Trends in Selectivity. Evidence from Rates and Products for Simultaneous Reaction Channels in Solvolyses of Benzoyl Chloride and Substituted Derivatives

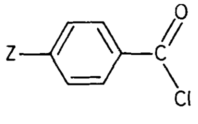
T. William Bentley* and In Sun Koo†
Department of Chemistry, University College of Swansea, Singleton Park, Swansea, SA2 8PP

Rates of solvolyses of *para*-Z-substituted benzoyl chlorides (Z = OMe, Me, or Cl) are reported for highly aqueous binary mixtures (with acetone, ethanol, and methanol cosolvents). Product data (ester and acid) are reported for a wide range of compositions of the aqueous binary alcohol mixtures (for Z = Me, H, or Cl). As water is added to alcohol, the selectivity *S* ([ester][water]/[acid][alcohol] initially increases but then reaches a plateau and/or decreases. This reversal of the trend in *S* occurs at different solvent compositions for each substrate (Z = Me, H, or Cl) and is very close to the region of mechanistic change predicted previously from rate–rate profiles; these predictions have now been refined by replacing solvolyses of 1-adamantyl chloride by *p*-methoxybenzoyl chloride as the model S_N1 process. The results provide new and sharply defined evidence for mechanistic change in nucleophilic substitutions at acyl carbon, supporting the co-existence of two different mechanisms or reaction channels, each of which could show variable structures of transition states. A quantitative dissection of observed rates into contributions from two reaction channels is described, and an attempt is made—with partial success—to calculate variations in *S* values occurring as the mechanism changes. Trends in *S* values are calculated successfully.

Nucleophilic substitutions at acyl carbon may proceed either by addition–elimination, by S_N1, or by direct S_N2 displacement.[1,2] From analyses of rate–rate profiles it was proposed that solvolyses of benzoyl chloride in aqueous alcohol (ethanol or methanol) occurred by two mechanisms—a carbonyl addition–elimination mechanism in less aqueous alcohol, and by a more polar mechanism having weak S_N2 character in more aqueous media.[3] The 'weak S_N2' mechanism differs from the carbonyl addition mechanism in that it involves the development of positive charge on the carbonyl group,[3a] and hence is favoured by electron-donating substituents in the benzene ring.[3b,4,‡] Each of these two mechanisms could show variable transition state structure,[4a] *e.g.* S_N2 tends towards S_N1 as nucleophilic assistance decreases.[5] It may be considered[4] that variations in transition states within only one mechanism may be sufficient to account for the results. We now report further evidence from rate–rate profiles and independent evidence from product selectivities supporting the simultaneous operation of two distinct mechanisms or reaction channels. A straightforward mechanistic pattern will be revealed. These results are also of wider significance because, in current discussions of reaction mechanisms, it is generally assumed that there is only one reaction channel.

Early proposals[1] for mechanistic changes from S_N2 to S_N1 in solvolyses of acid chlorides require modifications. Previous arguments for an S_N1 mechanism for solvolysis of benzoyl chloride in 50% w/w aqueous acetone,[6] have not been supported by recent attempts to trap a cationic intermediate.[3a] Interpretation of the earlier trapping experiments[6] is complicated by the medium effect of the added nucleophile,[3a] and by the possibility that an added nucleophile could induce a new substitution pathway.

We now consider that the mechanistic change from S_N2 to S_N1 reflects variations within a single mechanistic spectrum (or reaction channel), which should fit one linear free energy relationship (LFER).[4,5] Deviations from an expected LFER for solvolytic rate data for benzoyl chloride versus *Y* values led to proposals[2a,3a,7] that there were two competing mechanisms. If it is accepted that kinetic data for the S_N2–S_N1 spectrum of mechanisms can be correlated by one appropriate LFER,[5] then the competing mechanism must be different—presumably a carbonyl addition process.[2a,3a,7] The point of mechanistic change from predominantly carbonyl addition to predominantly S_N2–S_N1, as predicted from rate–rate profiles,[3,7] occurred at increasingly aqueous solvent compositions for more electron-donating substituents in the benzene ring;[3b] a more precise LFER was recently reported for solvolyses of benzoyl chloride,[3c] and details of the improved method of analysis of these rate–rate profiles are reported here.



(1)

A point of mechanistic change was not observed for solvolyses of *p*-nitrobenzoyl chloride (**1**; Z = NO_2) in aqueous ethanol or methanol,[3b] and the rates and products can be correlated assuming third-order kinetics.[8a] There appear to be at least four similar pathways differing only in the way two alcohol or water molecules participate in the reaction (see later discussion). All of these reactions are favoured by electron withdrawal, are probably general base catalysed,[8a] and may be broadly described as carbonyl additions. As changes in contributions from the four pathways are mechanistic changes, we will use terms like 'change in reaction channel' when more extensive changes in mechanisms are discussed. Solvolyses of (**1**; Z = NO_2) model the carbonyl addition reaction channel and provide useful data with which the other solvolyses will be compared.

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† On study leave from Department of Chemical Education, Gyeongsang National University, Chinju, Gyeongnam 620, Korea.

‡ *Corrigendum. J. Chem. Soc., Perkin Trans. 2*, 1986, 619, Table 2, [ref. 3(*b*)]. Entries on the first four and final five rows are correct; the other ten entries are printed one row too low. The editor apologises for this error.

Table 1. Rate constants (k) for solvolyses of *p*-methoxybenzoyl chloride (**1**; Z = OMe) in aqueous alcohols and aqueous acetone.[a]

Solvent[b]	T/°C	k/s^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}
50E	25.0[d]	5.4×10^{-1}	17.7	−0.3
40E	−10.0	$(3.50 \pm 0.22) \times 10^{-2}$		
	0.1	$(1.41 \pm 0.01) \times 10^{-1}$	18.5	5.4
	10.0	$(4.57 \pm 0.14) \times 10^{-1}$		
	25.0[c]	2.6		
30E	−10.0	$(2.06 \pm 0.09) \times 10^{-1}$		
	0.0	$(6.73 \pm 0.10) \times 10^{-1}$	18.2	7.8
	5.0	1.48 ± 0.01		
	25.0[c]	14		
20E	−9.9	$(5.71 \pm 0.15) \times 10^{-1}$		
	−5.0	1.02 ± 0.04	17.7	7.8
	0.0	2.02 ± 0.02		
	25.0[c]	34		
60M	25.0[d]	8.4×10^{-1}	16.2	−4.5
50M	25.0[c,e]	2.4	16.1	−2.8
40M	25.0[c,e]	5.9	16.5	0.2
30M	−20.0[f]	$(6.53 \pm 0.30) \times 10^{-2}$		
	−10.0	$(2.69 \pm 0.09) \times 10^{-1}$	18.2	8.4
	25.0[c]	18		
20M	−9.9	$(5.71 \pm 0.27) \times 10^{-1}$		
	−4.9	1.13 ± 0.02	18.7	11.5
	0.0	2.16 ± 0.07		
	25.0[c]	42		
40A	25.0[e]	9.8×10^{-1}	16.0	−4.9
30A	−10.0	$(8.25 \pm 0.04) \times 10^{-2}$		
	0.0	$(2.8 \pm 0.02) \times 10^{-1}$	17.2	2.0
	25.0[c]	4.4		
20A	−10.0	$(2.49 \pm 0.01) \times 10^{-1}$		
	0.0	$(8.78 \pm 0.6) \times 10^{-1}$	17.5	5.3
	25.0[c]	14		

1 cal = 4.184 J. [a] Determined conductimetrically in duplicate except where noted otherwise; errors shown are average deviations. [b] Solvent codes: E = % v/v ethanol–water; M = % v/v methanol–water; A = % v/v acetone–water. [c] Calculated from data at other temperatures. [d] Reference 3(*a*). [e] Reference 3(*b*). [f] Triplicate measurement of rate constant.

Table 2. Additional rate constants (k/s^{-1}) for solvolyses of *p*-methoxybenzoyl chloride (**1**; Z = OMe) in aqueous alcohols at 25 °C.[a]

% v/v Alcohol	Ethanol	Methanol
98	$(1.55 \pm 0.02) \times 10^{-3}$	$(1.42 \pm 0.01) \times 10^{-2}$
95	$(2.66 \pm 0.05) \times 10^{-3}$	$(2.09 \pm 0.01) \times 10^{-2}$

[a] Determined conductimetrically in duplicate; errors shown are average deviations.

Electron-donating substituents and increases in solvent ionizing power favour the S_N1 mechanism *e.g.* hydrolysis of *p*-dimethylaminobenzoyl fluoride shows common-ion rate depression.[9] Solvolyses of *p*-methoxybenzoyl chloride (**1**; Z = OMe) in aqueous ethanol or methanol showed a slightly non-linear rate–rate profile *vs.* Y_{Cl}, possibly indicating a point of mechanistic change.[3b] However, more detailed studies and comparisons with solvolyses of 2,6-dimethylbenzoyl chloride showed that the slight non-linearity was due to a solvation effect.[10] From substituent and solvent effects it appears that these solvolyses are close to S_N1;[3b] product formation may occur *via* solvent-separated ion pairs because selectivity for ethanol is less than that for water.[10] Hence solvolyses of (**1**; Z = OMe) model the S_N2–S_N1 reaction channel and provide data for a second model compound for comparison with the other solvolyses.

Table 3. Rate constants (k/s^{-1}) for solvolyses of *para*-Z-substituted benzoyl chlorides (**1**) in highly aqueous media[a] at 25 °C.

Solvent[b]	Z = Cl	Z = H[c]	Z = Me	Z = OMe[d]
60E		0.0078[e]		0.19[f]
50E	0.0097[g]	0.017	0.0584[g]	0.54
40E	0.0155	0.048	0.199	2.6
30E	0.0384	0.18	0.83	14
20E	0.0890	0.37	2.5[h]	34
70M	0.0220	0.0197	0.0415	0.32
60M	0.0254[g]	0.035	0.0844[g]	0.84
50M	0.0295	0.063	0.242[g]	2.4
40M	0.0428[g]	0.134	0.554[c]	5.9
30M	0.0635	0.29	1.2[c]	18
20M	0.0994[g]	0.54	3.1[c]	42
40A	0.0091[g]	0.025	0.103[g]	0.98
30A	0.0201[g]	0.083		4.4
20A	0.0479[g]	0.25	1.42[g]	14
10A	0.110[g]	0.55		

[a] New results determined conductimetrically in duplicate; errors for this new work are not shown but are typically < ± 2%. [b] As for Table 1. [c] Ref. 3(*a*). [d] Data from Table 1. [e] Ref. 4(*b*). [f] Interpolated from a slightly curved plot of $\log(k/k_0)$ for (**1**; Z = OMe) *versus* Grunwald–Winstein Y values from ref. 13. [g] Ref. 3(*b*). [h] Direct measurement at 25 °C supported by the following additional kinetic data k/s^{-1} (°C): $(1.63 \pm 0.02) \times 10^{-1}$ (0.0 °C); $(5.32 \pm 0.07) \times 10^{-1}$ (10.0 °C); $\Delta H^{\ddagger} = 17.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = 2.6$ cal K^{-1} mol^{-1}; extrapolation of these two results to 25.0 °C gives $k = 2.7$ s^{-1}.

Because of possible complications in the interpretation of rate–rate profiles, independent evidence for competing mechanisms was obtained from product selectivities. Products of solvolyses of acid chlorides in aqueous alcohols are the parent acid and an ester. Selectivities (S) are defined by equation (1).[10]

$$(S) = [\text{ester}]_{\text{prod}}[\text{water}]_{\text{solv}}/[\text{acid}]_{\text{prod}}[\text{alcohol}]_{\text{solv}} \quad (1)$$

Results

To complete the set of kinetic data required for this work, additional results were obtained for solvolyses of (**1**; Z = OMe) (Tables 1 and 2) and (**1**; Z = Cl, Me) (Table 3). Solvent codes are shown in Table 1, footnote *b*. Additional rate constants in s^{-1} (not tabulated) are: (**1**; Z = Me); 90A, $k = 1.02 \times 10^{-4}$; (**1**; Z = Cl); 90A, $k = 4.9 \times 10^{-4}$; 90M, $k = 1.16 \times 10^{-2}$. Additional literature data have been added to Table 3 to show the substituent effects on reactivity as well as the consistency of the experimental data. The activation parameters further support the reliability of the difficult measurements on solvolyses of (**1**; Z = OMe) (Table 1); the increase in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in highly aqueous alcohols has been observed for solvolyses of t-butyl chloride.[11,12] More detailed evidence supporting the reliability of the relatively large rate constants ($k > 2$ s^{-1}), obtained by extrapolation of data at lower temperatures, has been reported elsewhere.[10] The highest reliable value of k that we have obtained by direct measurements is 2.5 s^{-1} for (**1**; Z = Me) in 20E at 25 °C (Table 3, footnote *h*).

Selectivities (S) are reported in Table 4. Trends for each substrate are more reliable than absolute values because of small (up to 5%) uncertainties in response calibration which at least partly accounts for the *ca.* 10% higher values reported previously for benzoyl chloride.[3a] Also, rapid mixing is now known to be important for these product studies; less rapidly mixed solutions tend to give higher S values.[10]

Discussion

Selectivities.—Mechanistic changes for solvolyses of the three substrates (**1**; Z = Cl, H, Me) can be seen directly from the

Table 4. Pattern of selectivity (S) for product formation in solvolyses of *para*-Z-substituted benzoyl chlorides (**1**) in alcohol–water at 25.0 °C.[a]

Alcohol (%v/v)	Substituent Z NO_2	 Cl	 H	 Me	 OMe
Ethanol					
98	0.7	0.9	1.3	1.6	0.6
95	0.9	1.3	1.7	1.7	0.7
90	1.3	1.8	1.9	**1.7**	0.7
80	2.0	2.6	2.3	**1.3**	0.6
70	2.5	3.4	**2.1**	**1.1**	0.7
60	3.1	3.7	**1.6**	**1.0**	0.7
50	3.6	3.8	**1.3**	1.0	0.7
40	4.2	**3.0**	**1.1**	1.0	0.7
20	5.2	**1.5**	0.7	0.8	0.8
Methanol					
98	1.9	2.0	4.0	2.7	1.3
95	2.4	2.6	4.2	2.6	1.4
90	3.5	3.4	4.3	**2.5**	1.4
80	4.9	4.8	**4.3**	**2.1**	1.3
70		5.4	**3.6**	**1.6**	
60	7.9	5.7	**2.7**	**1.6**	1.2
50		**5.2**	**2.0**	1.4	
40	9.9	**4.1**	**1.6**	1.4	1.4
20	10.0	**2.7**	1.3	1.4	1.4

[a] Data from this work and references 8(*a*) and 10; experimental values have been rounded off to emphasise trends in a compact form. Values in bold show deviations from expected trends based on data for solvolyses of (**1**; Z = NO_2 and (**1**; Z = OMe).

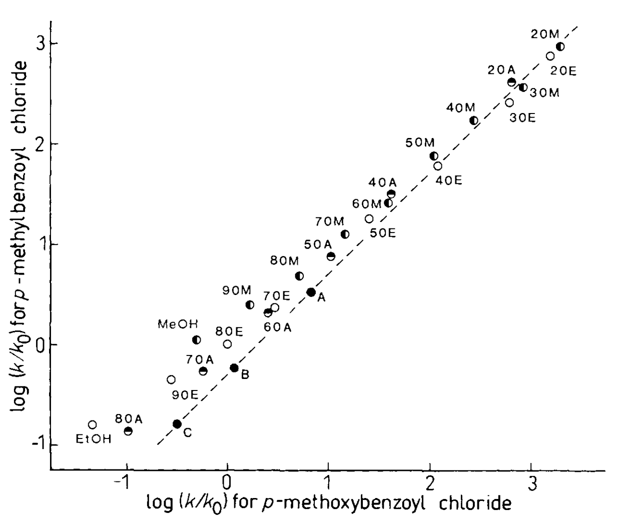

Figure 1. Correlation of logarithms of solvolysis rates for *p*-methylbenzoyl chloride (**1**; Z = CH_3), relative to rates in 80% v/v ethanol–water (k_0) at 25 °C *versus* corresponding rates for *p*-methoxybenzoyl chloride (**1**; Z = OMe); solvent codes given in Table 1; kinetic data from Tables 1–3 and refs. 3, 4, and 10. The hatched line is predicted for S_N2–S_N1 solvolyses from a least-squares calculation for points A, B, and C (see the text) and experimental data points for 20A, 20E, and 20M: slope, 1.01 ± 0.02; correlation coefficient 0.9995.

selectivity data when comparisons with solvolyses of (**1**; Z = OMe) and (**1**; Z = NO_2) are made (Table 4). The expected trend for the carbonyl addition reaction channel is an increase in S as water is added to alcohol—see data for (**1**; Z = NO_2) (Table 4). Departures from this trend (shown in bold typeface) occur in 40E and 50M (**1**; Z = Cl), in 70E and 80M (**1**; Z = H), and in 90E and 90M (**1**; Z = Me). Although S values for the S_N2–S_N1 reaction channel are not known, it appears that for ethanol–water mixtures an S value of 0.7 ± 0.1 can be reached as a lower limit (**1**; Z = OMe) in all compositions; (**1**; Z = H and Me) in 20E, when the carbonyl addition processes becomes insignificant. Similar results are observed for methanol–water mixtures with S = 1.3 ± 0.1 for (**1**; Z = OMe) in all compositions and for (**1**; Z = H and Me) in highly aqueous media.

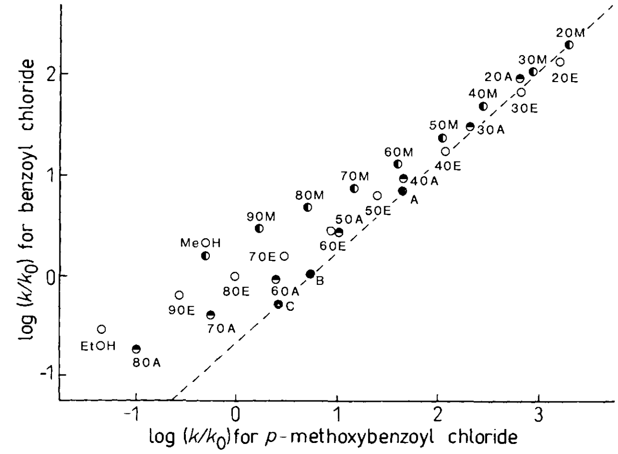

Figure 2. As for Figure 1, except the substrate is benzoyl chloride. For the hatched line: slope, 0.90 ± 0.02; correlation coefficient, 0.9986.

Rate–Rate Profiles.—Mechanistic changes for solvolyses of benzoyl chloride have previously been predicted from mass law effects (*NB* solvent effects ignored),[6b] and from solvent effects *e.g.* Grunwald–Winstein plots[2a,7] and comparisons of logarithms of rate constants for solvolyses of various acid chlorides *versus* Y_{Cl}.[3b] These predictions can now be modified slightly to improve further the allowance made for solvation effects.[10] Of the alternative model substrates for which data suitable for rate–rate profiles are available,[10] we chose solvolyses of (**1**; Z = OMe) because a wider range of data was accessible. The new rate–rate profiles are shown in Figures 1–3. Discussion of the hatched lines will be given later. Considering results for individual binary mixtures, changes in slopes for (**1**; Z = Me) (Figure 1) occur close to 80M and close to 80E, and for benzoyl chloride (Figure 2) close to 60M and between 60E and 70E. These are the solvent compositions where a change of reaction channel is predicted to occur, *i.e.* at that composition the two reaction channels both contribute 50% towards the observed rate of reactions. These predicted values for solvent compositions are all of slightly higher alcohol content than previous predictions based on Y_{Cl};[3b] *e.g.* for benzoyl chloride in methanol–water we previously predicted[3b] the change to be at 50M whereas 60M is now predicted (see Figure 2).

Interpretation of kinetic data for (**1**; Z = Cl) and (**1**; Z = NO_2) is now known[8a] to be more complex than that given previously.[3b] In less aqueous media, rates and products (Table 4) of solvolyses of (**1**; Z = Cl) resemble those of (**1**; Z = NO_2). For solvolyses of (**1**, Z = NO_2) over the whole range of aqueous alcohol mixtures, rates fit the third-order equation (2), in which

$$k_{obs} = k_{aa}[ROH]^2 + (k_{aw} + k_{wa})[ROH][H_2O] + k_{ww}[H_2O]^2 \quad (2)$$

k_{aa} is the rate constant for attack by two alcohol molecules, k_{ww} refers to water, k_{aw} refers to alcohol as nucleophile and k_{wa} refers to water as nucleophile. Products can be calculated directly if the (k_{aw} + k_{wa}) term is assumed to lead only to ester product;[8a] *i.e.* the k_{wa} term leading to acid product is relatively small. In more aqueous media (*e.g.* 60M ⟶ water), rates of solvolyses

Table 5. Comparisons of third-order rate parameters [equation (2)] for solvolyses of *p*-nitrobenzoyl chloride (**1**; Z = NO_2) and *p*-chlorobenzoyl chloride (**1**; Z = Cl).[a]

Parameter	Z = NO_2[b]	Z = Cl	Ratio
k_{aa} (for MeOH)/mol^{-2} dm^6 s^{-1}	6.69×10^{-5}	9.95×10^{-6}	6.7
k_{aa} (for EtOH)/mol^{-2} dm^6 s^{-1}	3.95×10^{-5}	4.16×10^{-6}	9.5
k_{ww} (in water)/mol^{-2} dm^6 s^{-1}	2.18×10^{-5}	2.00×10^{-6}[c]	10.9
m	−0.176	−0.168[d]	

[a] Summarised in the text but full details given in ref. 8(*a*). [b] From ref. 8(*a*). [c] Extrapolated from a plot (Figure 4) of third-order hydrolysis rate constants in 90A, 80A, and 70A for (**1**; Z = Cl). [d] Slope of plot described in footnote *c*; standard error in slope ± 0.003, correlation coefficient 0.99986.

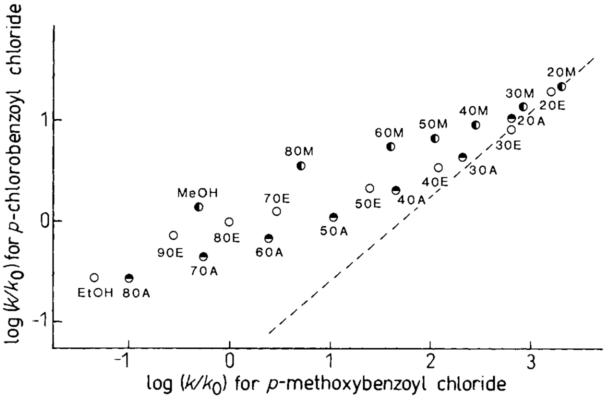

Figure 3. As for Figure 1, except the substrate is *p*-chlorobenzoyl chloride (**1**; Z = Cl); the hatched line is predicted for S_N2–S_N1 solvolyses (see text and Figure 5).

of (**1**; Z = NO_2) decrease, in contrast with the rate increase observed for solvolyses of (**1**; Z = Cl) (Figure 3). Relative rates of solvolyses for (**1**; Z = NO_2)/(**1**; Z = Cl) are between 6 and 13 for solvolyses in less aqueous media (*e.g.* pure alcohols, Table 5). In more aqueous media these relative rates decrease sharply, so that in 20E the rate ratio is <1. A mechanistic change appears to be taking place, but the plot of the data (Figure 3) provides no clearly defined evidence that this change has been completed in 20E and 20M.

These conclusions can be compared with the independent predictions based on changes in trends in the selectivity data (Table 4) [*i.e.* for (**1**; Z = H), mechanistic change appears to be in the region 70E ⟶ 40E, and 80M ⟶ 40M; for (**1**; Z = Me), 90E ⟶ 60E, and 90M ⟶ 60M]. These predictions are in good agreement with those predicted from Figures 1 and 2. For (**1**; Z = Cl) the lowest *S* values are 1.5 in ethanol–water and 2.7 in methanol–water (Table 4), significantly greater than the lower limits of 0.7 ± 0.1 and 1.3 ± 0.1 for ethanol–water and methanol–water, respectively. This may be another indication that the change of the reaction channel for solvolyses of (**1**; Z = Cl) is incomplete in 20% v/v alcohol–water (an alternative and preferred explanation is discussed later).

Towards a More Quantitative Analysis of Rate and Product Data.—The pattern of results (Table 4) suggests a high level of consistency in the *S* values. For (**1**; Z = Cl, NO_2) *S* values for methanol–water and trends in *S* values for ethanol–water (Table 4) are very similar when carbonyl addition is dominant. Slightly higher *S* values are observed for (**1**; Z = H) (98E ⟶ 80E) and (**1**; Z = Me) (98E ⟶ 95E). Hence, as first approximations, we assume: (*a*) data for (**1**; Z = NO_2) (Table 4) provide reasonable estimates of the *S* values expected for the carbonyl addition reaction channel in each solvent and (*b*) data for (**1**; Z = OMe) provide solvent-independent *S* values of 0.70 in ethanol–water and 1.3 in methanol–water for the S_N2–S_N1 reaction channel. For solvolyses of (**1**; Z = H) in 60E–70E, the two reaction channels are predicted from the kinetic data (Figure 2) to occur equally. Using the two assumptions stated above, *S* can be calculated for solvolyses of (**1**; Z = H). For 60E the observed ester/acid concentration ratios are 1.44 for (**1**; Z = NO_2)[8a] and 0.32 for (**1**; Z = OMe).[10] If 50% of the total reaction goes by each reaction channel, then 29.5% of the total product will be ester formed by the carbonyl addition channel and 12.1% will be formed by the S_N2–S_N1 reaction channel. From these yields of ester the *S* value is calculated to be 1.54, in good agreement with the experimental result of 1.6 for (**1**; Z = H) in 60E. For methanol–water, the mechanistic change is predicted to occur close to 60M (Figure 2) and the calculated *S* value is 2.8, again in good agreement with the experimental value of 2.7.

The above results illustrate that, in the region of mechanistic change, the *S* values can be calculated quite well. It would be possible to use only the *S* values (Table 4), with the assumptions given above, to predict the solvent composition when the mechanistic change occurs (*i.e.* 50% of each reaction channel). However, this is probably less reliable than the analysis given above, based on the kinetic data (Figures 1–3). Because *S* is based on product ratios [equation (1)], contributions of 50% from a reaction having for example $S = 9$ (*i.e.* 90% of the product formed by this pathway will be ester, when [ROH] = [H_2O]) and of 50% from a reaction having $S = 1$ (50% ester when [ROH] = [H_2O]) will give an overall value of 70% of the total product for the yield of ester *i.e.* $S = 2.3$, not the average *S* of 5.0. Hence the maximum *S* value is not the point of mechanistic change, and appropriate *S* values cannot be predicted simply by taking an average of the two *S* values for the competing reaction channels.

Precise Quantitative Analysis of Rate Data.—Further information can be obtained from the kinetic data about the changeover from the carbonyl addition reaction channel to the S_N2–S_N1 reaction channel. Logarithms of rate constants for the S_N2–S_N1 reaction channel should plot linearly against logarithms of rate constants for solvolyses of (**1**; Z = OMe), an appropriate model compound for correlating reactions occurring *via* the S_N2–S_N1 channel.[10] Solvolyses of benzoyl chloride in highly aqueous media (50M ⟶ 20M; 40E ⟶ 20E; see Figure 2) show a linear region. Fortuitously, other linear plots are also observed for MeOH ⟶ 70M and EtOH ⟶ 70E. Extrapolated correlation lines for MeOH ⟶ 70M and 50M ⟶ 20M intersect close to the point for 60M. The exact intersection point is calculated to be at $y = 1.10$, $x = 1.65$, values which represent logarithms of solvolysis rates relative to rates observed in the standard solvent, 80E.[11,13] If these extrapolations are reliable, then for the solvent composition corresponding to this point on the *x* axis, the two reaction channels each contribute 50% to the overall reaction. The S_N2–S_N1 channel is then contributing half of the observed rate (k_{obs}); *i.e.*

$$k_{obs}/2 = k_{S_N2-S_N1}$$

Hence, $\log k_{obs}\ (\text{at } x = 1.65) - \log 2 = \log k_{S_N2-S_N1}$

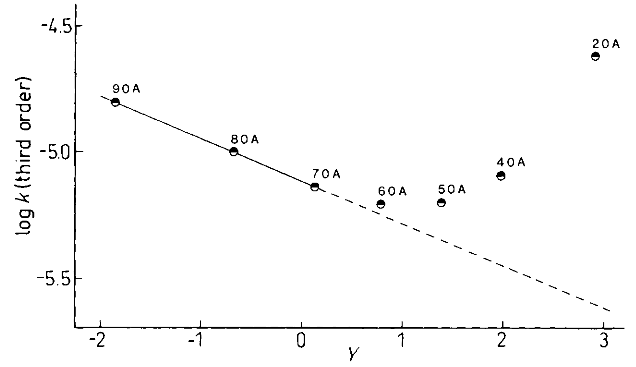

Figure 4. Correlation of logarithms of calculated third-order rate constants for solvolyses of *p*-chlorobenzoyl chloride (**1**; Z = Cl) in acetone–water *versus* Grunwald–Winstein *Y* values (ref. 13). The hatched line is an extrapolation to predict the rates of solvolysis occurring *via* the carbonyl addition reaction channel in the more aqueous media (see also Table 4, footnotes *c* and *d*).

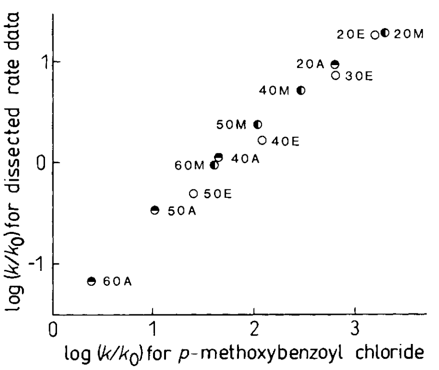

Figure 5. As for Figure 1, except the substrate is *p*-chlorobenzoyl chloride (**1**; Z = Cl) and the rate constants are the dissected contributions to the S_N2/S_N1 reaction channel; least-squares analysis slope 0.83 ± 0.03, correlation coefficient 0.994.

The logarithm of the rate constant k_{obs} (at $x = 1.65$) was estimated by linear interpolation between the logarithms of observed rate constants for the two closest solvent compositions for which experimental data had been obtained. The dissected contribution ($\log k_{S_N2-S_N1}$) can be plotted on the graph (Figure 2) at point A, $y = (1.15 - \log 2)$, $x = 1.65$. Rate constants for the carbonyl addition channel in highly aqueous media cannot be obtained by extrapolation of the MeOH ⟶ 70M line because after 60M the rate decreases—see Figure 3 and particularly data published elsewhere for (**1**; Z = NO_2).[8a] This decrease introduces a small uncertainty into the location of point A. From expected trends it can be estimated that in 20M the S_N2–S_N1 channel contributes over 90% of the observed rate, and we approximate this to 100%. A line through the data point for 20M (Figure 2) and point A should then be the dissected contribution from the S_N2–S_N1 reaction channel. If this line is both interpolated and extrapolated, dissected contributions in other solvent compositions and corresponding *S* values could be predicted.

The above arguments can be strongly supported by the following additional evidence. Calculations repeated for the ethanol–water data (Figure 2) give point B, well separated from point A. Different aqueous binary mixtures may give slight 'dispersion' of correlation lines, and to check that this effect was minor, data for acetone–water mixtures have been added (point C, Figure 2) to the results communicated previously.[3c] The correlation line shown in Figure 2 is a least-squares fit to the experimental data points for 20M, 20E, and 20A and the corresponding calculated points A, B, and C respectively. These calculations were repeated for solvolyses of (**1**; Z = Me) (Figure 1). Extrapolation of the lines through points A, B, and C to $x = 0$ permits calculation of the rates of S_N2–S_N1 solvolyses in 80E; this is calculated to be 0.5 k_{obs}, for (**1**; Z = Me) and 0.22 k_{obs} for (**1**; Z = H).

The self consistency of the above results for (**1**; Z = H, and Me) prompted a more difficult analysis of the data for (**1**; Z = Cl) (Figure 3), for which no convincing linear plots through the data points were seen. As most of these solvolyses resemble those of (**1**; Z = NO_2) more closely than those of (**1**; Z = OMe) (Figure 3), allowance can be made for the carbonyl addition channel [equation (2)] as in previous work.[8a] Third-order rate constants for solvolyses of (**1**; Z = Cl) in pure alcohols [k_{aa}, equation (2)] are calculated from the observed pseudo-first order rate constants and the molar concentrations of alcohol (Table 5). Third-order rate constants in the less aqueous compositions of acetone–water can be extrapolated to pure water (Figure 4) to obtain the k_{ww} term [equation (2)], and the medium effect (*m*). Strong similarities with solvolyses of the more reactive substrate (**1**; Z = NO_2) can be seen from the rate ratios and *m* values (Table 5). Following our earlier work,[8a] we have retained the use of *Y* values (Figure 4) for the small medium effect on rate constants. Very similar rate-product correlations to those previously reported[8a] have now been obtained by replacing *Y* values with logarithms of rate constants for solvolyses of (**1**; Z = OMe).[8b]

For solvolyses of (**1**; Z = NO_2), a plot[8a] analogous to Figure 4 is linear over a wide range of acetone–water mixtures (90–20%), and the extrapolated line for (**1**; Z = Cl) (Figure 4) from 60A to 20A gives the predicted rates in the various solvent mixtures for solvolyses of (**1**; Z = Cl) occurring *via* the carbonyl addition channel. The difference between the observed and predicted rate constants for solvolyses of (**1**; Z = Cl) is assumed to be the contribution from the S_N2–S_N1 reaction channel.

A very similar result for the dissected contribution from the two reaction channels could have been obtained by assuming that the k_{ww} term [equation (2)] was 11 times greater in all solvents for (**1**; Z = NO_2) than for (**1**; Z = Cl) (see Table 5). This alternative approach gave good results for ethanol–water mixtures, assuming a rate ratio of ten as an approximate weighted average of k_{aa}, k_{aw}, k_{wa}, and k_{ww} terms [equation (2)]. A lower rate ratio of 7.5 was assumed for methanol–water mixtures—these solvolyses are dominated by the k_{aw} term,[8a] which we cannot evaluate directly for (**1**; Z = Cl).

The dissected rate constants calculated for solvolyses of (**1**; Z = Cl) *via* the S_N2–S_N1 reaction channel give a satisfactory linear rate–rate profile *versus* solvolyses of (**1**; Z = OMe) (Figure 5), considering the uncertainties in these calculated rate constants. The slope of a correlation line through all of the data points (Figure 5) is 0.83 ± 0.03, lower than for benzoyl chloride (0.90 ± 0.02, Figure 2).

The correlation line (Figure 5) has been added to Figure 3 as a hatched line to provide a comparison with the undissected rate data. In retrospect, it was seen that a similar line could have been constructed by linear extrapolations leading to points A, B, and C, as described for the hatched lines in Figures 1 and 2. These results imply that the gradual increase in upward curvature in highly aqueous media (Figure 3) has ceased in 20A, 20E, and 20M.

Calculation of Trends in S *Values.*—A very demanding test of the reliability of the above evidence for the dissected S_N2–S_N1 contributions is the calculation of variations in *S* values as the S_N2–S_N1 reaction channel gradually supersedes the carbonyl addition channel. The calculated results are summarised in

Table 6. Dissected contributions of two reaction channels to observed rates and products for solvolyses of *p*-Z-substituted benzoyl chlorides (**1**) in alcohol–water.

	Ethanol		Methanol	
Alcohol (% v/v)	% ($\mathrm{S_N}2$–$\mathrm{S_N}1$)[a]	S_{calc}	% ($\mathrm{S_N}2$–$\mathrm{S_N}1$)[a]	S_{calc}
p-Methylbenzoyl chloride				
98[b]	17	0.7	24	1.8
95[b]	21	0.9	28	1.9
90	30	1.06	34	2.3
80	50	1.15	55	2.1
70[c]	66	1.09	58	2.2
60			74	1.9
50[c]	81	1.0	83	1.8
40	95	0.8	92	1.6
20	100[d]	0.7	100[d]	1.3
Benzoyl chloride				
98[b]	6	0.7	8	1.9
95[b]	7	0.9	10	2.3
90	11	1.2	12	3.0
80	22	1.53	20	3.4
70[c]	39	1.51	33	3.3
60	54	1.46	48	2.9
50[c]	68	1.3	63	2.5
40	86	1.0	72	2.3
20	100[d]	0.7	100[d]	1.3
p-Chlorobenzoyl chloride				
98[b]	1	0.7	2	1.9
95[b]	1	0.9	2	2.3
90	2	1.3	2	3.4
80	4	1.9	4	4.5
70[c]	12	2.1	7	5.4
60			15	5.5
50[c]	27	2.5	30	4.6
40	62	1.7	45	3.9
20	92	1.0	98	1.4

[a] The contribution from the carbonyl addition channel is 100 − % ($\mathrm{S_N}2$–$\mathrm{S_N}1$). [b] Rate constants interpolated from data in pure alcohol and 90% v/v alcohol–water by comparison with rate data for (**1**; Z = OMe) (Table 2). [c] Product data for (**1**; Z = NO_2) in this composition of methanol–water were estimated from the trends in a data for other solvent compositions. [d] Assumed.

Table 6, but one such calculation is now outlined. For benzoyl chloride in 90M the distance between the point for 90M and the extrapolated line (hatched, Figure 2) is 0.94 log unit. For illustration, we approximate this to 1 log unit, so the $\mathrm{S_N}2$–$\mathrm{S_N}1$ process is calculated to contribute 10% of the observed rate. As before, solvent dependent S values were obtained from data for (**1**; Z = NO_2) to model the carbonyl addition reaction channel (S = 3.50[8a]) and S values for (**1**; Z = OMe) modelled the $\mathrm{S_N}2$–$\mathrm{S_N}1$ reaction channel (S = 1.3 in methanol–water). Ester/acid concentration ratios for the two reaction channels are 14 and 5.2 respectively, corresponding to 93.3 and 83.9% ester. Taking 90% of 93.3 and 10% of 83.9 gives a total yield of ester of 92.4% and a calculated S value [equation (1)] of 3.0. The calculated results (Table 6) reproduce the trends in S values including the solvent compositions giving maximum S for (**1**; Z = Cl and H). The calculated S values are particularly good for solvolyses of (**1**; Z = Cl) in methanol–water (except for low values in 20M and 50M). Two deficiences in absolute values are discussed below.

In less aqueous media (*e.g.* 98 ⟶ 90E), observed S values for solvolyses of (**1**; Z = Cl, H, Me) are higher than for (**1**; Z = NO_2). However, S values calculated from our rate-product correlation for (**1**; Z = NO_2),[8a] assuming zero contribution from the k_{wa} [leading to acid product, equation (2)] are at least double the observed values. A few % contribution from the k_{wa} pathway has a large effect on S values when, as in these cases, the total yield of acid is low (< 10%). Hence the increase in S values for Z = NO_2 < Z = Cl < Z = H < Z = Me could be due to increasing (but small overall) contributions from the k_{wa} pathway.

A second deficiency is the choice of S values for solvolyses in highly aqueous media. For solvolyses of (**1**; Z = Cl) in 20% v/v alcohol the $\mathrm{S_N}2$–$\mathrm{S_N}1$ mechanism is dominant, but S has not reached such low values as those obtained for solvolyses of (**1**; Z = H, Me, and OMe) *e.g.* 0.7—0.8 in 20% ethanol–water (Table 4). These results are consistent with greater $\mathrm{S_N}2$ character for solvolyses of (**1**; Z = Cl), so that product formation does not occur from solvent-separated ion pairs (proposed when S < 1).[10] Conversely, for solvolyses of (**1**; Z = H and Me) in 20% v/v alcohol–water, a prediction arising from this work is that it may be possible to trap a cationic intermediate; previous attempts were made using much less aqueous media (*e.g.* 50% w/w acetone–water).[3a,6a]

Dissections of kinetic data for solvolyses of benzoyl chloride in 30A ⟶ 95A were made by A. H. Fainberg and reported in a later doctoral thesis.[14] For 50A the percentage of the $\mathrm{S_N}2$–$\mathrm{S_N}1$ pathway was calculated[14] to be 63%, in very good agreement with our calculated value of 66%. However, in 80A, we predict 15% $\mathrm{S_N}2$–$\mathrm{S_N}1$ in comparison with the earlier prediction[14] of 3%. Although the exact procedure[14] was not reported, calculations were probably based on a correlation with Y values. No allowance could have been made for the recently discovered differences in solvation effects in less aqueous media.[10]

Table 7. Substituent effects on the dissected rate constants ($k/10^{-3}$ s^{-1}) for S_N2–S_N1 solvolyses of *p*-Z-substituted benzoyl chlorides (**1**).[a]

	Substituent Z			
Solvent	Cl	H	Me	OMe
80E	0.18	0.59	1.64	21.7[b]
EtOH	0.014	0.04	0.07	0.99[b]
20M	99.4[b]	540[b]	3 100[b]	42 000[b]
MeOH	0.10	0.31	0.79	10.7[b]

[a] Calculated by extrapolation of the hatched correlation lines (Figures 1–3), except where noted otherwise. [b] Observed rate constants.

Table 8. Substituent effects on the dissected rate constants ($k/10^{-3}$ s^{-1}) for carbonyl addition solvolyses of *p*-Z-substituted benzoyl chlorides (**1**).[a]

	Substituent Z			
Solvent	NO_2	Cl	H	Me
80% EtOH	49.0[b]	4.31	2.08	1.67
EtOH	11.6[b]	1.20	0.72	0.45
MeOH	40.8[b]	5.95	3.99	2.41

[a] Calculated from the difference between observed rate constants and those calculated for the S_N2–S_N1 reaction channel (Table 7), except where noted otherwise. [b] Observed rate constants.

Solvation effects were ignored in an independent published analysis of similar data, in which an empirical mass law relationship was derived for contributions from unimolecular and bimolecular pathways.[6b] From the equation given for the two pathways,[6b] there is again agreement for 50A. However, we calculate that in 60A there is a contribution of 69% from the bimolecular (presumably carbonyl addition) pathway, significantly greater than the value of 47% obtained by our method[3c] of dissecting the rate data. Also in 80A, the bimolecular pathway is calculated to contribute 99.5% of the observed rate constant (*cf.* our predicted value of 85%). It is difficult to devise experimental checks of these predictions for acetone–water mixtures. In contrast, our studies of rates and products in alcohol–water mixtures have provided more experimentally accessible checks.

Substituent Effects.—Having separated the contribution from the S_N2–S_N1 reaction channel, the rates of solvolyses in other solvents can be predicted by linear extrapolation of the correlation line (Figures 1–3) for the separated channel. Example calculations have been made for 80E, ethanol, methanol, and 20M (Table 7). The relative rates depend on the slopes (m) of the correlation lines (Figure 1–3) and when $m = 1.01$ (Figure 1) relative rates are independent of solvent (*e.g.* for **1**; Z = Me and OMe). As m decreases, rates in less polar solvents drop less sharply (perhaps because of nucleophilic solvent assistance) and the magnitudes of substituent effects are reduced. There is a consistent trend that rates of S_N2–S_N1 solvolyses are favoured by electron donation by the substituent (Z), particularly so when Z = OMe (Table 7). Also the dissected rate constants for the carbonyl addition reaction channel increase with electron withdrawal by the substituent Z, particularly when Z = NO_2 (Table 8).

General Implications.—Modern interpretations of reaction mechanisms often involve detailed kinetic or theoretical studies to characterise the structures of transition states, which can vary so widely that three-dimensional contour diagrams may be required.[15–17] These developments have made it increasingly difficult to establish the alternative possibility that competition between two distinct reaction channels can occur. This alternative has now been strongly supported by studying rates, products, substituent effects and solvent effects for solvolyses of (**1**). However, it may still be argued that instead of two or more different transition states, at least one for each of the two reaction channels, there is only one transition state of hybrid character.[2b,4a] As the contributions from the dual reaction channels change, a single transition-state model would change in accordance with the weighted average of the two transition-state model. Because the single transition-state model is not predictive, it is very difficult to disprove conclusively. However, interpretation of the selectivity data (Table 4) would be very difficult without postulating several product-determining steps.[18] Changes in rate-limiting step with the same product-determining step, proposed for reactions of morpholine with benzoyl halides,[19] cannot explain all of these results adequately.

Additional mechanistic studies are now required to characterise further the mechanistic changes occurring within each of the two proposed reaction channels. An important challenge is to explain why the carbonyl addition channel shows high Br/Cl rate ratios.[2b,2d,8a,19] Hence, it should be emphasised that use of the term 'carbonyl addition reaction channel' is a convenient way to discuss the results in this paper, not an explicit statement about exactly how these reactions occur. Related mechanistic studies of activated carboxylic esters[2c] include consideraton of tetrahedral 'intermediates' with little or no barrier to decomposition.

Conclusions

Solvolyses of *p*-Z-substituted benzoyl chlorides (**1**; Z = Me, H, Cl) in aqueous ethanol and in aqueous methanol can be related to solvolyses of (**1**; Z = NO_2) and (**1**; Z = OMe). Rate–rate profiles (Figures 1–3) are consistent with two competing reaction channels, as discussed previously.[3b] The accuracy of these profiles has now been improved and rate constants for the S_N2–S_N1 reaction channel have been dissected from the observed rate constants; the dissected rate constants show the expected[10] single correlation lines (Figures 1, 2, and 5) for aqueous acetone, aqueous ethanol, and aqueous methanol. The carbonyl addition reaction channel is more complex[8a] and shows a dispersion between plots of data for aqueous acetone, ethanol and methanol (Figures 1—3). Dispersion may be caused by greater contributions from solvent nucleophilicity,[5b,20] and by possible contributions from general base catalysis.[8a] Changes in the contributions from the two reaction channels, occurring as water is added to alcohol, can be calculated (Table 6).

Trends in product ratios and selectivities (S) [equation (1)] independently confirm the main conclusions from rate–rate profiles. For the carbonyl addition channel, S increases as water is added to alcohol (data for **1**; Z = NO_2). For (**1**; Z = OMe), the model substrate for the S_N2–S_N1 reaction channel, S is constant. For solvolyses of (**1**; Z = Me, H, Cl), S increases then reaches a plateau and/or decreases. Deviations from expected trends occur in the range of solvent compositions predicted independently from rate–rate profiles. Taking S values from solvolyses of (**1**; Z = NO_2 and OMe) as typical of the corresponding reaction channels, combined with the calculated contributions from each reaction channel, it was possible to calculate satisfactory trends in S for solvolyses of (**1**; Z = Cl, H, Me). Some of the calculated values were too low, suggesting that the choice of S value has been oversimplified. A general implication of these results is that the possibility of competing reaction channels should be considered in addition to variations in transition states within a particular reaction channel.

Experimental

Materials.—Acid chlorides were commercial samples purified by distillation under reduced pressure and shown to be pure ($\geqslant 99.7\%$) by h.p.l.c. analyses of methanolysis products. Because of these small impurities corrections were required for solvents containing $>90\%$ alcohol. Acids and esters were obtained and purified by standard methods.

Rates and Products.—The experimental methods were as described previously.[10]

Calculations.—Details of slopes of correlations and dissections for (**1**, Z = Cl) are available on request.

Acknowledgements

This work was supported by the SERC and by the Korean Science and Engineering Foundation. Preliminary product studies were carried out by Mr. N. Jones (Swansea, 1986) and H. C. Harris. Helpful discussions with H. C. Harris and D. N. Kevill are gratefully acknowledged.

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Received 14*th July* 1988; *Paper* 8/02844C