^{-4}$
50% w/w	0	0.2	−0.1	$(2.14 \pm 0.01) \times 10^{-4}$
50% w/w	0.05	0.05	−0.1	$(3.17 \pm 0.01) \times 10^{-4}$
50% w/w	0.1	0.1	−0.1	$(3.21 \pm 0.01) \times 10^{-4}$
80% w/w[e]	0	0	−0.1[f,g]	$(5.14 \pm 0.25) \times 10^{-5}$
80% w/w[e]	0	0.2	−0.1[f]	$(4.82 \pm 0.29) \times 10^{-5}$
80% w/w[e]	0	0	25.0[h,i]	$(3.84 \pm 0.01) \times 10^{-4}$
80% w/w[e]	0	0.2	25.0	$(3.70 \pm 0.10) \times 10^{-4}$

[a] Determined conductimetrically in duplicate except where noted otherwise; errors shown are average deviations. [b] Literature values: 10^3k/s^{-1} = 4.31, $\Delta H^‡$ = 16.3 kcal mol^{-1}, $\Delta S^‡$ = −14.7 cal mol^{-1} K^{-1} (ref. 12*f*); our values from k at 25 and 0 °C, $\Delta H^‡$ = 16.4 kcal mol^{-1}, $\Delta S^‡$ = −14.6 cal mol^{-1} K^{-1}. [c] Triplicate measurement of rate constant; further duplicate measurements in another batch of solvent gave 10^4k/s^{-1} = 2.98 ± 0.05. [d] Literature values: 10^4k/s^{-1} = 2.77 (ref. 9), 3.08 (from ref. 12*f* by extrapolation). [e] We established a linear relationship at 0 °C between change in conductance and molar concentration of fully hydrolysed benzoyl chloride up to 10^{-3}M. [f] Triplicate measurement of rate constant. [g] Literature value: $10^5 k$/s^{-1} = 3.90 (ref. 9). [h] A single measurement in another batch of solvent gave 10^4k/s^{-1} = 3.89 ± 0.02. [i] $\Delta H^‡$ = 12.4 kcal mol^{-1}, $\Delta S^‡$ = −32.6 cal mol^{-1} K^{-1}; literature value for 85% v/v acetone–water: $\Delta H^‡$ = 13.2 kcal mol^{-1}, $\Delta S^‡$ = −30.5 cal mol^{-1} K^{-1}. (ref. 12*d*).

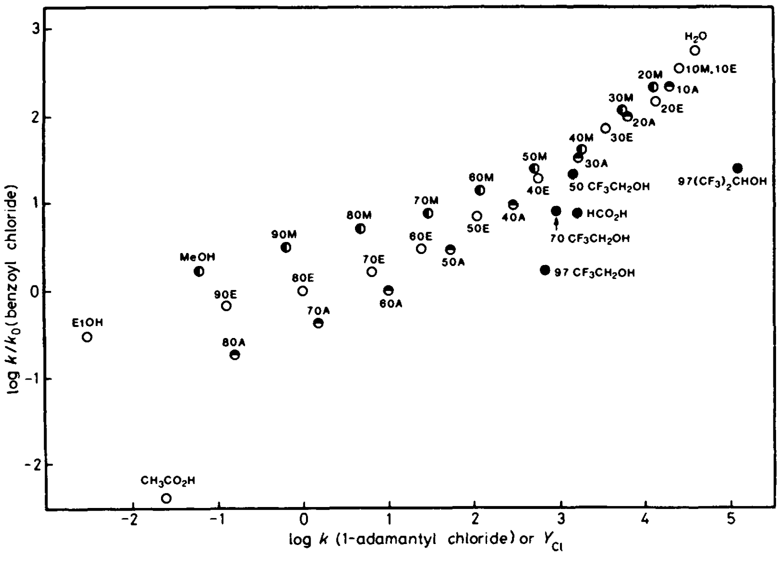


Figure 1. Correlation of logarithms of rate constants for solvolyses of benzoyl chloride [relative to rates in 80% (v/v) ethanol–water] at 25 °C *versus* Y_{Cl}; data from Table 2 and ref. 3*b*. The symbols A, E, and M refer to % acetone–, % ethanol–, and % methanol–water (v/v), respectively; fluorinated alcohols are % alcohol–water (w/w)

values, provides important evidence to support our discussion. In Figure 1, a similar plot *versus* Y_{Cl} shows considerable scatter even for solvents of high ionizing power, in contrast to the plot *versus* Y.[8] Interpretation of these plots is based on the considerable information available on the expected trends in S_N2–S_N1-type solvolytic reactivity in a wide range of protic media.[12b,15,16] To allow for leaving-group effects it is preferable to compare substrates having the same leaving group.[3b,7b,15a] Particularly relevant to the interpretation of data for benzoyl chloride are data for the structurally similar substrate, α-phenylethyl chloride, which correlate linearly with Y_{Cl} over the whole range of aqueous alcohols with only a small dispersion into separate lines for various binary mixtures.[16] As Y_{Cl} models S_N1 reactivity we conclude that hydrolyses of benzoyl chloride are not S_N1 reactions. As most of the data in Figure 1 can be correlated with the original Y values,[8] it appears that many solvolyses of benzoyl chloride are weakly nucleophilically solvent-assisted (S_N2) to about the same extent as solvolyses of t-butyl chloride. Rate ratios in solvents of the same Y_{Cl} value and different nucleophilicities provide measures of the minimum extent of nucleophilic solvent assistance (*e.g.*, $[k_{40EW}/k_{97TFE}]_Y = 13$, EW = ethanol–water, TFE = trifluoroethanol). The low nucleophilicities of the fluorinated alcohols, CF_3CH_2OH and $(CF_3)_2CHOH$, are apparent in both the rates (deviations from Figure 1) and the products (S values, Table 2).

The curvature of the correlation lines for the less aqueous compositions of $MeOH–H_2O$, $EtOH–H_2O$, and acetone–water is similar for correlations *versus* Y_{Cl} (Figure 1) or *versus* Y.[8] From the latter plot we can estimate the solvolytic reactivity, within the usual S_N2–S_N1 spectrum, expected for reactions of benzoyl chloride in any solvent. It appears that solvolyses in the following ranges of solvents (50% $MeOH–H_2O \longrightarrow MeOH$; 60% $EtOH–H_2O \longrightarrow EtOH$; 70% acetone–water $\longrightarrow$ less aqueous mixtures) are faster than expected for solvolyses in the S_N2–S_N1 spectrum.[15,16] Another mechanistic pathway (presumably carbonyl addition), much less sensitive to changes in solvent ionizing power, becomes dominant in nucleophilic solvents of low ionizing power (not in acetic acid).

Distinction between S_N2 *and Carbonyl Addition Pathways.*— The above mechanistic analysis implies that S_N2 and carbonyl-addition pathways are independent and competitive. Although several workers have considered the possibility that carbonyl compounds may react *via* S_N2 reactions,[15b,17] proposals for carbonyl-addition mechanisms appear to have become dominant since Bender's classical work on ^{18}O exchange in carbonyl compounds.[2] It is not always clear from the literature whether the term 'S_N2' encompasses carbonyl-addition mechanisms. An S_N2-like transition state could occur by partial heterolytic cleavage of the C–Cl bond, making available a *p*-type orbital capable of interacting with an incoming nucleophile in the COCl plane.[17b,18a] Carbonyl addition probably occurs in the plane of the C=O bond, perpendicular to the COCl plane.[17g,18] A complication is the possibility (examined by molecular orbital calculations) that initial attack as a carbonyl addition could lead directly to an S_N2-like transition state, by a small rotation of atoms as the attack proceeds.[18a]

A crucial difference between S_N2 and carbonyl-addition mechanisms is the role of the oxygen atom of the carbonyl group in the transition states. During the carbonyl-addition mechanism the double bond of the carbonyl group begins to cleave and the oxygen atom must bear a partial negative charge (possibly delocalised on to the electronegative substituent, *e.g.*, chlorine) and/or become protonated. This process may show a low sensitivity to changes in solvent ionizing power. In the S_N2 or S_N1 mechanisms, the oxygen atom may bear a positive charge as it assists with the direct expulsion of the chloride ion. Consequently, the negative charge is less delocalised and the leaving group will require more electrostatic stabilisation by solvent; this explains the increasing slope as solvent ionizing power increases [see equation (1) and Figure 1].

The feasibility of an S_N reaction (with heterolytic cleavage of the C–Cl bond) for benzoyl chloride can be compared with that for t-butyl chloride using equation (2) and published gas-phase

$$PhCOCl + Bu^{t+} \rightleftharpoons PhCO^+ + Bu^tCl \qquad (2)$$

thermochemical data: ΔH_f/kcal mol^{-1} = -26 ± 1,[19a] 164 ± 3,[19b,c] 168.5 ± 2,[19d] and -43.7 ± 0.6,[19a] respectively. The above results show that direct heterolytic cleavage of benzoyl chloride to the benzoyl cation is more favourable by 13 ± 7 kcal mol^{-1} than the corresponding cleavage of t-butyl chloride.* In solution we have proposed that both of these processes are assisted by nucleophilic solvation;[3b,8] general solvation forces will also be large. However, equations such as (2) give a good indication of heterolytic reactivity *in solution* because of the similarity between solvation of carbocations in solution and in the gas phase.[3b,20] The prediction from equation (2) is that an S_N reaction of benzoyl chloride should occur more rapidly than the corresponding reaction of t-butyl chloride, in agreement with the observed rate ratio in water at 25 °C ($k_{PhCOCl}/k_{t-BuCl} \sim 50$). Consequently the high reactivity of benzoyl chloride in water and in other solvents of high ionizing power can readily be explained by the relatively good stabilisation of the incipient benzoyl cation, *e.g.*, in an S_N1 or an S_N2 pathway *via* a transition state with high carbocation character.[15a,21a]

Distinction between S_N1, S_N2 *and Ion-pair Mechanisms.*— Independent evidence against an S_N1 reaction can be obtained from the effects of added nucleophiles on the rates and products of displacement reactions.[9,10,13a,21] Both carbonyl-addition and S_N2 mechanisms should show rate–product correlations,[13a] in which rate enhancements due to added nucleophiles lead to corresponding amounts of extra product, *e.g.*, added amines convert benzoyl chloride into amides.[13a] Rate–product correlations have been observed for benzoyl chloride in 80% w/w acetone–water with added *o*-nitroaniline,[9] and in methanol with added *m*-nitroaniline.[13a] S_N1 and ion-pair mechanisms are characterised by a lack of rate–product correlation.[9,10] An apparent lack of rate–product correlation for benzoyl chloride in 50% w/w acetone–water with added *o*-nitroaniline has previously been discussed in terms of a competing S_N1 mechanism[9] or an ion-pair mechanism.[10a] The former proposal[9] is not consistent with our recent work,[8,13a] nor with the results discussed below. We also show that the results *do not require* an ion-pair mechanism.

The most distinctive feature of an ion-pair mechanism is the non-linearity of a plot of rate *versus* concentration of added nucleophile.[10a] We obtained kinetic data at constant molar concentration of nitroaromatic, paralleling similar studies of electrolytes at constant ionic strength (Figure 2). The non-linear plot (points A, B, and C) becomes linear when nitrobenzene is added (lines DB and EC). These results can be explained quantitatively (see below) by medium effects on competing aminolysis and solvolysis reactions, without postulating a 'trapping' pathway.

The second-order rate constants (Table 4) lead to predictions of percentage amide product slightly higher than the observed values; *e.g.*, for 0.188M-*o*-nitroaniline in 50% w/w acetone–water at 0 °C, S (selectivity) = 115 (from rate data alone, see Table 4) gives the predicted amount of amide to be 46% compared with the observed value of 44%.[9,13a] Direct comparisons of S values predicted from kinetic data (115—127, Table 4) with those previously obtained from product data (98—106[13a]) emphasise these discrepancies, which are now in the opposite direction from those expected for a trapping mechanism. We suggest that there is a satisfactory rate–product correlation at 0 °C. Presumably our attempts to model the medium effect of *o*-nitroaniline by adding nitrobenzene (Figure 2) are slightly imperfect (see below), particularly at 25 °C where the predicted S values (46—51, Table 4) are again higher than the observed values (33—36[13a]). If these reactions were base-catalysed by nitroaniline the predicted S values would be too high, but it is not clear why base catalysis should occur in 50% acetone–water and not in 80% acetone or in methanol.[13a]

Two additional observations support the above argument: (*i*) the medium effect of nitrobenzene is similar for both hydrolysis (Table 3, entries 9 and 10) and aminolysis (Table 4, entries 4 and 5); (*ii*) the temperature dependence of S values (Table 4), which

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* Entropy effects make a small but significant additional contribution to gas-phase equilibria.[19e]

arises from the *ca.* 5 kcal mol^{-1} lower $\Delta H^{\ddagger}$ (Table 1) for aminolysis than for solvolysis.

Medium Effects of Non-electrolytes.—Previous workers[9] made insufficient allowance for the medium effects in 50% acetone–water, for which the rate-retarding medium effect of added 0.2M-nitrobenzene is unexpectedly large (*ca.* 24%)—there is a corresponding effect of only *ca.* 5% for 80% acetone–water, so previous mechanistic analyses ignoring the medium effect in 80% w/w acetone–water seem justified.[9,13a] There are isolated literature reports of other medium effects of non-electrolytes. Three dissimilar non-electrolytes (>0.1M) each reduce the rates of nitration of benzenesulphonic acid in anhydrous sulphuric acid, but do not affect the nitration of protonated benzoic acid.[22a] In contrast, for aminolyses of alkyl perchlorates in benzene, the medium effects of added *N,N*-dimethylanilines are rate-enhancing.[22b]

Because of the complexities of these unexpected medium effects, the precision of the above rate-product correlations is reduced. Previously published product data were obtained in the absence of nitrobenzene.[9,13a] Predictions of these products from rate data requires the hydrolysis rate constant and an estimate of the second-order aminolysis constants in the absence of the medium effect. At amine concentrations (*e.g.*, <0.01M) sufficiently low to exclude medium effects, mass law effects are comparable in magnitude with experimental errors, so our aminolysis rate constants were obtained by linear extrapolations to zero nitroamine concentrations (Table 4); it seems likely that both they and the derived S values (Table 4) are slightly too large because they have been 'overcorrected' for the medium effect.

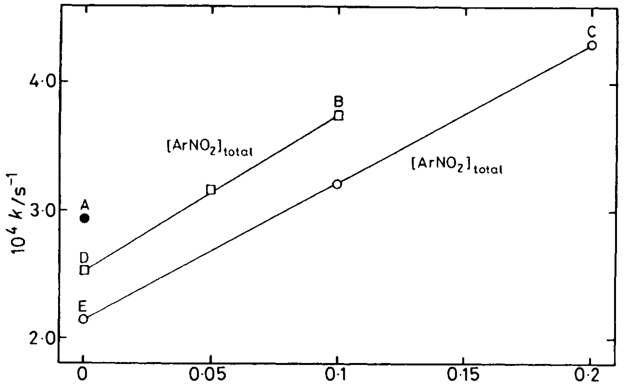

Figure 2. Rate constants for solvolysis and aminolysis of benzoyl chloride in 50% w/w acetone–water at −0.1 °C *versus* molar concentration of *o*-nitroaniline. Nitrobenzene added to maintain the total molar concentration of nitroaromatic $[ArNO_2]_{total}$ at either 0.1M (line DB) or 0.2M (line EC). The slopes of the correlation lines are presented in Table 4. See text for discussion of points A—E

Other Mechanistic Evidence.—Typical solvolyses of benzoyl chloride in the presence of 10^{-2}—10^{-5}M-HCl do *not* show acid catalysis,[17c] and give high ratios of hydrolysis to ^{18}O exchange;[23] the latter mechanistic probe does not provide direct evidence for an intermediate on the solvolysis pathway.[15a,23b] Because of the apparent absence of mechanistic complications, we have successfully applied ideas based on the S_N2–S_N1 spectrum[3b,15] to the reactions of benzoyl chloride. The additional competing carbonyl-addition pathway produces curvature and dispersion of the correlation lines (for the less aqueous mixtures of MeOH–H_2O and EtOH–H_2O) much greater than expected for the S_N2–S_N1 spectrum.[15,16] The greater reactivity of MeOH–H_2O compared with EtOH–H_2O mixtures of the same Y_{Cl} value (Figure 1) is also reflected in the greater product selectivities (S values, Table 2); *i.e.*, it appears to be a mass law effect not a solvation effect, consistent with previous discussions of second- and third-order dependence on solvent for carbonyl addition reactions.[18b] Relatively little work has been published on selectivities of MeOH–H_2O *and* EtOH–H_2O, but they have been found to be very similar for 2-octyl[24a] and 1-adamantyl[24b] substrates; at least a consistent order: H_2O, MeOH, EtOH (or the reverse) might have been expected,[18b] but our results for benzoyl chloride (S, Table 2) generally follow the order: MeOH > EtOH > H_2O > CF_3CH_2OH > $(CF_3)_2CHOH$. Solvent molecules may be required to act both as nucleophiles and proton donors, when the carbonyl-addition pathway becomes dominant. More detailed discussion of the carbonyl-addition pathway, particularly the effect of substituents,[8] will be presented elsewhere.

Interestingly, the increase in S, from 20 in 80% acetone to 34 in 50% acetone at 25 °C,[13a] is in the opposite direction to that expected from decreasing nucleophilic assistance (*e.g.*, the S values for MeOH–H_2O in Table 2 decrease as water is added). Possibly, this indicates that the amine is attacking a carbon atom having substantial cationic character,[15a,21a] but an ion-pair intermediate would also explain these results. In more highly ionizing and/or less nucleophilic solvents a change in mechanism from S_N2 to S_N2(intermediate) to S_N1 would be expected.[15a] The S_N2(intermediate) mechanism is an ion-pair mechanism, significantly different from that of Sneen and Larsen[10a] but further work is required to establish evidence for nucleophilic assistance *and* a trappable intermediate.

Conclusion

Our work on the correlation of solvent effects on reactivity has now reached the stage where predictions can be attempted. These predictions are useful for identifying anomalous be-

Table 4. Second-order rate constants for aminolysis (*o*-nitroaniline) of benzoyl chloride in 50% w/w acetone–water[a]

T/°C	$[ArNO_2]_{total}$/M[b]	k/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}	S[c]
25.0	0.2	6.7×10^{-3}			51
25.0	0.1	7.3×10^{-3}			46
25.0	0[d]	7.9×10^{-3}			48
−0.1	0.2[e]	1.09×10^{-3}	11.2[f]	−31.1[f]	127
−0.1	0.1[e]	1.22×10^{-3}	11.0[f]	−31.5[f]	121
−0.1	0[d]	1.35×10^{-3}			115

[a] Kinetic data from Table 3. [b] Nitrobenzene added to maintain constant total molar concentration of nitroaromatic (nitrobenzene + *o*-nitroaniline). [c] Selectivity calculated from the ratio of second-order aminolysis and hydrolysis rate constants, assuming $[H_2O]$ = 25M: see equations (5) and (6) of ref. 13*a*. [d] Rate constant extrapolated from above two values. [e] See also Figure 2. [f] From data at −0.1 and 25.0 °C.

Table 5. A typical calculation of first-order rate constant for relatively fast solvolytic reactions studied conductimetrically

Input readings[a]		Calculated conductance[c]	Error in conductance[c]
Time (min)	Conductance[b] 5×10^4/ohm^{-1}	5×10^4/ohm^{-1}	5×10^7/ohm^{-1}
0.000[d]	1.0105[d]	1.0480	−37.52
0.005[d]	1.3220[d]	1.3318	−9.80
0.010	1.5945	1.5963	−1.82
0.015	1.8433	1.8429	0.41
0.020	2.0768	2.0727	4.07
0.025	2.2897	2.2870	2.74
0.030	2.4827	2.4867	−3.95
0.035	2.6749	2.6728	2.11
0.040	2.8445	2.8463	−1.80
0.050	3.1554	3.1588	−3.38
0.060	3.4248	3.4303	−5.48
0.070	3.6704	3.6662	4.22
0.085	3.9666	3.9633	3.29
0.100	4.2034	4.2040	−0.55
0.120	4.4572	4.4552	2.00
0.150	4.7182	4.7215	−3.28
0.195	4.9608	4.9594	1.36

[a] Experimental conditions: immediately following an audible signal, 15 µl of *p*-methoxybenzoyl chloride (2% solution in dry dioxane) were injected into rapidly stirred 50% v/v acetone–water at 25.0 °C; the initial reading (time zero) was taken 1.00 s after the audible signal and further readings were taken at intervals of 0.300 s. [b] Readings tabulated are direct measurements in volts; the settings on the conductivity amplifier were range 4 and scale factor 5. [c] From the LSKIN computer program with least-squares minimisation of the logarithm of conductance: $k = (2.34 \pm 0.01) \times 10^{-1}$; standard deviation of log conductance 0.0012; correlation coefficient 0.999 99; calculated conductance at infinity 5.229, measured 5.382 after 2 h. [d] Readings omitted from the least-squares calculation; inclusion of these two readings in LSKIN gave: $k = (2.42 \pm 0.03) \times 10^{-1}$; standard deviation of log conductance 0.0049; correlation coefficient 0.999 77; calculated conductance at infinity 5.186.

haviour and for guiding further experimental work. The solvolytic reactions of benzoyl chloride proceed by two distinct and competing mechanisms, differing markedly in susceptibility to solvent ionizing power. In solvents of high ionizing power and/or low nucleophilicity the reactions conform to the S_N2–S_N1 spectrum.[15a,16] In 50% w/w acetone–water (*ca.* 56% v/v) rate–product correlations are observed consistent with S_N2 and/or carbonyl-addition mechanisms (no trappable intermediate). This conclusion is supported by our previous work on product selectivities[13a] and rate–rate profiles.[8] An S_N2–S_N1-type of mechanism is feasible in solvents of high ionizing power and/or low nucleophilicity [see equation (2)]. In nucleophilic solvents of lower ionizing power, carbonyl-addition mechanisms become dominant. Two important features of the carbonyl-addition mechanism are: (*i*) a very low sensitivity to solvent ionizing power [*m*, equation (1) is *ca.* 0.3]; and (*ii*) a tendency for greater nucleophilic reactivity of methanol compared with ethanol or water in the product-determining step. In studies of rate–product correlations in highly aqueous media, the medium effects on reactivity of non-electrolytes are expected to be significant.

Experimental

Chemicals.—Benzoyl chloride, methyl benzoate, *o*-nitroaniline, and t-butyl bromide were purified as described previously.[7a,13a] Nitrobenzene was a microanalytical standard (BDH Chemicals). Solvents for kinetics were prepared as described elsewhere,[25] with additional precautions to minimise levels of carbon dioxide impurities. Commercial samples of benzoic acid (sublimed) and ethyl benzoate (distilled) were purified for use as h.p.l.c. standards; also two benzoates of fluorinated alcohols were obtained by standard methods: 2,2,2-*trifluoroethyl benzoate*,[26a] b.p. 190 °C (Found: C, 52.8; H, 3.2. $C_9H_7F_3O_2$ requires C, 52.95; H, 3.45%); and hexafluoroisopropyl benzoate, m.p. 55—56 °C (from pentane), lit.,[26b] 53.9 °C (Found: C, 43.9; H, 2.1. Calc. for $C_{10}H_6F_6O_2$: C, 44.1; H, 2.2%).

Kinetic Methods.—As an alternative to data collection by chart recorder,[7] we utilised a high-precision digital voltmeter (SOLARTRON 7066 DATASTORE), which could be set to sample every second (or less frequently). Under computer control (Prime 750 or BBC Model B Microcomputer), up to 30 readings per second could be triggered and up to 50 readings could be stored in the voltmeter. Typically ten readings were triggered during the first half-life of reaction, and an additional five or ten readings equally spaced in extent of reaction were included in the calculation of the rate constant. For the fastest reactions so far examined by this technique, up to 10 readings per second were taken. The readings stored in the voltmeter were transferred *via* the RS232 interface to filestore in the Prime 750 either directly or *via* the disc store of the microcomputer, fitted with the UNITERM terminal emulator supplied by the Wolfson Microelectronics Unit (Swansea). After further manipulation and editing of files, the rate constant was obtained using LSKIN.[27] The input data and results for a typical kinetic run are shown in Table 5, which also illustrates the excellent performance of the amplifier required to obtain the conductance readings.[28]

In our most recent kinetic work we have reverted to Watt and Tranter's technique,[6b,28] using rapidly and continuously stirred conductivity cells, fitted with Quickfit B10 nitrogen-driven stirrers placed in the solution above the electrodes. Samples in dilute dioxane solution were injected rapidly by syringe *via* a side arm in the thermostatted cell. Injections were made immediately following an audible signal generated by the microcomputer. Trial experiments with injections of dilute hydrochloric acid showed that the initial increase in conductance began 0.4—0.5 s after the audible signal and that complete mixing required a further 0.8—1.0 s. Visual tests, made by injecting an aqueous solution of Methylene Blue, confirmed that the distribution of sample very rapidly became uniform throughout the conductivity cell.

Liquid Chromatrography and Product Studies.—In addition to the apparatus and techniques described previously,[13a] we also utilised a system comprising a Waters Solvent Metering Pump (M45), a Cecil Double Beam u.v. detector (CE 2112) and an Hewlett Packard electronic integrator (HP 3090A). Satisfactory chromatography columns having $N > 8\,000$ were packed with 5 µm SPHERISORB ODS (Phase Separations) in 15 cm × 1/4 in columns. Results were obtained by eluting with MeOH–H_2O (60—85%, containing 1% acetic acid); flow-rate 1 ml min^{-1}, $\lambda = 270$ nm.

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