Dual Reaction Channels for Solvolyses of Acyl Chlorides in Alcohol–Water Mixtures

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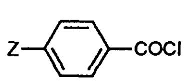
Rate constants are reported for solvolyses at 0 °C of trimethylacetyl chloride (**3**) in 90–30% v/v acetonitrile–, acetone–, ethanol– and methanol–water mixtures, of adamantane-1-carbonyl chloride (**4**) in 90–60% acetone–, ethanol– and methanol–water mixtures, and of cyclopropanecarbonyl chloride (**5**) in 90–40% acetone–water. Quantitative product data (acid and ester) are also reported for solvolyses of trimethylacetyl chloride in 98–20% ethanol– and methanol–water mixtures. Product selectivities (*S*) show maxima in 90–95% alcohol–water mixtures, similar to those, reported previously for solvolyses of *p*-chlorobenzoyl chloride (**1a**), benzoyl chloride (**1b**), 2,4,6-trimethylbenzenesulfonyl chloride (**2a**) and 4-methoxy-2,6-dimethylbenzenesulfonyl chloride (**2b**). Using rate–rate profiles, logarithms of rate constants are dissected into the competing reaction channels. Given the sharp maxima in *S* that occur at different alcohol compositions for different substrates, and the link to 'breaks' in rate–rate profiles, the results are consistent with competing mechanisms having different rate-limiting steps. The competing mechanisms involve two broad reaction channels: (1) nucleophilic attack by one molecule of solvent assisted by a second molecule of solvent acting as a general base catalyst—consequently, in aqueous alcohols there are four mechanistic combinations operating simultaneously within this *one* reaction channel; (2) nucleophilic attack by solvent occurs *via* a carbocationic reaction within the S_N2–S_N1 mechanistic spectrum, involving for example, a solvent-separated ion pair intermediate (S_N1) or a concerted nucleophilic attack (S_N2).

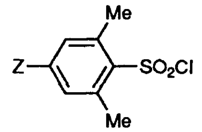
Solvolyses of acid chlorides in alcohol–water mixtures give ester and acid products, and product selectivities (*S*) can be defined using eqn. (1), which relates the molar product ratio to the molar ratios of the two components of the solvent.

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

S Values reach sharp maxima for solvolyses of *p*-chlorobenzoyl chloride (**1a**) in 50–60% ethanol- or methanol-water and of benzoyl chloride (**1b**) in 80% alcohol-water.[1a] Extending this work to acyl halides, we now report rate and selectivity data for solvolyses of trimethylacetyl chloride (3), and we strengthen the previously proposed[1] link between maxima in *S* values and mechanistic changes due to competing *dual* reaction channels; this interpretation is in marked contrast to the current tendency to interpret mechanistic changes by transition state variations within a *single* reaction channel.[2]



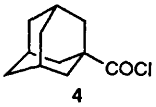
1a Z = Cl
b Z = H
c Z = Me
d Z = NO_2
e Z = OMe



2a Z = Me
b Z = H

$(CH_3)_3C–COCl$

3



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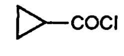

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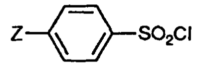

6a Z = NO_2

Recent mechanistic work on acyl chlorides has been concerned with methanolysis and phenolysis of acetyl chloride[3] along with chloro- and methyl-substituted derivatives. Second and third order rate coefficients were established in acetonitrile containing up to 0.5 mol dm^{-3} (~ 1%) methanol in acetonitrile, and methanolysis of acetyl chloride was proposed to proceed *via* a loose S_N2 transition state.[3] Earlier related research has been summarised.[3] The rate-retarding effect of methyl substitution was shown to be appreciable only upon introduction of a third methyl group, *i.e.* in trimethylacetyl chloride (**3**).[3] Using a fast-response conductimetric method, we have now extended kinetic work to typical solvolysis conditions, and we have investigated solvolyses of **3** in aqueous mixtures containing up to 70% v/v water. Kinetic data for solvolyses of adamantane-1-carbonyl chloride (**4**) and cyclopropanecarbonyl chloride (**5**) are also reported.

Results

Rate constants for solvolyses of trimethylacetyl chloride (**3**) in aqueous binary mixtures at various temperatures (Table 1) give an approximately constant $\Delta H^‡$ and a less negative $\Delta S^‡$ as the water content increases. These activation parameters are typical for solvolyses in aqueous alcohols,[4,5] and show the reliability of the kinetic data. A wider range of data at 0 °C is shown in Table 2. Solvolysis rate constants for adamantane-1-carbonyl chloride (**4**) are given in Table 3 and for cyclopropanecarbonyl chloride (**5**) are given in Table 4.

Product selectivity data for solvolyses of trimethylacetyl chloride, determined by reverse phase high performance liquid chromatography (HPLC) are in Tables 5 and 6. Independent analytical methods for product analyses were also investigated. The esters appear to decompose on GC, but titrimetric analyses in degassed (CO_2 free) solutions were possible and provided an independent check (Table 5, footnote *e*).[6]

Table 1 Rate constants and activation parameters for solvolyses of trimethylacetyl chloride (**3**) in aqueous binary mixtures[a]

Solvent (% v/v)	T/°C	k/s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal mol^{-1} K^{-1} [c]
Ethanol (80)	0	$(1.34 \pm 0.01) \times 10^{-2}$		
	25.0	$(1.20 \pm 0.02) \times 10^{-1}$	13.6	−17.2
Ethanol (40)	−20.0	$(6.9 \pm 0.5) \times 10^{-2}$		
	−14.0	$(1.41 \pm 0.08) \times 10^{-1}$		
	−10.0	$(2.48 \pm 0.23) \times 10^{-1}$		
	0	$(6.67 \pm 0.06) \times 10^{-1}$	15.1	−3.7
Ethanol (30)	−15.0	$(4.59 \pm 0.05) \times 10^{-1}$		
	−10.0	$(8.30 \pm 0.14) \times 10^{-1}$	15.5	0.2
Methanol (50)	−20.0	$(7.96 \pm 0.15) \times 10^{-2}$		
	−10.0[b]	2.21×10^{-1}		
	0	$(5.73 \pm 0.05) \times 10^{-1}$	13.0	−11.7
Methanol (40)	−20.2	$(1.57 \pm 0.03) \times 10^{-1}$		
	−10.0	$(4.56 \pm 0.02) \times 10^{-1}$	13.3	−9.3
Methanol (30)	−15.0	$(4.52 \pm 0.07) \times 10^{-1}$		
	−10.0	$(7.89 \pm 0.12) \times 10^{-1}$	14.5	−3.6

[a] Determined conductimetrically at least in duplicate, except where stated otherwise; errors shown are average deviations. [b] Single measurement of rate constant. [c] 1 cal = 4.184 J.

Table 2 Rate constants for solvolyses of the trimethylacetyl chloride (**3**) in binary aqueous mixtures at 0 °C[a]

Solvent (% v/v)	Rate constant (k/s^{-1})			
	Ethanol	Methanol	Acetone	Acetonitrile
100	2.49×10^{-3}	1.74×10^{-2}		
90	7.01×10^{-3}	3.62×10^{-2}	4.89×10^{-4}	6.47×10^{-4}
80	1.34×10^{-2}[b]	6.95×10^{-2}	1.86×10^{-3}	3.27×10^{-3}
70	2.75×10^{-2}	1.49×10^{-1}	5.83×10^{-3}	9.40×10^{-3}
60	6.01×10^{-2}	2.65×10^{-1}	2.06×10^{-2}	2.29×10^{-2}
50	1.71×10^{-1}	5.73×10^{-1}	9.17×10^{-2}	6.31×10^{-2}
40	6.67×10^{-1}	1.20[c]	3.52×10^{-1}	1.87×10^{-1}
30	2.55[c]	2.26[c]	1.14	6.31×10^{-1}

[a,b] As for Table 1. [c] Calculated from data at lower temperatures.

Table 3 Rate constants for solvolyses of the adamantane-1-carbonyl chloride (**4**) in aqueous mixtures at 0 °C[a]

Solvent (% v/v)	Rate constant (k/s^{-1})		
	Ethanol	Methanol	Acetone
100	3.13×10^{-3}	2.33×10^{-2}	
90	9.93×10^{-3}	5.65×10^{-2}	5.13×10^{-4}
80	2.17×10^{-2}	1.24×10^{-1}	2.24×10^{-3}
70	4.24×10^{-2}	2.70×10^{-1}	8.26×10^{-3}
60	1.27×10^{-1}	6.80×10^{-1}	3.14×10^{-2}
50			1.70×10^{-1}
40			8.44×10^{-1}

[a] As in Table 1.

Table 4 Rate constants (k/s^{-1}) for solvolyses of the cyclopropanecarbonyl chloride (**5**) in acetone–water mixtures at 0 °C[a]

Acetone (v/v %)	k/s^{-1}
90	3.04×10^{-4}
80	2.62×10^{-3}
70	1.47×10^{-2}
60	7.17×10^{-2}
50	2.60×10^{-1}
40	9.63×10^{-1}

[a] As for Table 1.

Table 5 Product ratios and product selectivities (S) for solvolyses of trimethylacetyl chloride (**3**) in alcohol–water mixtures[a,b]

	Ethanol		Methanol	
Alcohol (%)	[Ester]/[Acid]	S[c]	[Ester]/[Acid]	S[c]
98	19.6	1.31[d]	78.6	3.61[d]
95	8.20	1.41[d]	40.8	4.83[d]
90	5.35	1.94[d]	18.29	4.57[d]
80	2.16	1.76	6.19	3.48
70	1.16	1.61	3.10	2.99
60	0.69	1.50	1.87	2.80
50	0.40	1.30	1.07[e]	2.40
40	0.23	1.13	0.60	2.02
30	0.13	1.00	0.32	1.68
20	0.086	1.12	0.15	1.35

[a] Determined at 210 nm by HPLC (Spherisorb ODS2, eluent 50% v/v methanol–water + 0.1% acetic acid; flow rate 1 cm^3 min^{-1}) analyses of *ca.* 10^{-2} mol dm^{-3} solutions at least in duplicate, error *ca.* ± 5%. [b] A 10% solution of acid chloride in acetonitrile was injected into a sample tube containing 1 cm^3 of solvent in an ultrasonic bath at ambient temperature (see also Table 6). [c] Calculated from eqn. (1). [d] Corrected for 0.5% acid impurity in the starting material. [e] In satisfactory agreement with an independent titrimetric analysis (ref. 6).

Table 6 Temperature dependence of product selectivity (S) for solvolyses of trimethyl acetyl chloride (**3**) in alcohol–water mixtures[a]

Solvent	Solvent composition (%/v/v)	S[b]	S[c]	S[d]
Ethanol	90	2.30[e]	1.80[e]	1.80[e]
	50	1.45	1.22	1.29
Methanol	90	4.09[e]	3.23[e,f]	4.16[e]

[a] As Table 5. [b] At 0 °C. [c] At ambient temperature. [d] In an ultrasonic bath, as in footnote *b*, Table 5. [e] Uncorrected for 0.5% acid impurity in the starting material. [f] Single measurement.

Discussion

Selectivities.—Product ratios and hence product selectivities are somewhat dependent on temperature and on the method of mixing (Table 6—see also ref. 7); hence the trends in S values (Table 5) are of more significance than the absolute values of S. Trends show maxima in S in 90–95% alcohol–water mixtures and absolute values of S are similar to those for corresponding solvolyses of benzoyl chloride (**1b**) and larger than for *p*-methylbenzoyl chloride (**1c**)[1a]—see Fig. 1. For solvolyses of **1b** and of **3**, as water is added to alcohol, S increases initially but then decreases; for solvolyses of **1c**, S decreases throughout (Fig. 1).

In contrast, an increase in S as water is added to alcohol is typical for solvolyses of *p*-nitrobenzoyl chloride **1d**[8a] and of *p*-

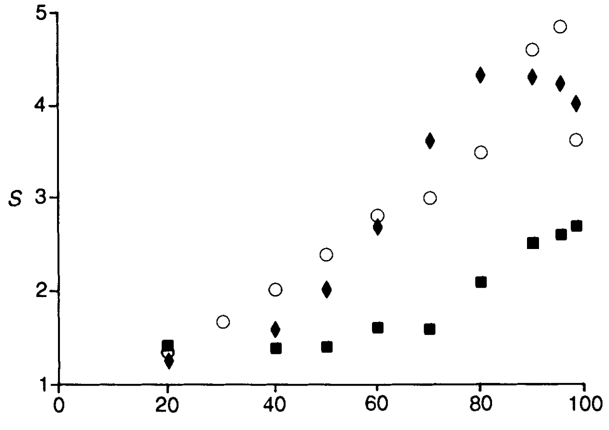

Fig. 1 Plot for *S* values (eqn. 1) for solvolyses of trimethylacetyl chloride (**3**) (○), and of benzoyl **1b** (◆) and *p*-methylbenzoyl chloride **1c** (■) *vs.* composition for methanol-water mixtures; selectivity data from Table 5 and ref. 1(*a*)

Table 7 Slopes of Grunwald-Winstein plots for solvolyses of trimethylacetyl chloride (**3**) in aqueous binary mixture at 0 °C[a]

Solvent	Solvent composition range (%/v/v)	Slope	Correlation coefficient (*r*)
Ethanol	100–80	0.36 ± 0.01	0.9998
	60–30	1.03 ± 0.05	0.998
Methanol	100–80	0.41 ± 0.01	0.9999
	60–30	0.74 ± 0.01	0.9997
Acetone	90–70	0.54 ± 0.04	0.998
	60–30	1.04 ± 0.01	0.9999
Acetonitrile	90–70	0.66 ± 0.01	0.9999
	50–30	1.07 ± 0.04	0.9993

[a] See Fig. 2.

nitrobenzenesulfonyl chloride (**6a**).[8b] The increase in *S* as water is added to alcohol continues to 20% alcohol-water (or less) and may be explained by general base catalysed reactions in which one molecule of solvent acts as a general base and another solvent molecule acts as a nucleophile.[8,9] In aqueous alcohols, there are four possible combinations because both water and alcohol can act as nucleophile or as base. We consider that these four similar mechanisms contribute to one reaction channel involving general base catalysis and possibly a carbonyl addition mechanism.[8] The most favoured of the four possible combinations is alcohol as nucleophile and water as general base.[8a] Hence, when even small amounts of water are added to pure alcohols, both rates and selectivities increase. This mechanism accounts for the increase in *S* for solvolyses of **3** as 10% v/v water is added to alcohol (Table 5).

A third trend in *S* values can be illustrated by solvolyses of *p*-methoxybenzoyl chloride (**1e**) in alcohol-water mixtures, which show a constant *S* of ~1 over the full range of solvent compositions from alcohol to water.[7] The results are explained by a carbocationic process involving nucleophilic attack on a solvent separated ion pair.[7] Solvolyses of trimethylacetyl chloride (**3**) in 40–20% ethanol-water reach a low and constant *S* of 1.1 (Table 5), consistent with a virtually complete mechanistic change. The higher and solvent-dependent *S* values, obtained in corresponding methanol-water mixtures, may be due to the greater effectiveness of methanol (compared with ethanol) in the competing general base catalysed reactions.[8] Hence, in this case, the carbocationic process is not yet overwhelmingly dominant.

Solvolyses of *p*-chlorobenzoyl **1a** [1a] and benzoyl chloride **1b** [1a] and of sulfonyl chlorides **2a** [10] and **2b** [11] show clear maxima in *S* in *different* alcohol-water mixtures, which we have explained by competition between two reaction channels.[1a,10,11] The term channel is used because there are mechanistic variations within both channels; *e.g.* in addition to the four possible competing mechanisms within the general base catalysed reaction channel,[8] there are mechanistic variations within the S_N2–S_N1 spectrum,[12] and the various processes may be grouped as a second reaction channel.

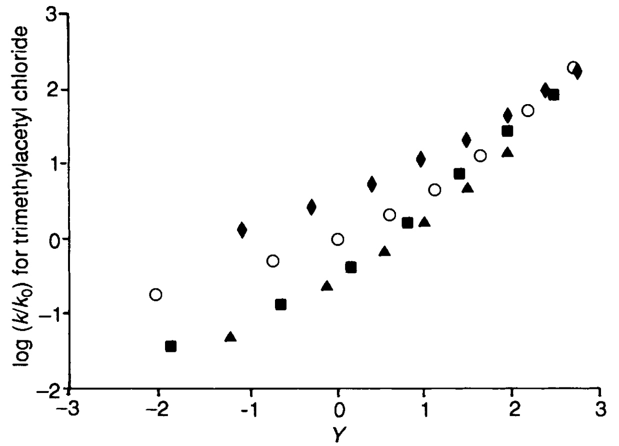

Fig. 2 Correlation of logarithms of rate constants for solvolyses of trimethylacetyl chloride *vs.* Grunwald-Winstein *Y* values; kinetic data from Table 1 and *Y* values from refs. 13 and 14: ◆, methanol; ○, ethanol; ■, acetone; ▲, acetonitrile

For solvolyses of *p*-methylbenzoyl chloride **1c**, *S* decreases as water is added to alcohol and there is not a clear maximum (Fig. 1). When compared with the behaviour of related substrates *p*-methoxybenzoyl chloride **1e** and **1b**, solvolyses of **1c** can also be explained satisfactorily by competing reaction channels.[1a] The results in Fig. 1, show that solvolyses of trimethylacetyl chloride (**3**) fit the pattern outlined above, if it is assumed that solvolyses are similar to those of **1b** and **1c**, so that the mechanistic change to a carbocationic process begins in high (>90) % alcohol-water and gradually becomes dominant as water is added.

Rate-Rate Profiles.—The curved plots of logarithms of solvolysis rate constants for trimethylacetyl chloride (**3**) *versus* Grunwald-Winstein *Y* values (Fig. 2) provide independent support for the mechanistic changes discussed above. In highly aqueous media, solvolyses in ethanol-, acetone- and acetonitrile-water mixtures give unit slopes (1.03, 1.04 and 1.07 respectively—see Table 7), suggesting that the change of reaction channel to a carbocationic process (modelled by the parameter *Y*, based on solvolyses of *tert*-butyl chloride[13]) is practically complete in solvents with $Y > 1$. In contrast, the lower slope of 0.74 in 60→30% methanol-water (Table 7) and the decreasing *S* values in this solvent range (Table 5) are consistent with an incomplete change in reaction channel.

Solvolyses in less aqueous alcohol mixtures show much lower slopes (0.36 and 0.41, Table 7), and aqueous acetone shows slightly higher values of 0.54. The change in slope in acetonitrile-water from 0.66 to 1.07 (Table 7) is the least sharp. Reactions of **3** in acetonitrile containing up to 0.5 mol dm^{-3} methanol (< 3% v/v) show competing second and third order processes. The third order process probably involves one molecule of methanol acting as nucleophile and a second molecule of methanol acting as a general base.[3] As nucleophilic attack by methanol may also be catalysed by chloride ion[3] acting as a general base, it is probable[9] that the second order process is catalysed by acetonitrile as base and, if so, a similar situation could apply in our work *i.e.* acetone as general base catalyst instead of acetonitrile, and water as nucleophile instead of methanol.

The phenomenon of dispersion[14] (the tendency for each cosolvent of a binary aqueous mixture to give a separate *mY*

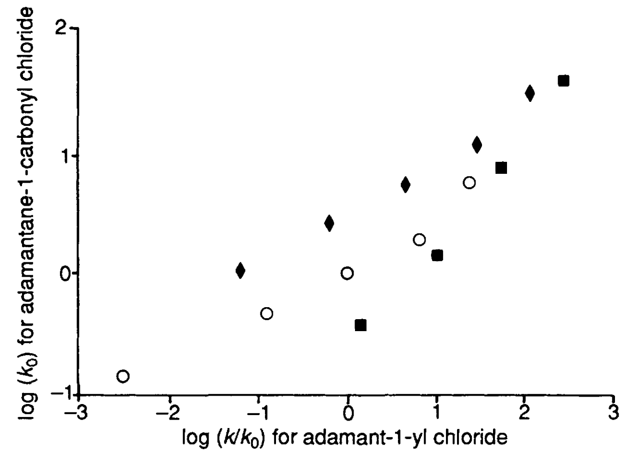

Fig. 3 Correlation of logarithms of solvolysis rate constants for adamantane-1-carbonyl chloride (**4**) *vs.* Y_{Cl} values; kinetic data from Table 3 and Y_{Cl} values from ref. 15: ◆, methanol; ○, ethanol; ■, acetone

correlation) complicates a detailed dissection of the rate–rate profiles (Fig. 2) into competing reaction channels, which has been achieved for solvolyses of benzoyl chloride (**1b**).[1] A partial further analysis of kinetic data for **3** can be achieved by extrapolating the two linear regions of the plots (Table 7) for aqueous ethanol or aqueous methanol to intersection points close to 70% alcohol. These intersection points represent the solvent compositions in which the two reaction channels contribute equally to the observed rate constant,[1] and these points occur at solvent compositions in between those observed for benzoyl chloride (**1b**) and *p*-methylbenzoyl chloride (**1c**),[1] consistent with our observations (Fig. 1) that *S* values for **3** are similar to those for **1b** and **c**.

Rate constants for solvolyses of adamantane-1-carbonyl chloride (**4**) (Table 3) are similar to those of trimethylacetyl chloride (**3**). The former solvolyses slightly faster (except in 90→70% acetone–water) and dissolves less rapidly, so a smaller range of data was accessible experimentally (Table 3). The plot (Fig. 3) of logarithms of solvolysis rate constants *vs.* Y_{Cl} (based on solvolyses of adamant-1-yl chloride) is qualitatively similar to Fig. 2. The largest **4**/**3** rate ratio is 2.5 in 60% methanol–water, consistent with a change of reaction channel by **4** in slightly less aqueous solvent mixtures than by **3**.

Logarithms of solvolysis rate constants for cyclopropanecarbonyl chloride (**5**) in acetone–water plot linearly against *Y* (Fig. 4) with a slope of 0.92 ± 0.02 ($r = 0.999$). However, if the data point for 90% acetone is excluded the slope increases to 0.97 ± 0.01 ($r = 0.9999$), very similar to the slopes seen for solvolyses of **3** and **4** in highly aqueous acetone (Fig. 4) and calculated for solvolyses of **3** in other highly aqueous media (Table 7). If there is a change in slope of the rate–rate profile for solvolyses of **5** in acetone–water due to a mechanistic change, the change occurs when only small amounts of water (~ 10% v/v) are present. As a convincing elucidation of the competing reaction channels would be much more difficult, this substrate was not investigated further.

Conclusions

Solvolyses of trimethylacetyl chloride (**3**) in ethanol, methanol and in alcohol–water mixtures are similar mechanistically to those previously reported for solvolyses of benzoyl chloride (**1b**) and of *p*-methylbenzoyl chloride (**1c**).[1] These results extend to acyl chlorides the concept of competing (dual) reaction channels, previously established for aroyl chlorides[1,9b,16] and aromatic sulfonyl chlorides.[10,11] In each case electron donation from the alkyl or aryl groups causes a shift of reaction channel in less aqueous solvent mixtures (*e.g.* electron donation by

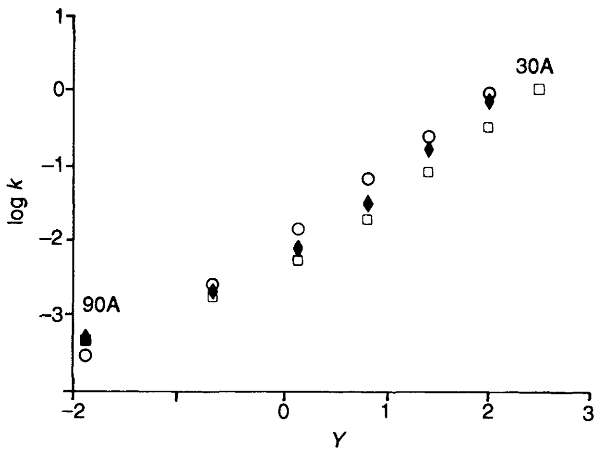

Fig. 4 Correlation of logarithms of rate constants for solvolyses of trimethylacetyl chloride, □ (**3**), adamantane-1-carbonyl chloride, ◆ (**4**), and cyclopropanecarbonyl chloride, ○ (**5**) in acetone–water mixtures at 0 °C *vs.* Grunwald–Winstein *Y* values; kinetic data from Tables 1–3 and *Y* values from ref. 13. For solvolyses of **5**, slope = 0.92 ± 0.02 ($r = 0.999$). Non linearity of the plots is discussed in the text—see also Table 7.

5 > **4** > **3** is the order of σ_p^+ values for the alkyl substituents although the values are very similar[17]). Electron donation by the alkyl (or aryl) group favours a carbocationic or an S_N2–S_N1 process, strongly sensitive to changes in solvent ionising power. Electron withdrawal (*e.g.* for solvolyses of *p*-nitrobenzoyl chloride **1d**[8a,9b] or of chloroacyl chlorides[3]) favours a general base catalysed process having a lower sensitivity to changes in solvent ionising power. Hence, a more electron donating alkyl group leads to a mechanistic change in less aqueous media. Alternative interpretations to dual reaction channels, such as a change in product-determining step or variations within a single transition state,[2] are becoming decreasingly probable.

Experimental

Materials.—Acid chlorides were commercial samples purified by distillation and traces of acid impurities in **3** were quantified by HPLC analysis of methanolysis products. Other materials were: pivalic acid (Aldrich); methyl trimethylacetate (Lancaster); ethyl trimethylacetate (synthesised by standard methods); methanol (Fisons, dried distilled for kinetics and BDH, AR grade for HPLC); ethanol (dried over magnesium ethoxide and distilled); and acetonitrile (Fisons, HPLC grade).

Rates and Products.—The experimental kinetic methods were as described previously.[7] The HPLC system was manufactured by LDC Milton Roy and comprised a Constametric 3000 solvent pump, a Spectromonitor 3100 variable wavelength detector, a CI 4100 computing integrator and a Promis autosampler. The HPLC column was 15 cm × 1/4″ (≈0.6 cm) Spherisorb S5 ODS2 with about 9000 theoretical plates. Response calibration was achieved by injecting known volumes of standard solutions of pivalic acid and of the corresponding ethyl and methyl esters. The reliability of injection volumes using the 'Microlitre' injection method was established.[18]

Under reverse phase HPLC conditions, acidic materials elute just before the injected solvent. A convenient way to increase the retention time is to add a small amount (*e.g.* 0.1%) of glacial acetic acid to the eluent.[19,20] However, subsequent washing of the column with water does not restore the ability of the column to separate acids before the injected solvent, unless buffer salts (*e.g.* from pH 7 buffer tablets) are present in the wash eluent.* Columns, regenerated by washing with aqueous pH 7 buffer for a few hours, retain their ability to separate acids for months (and also give sharp peaks for weak bases such as 2,6-lutidine). After many injections of acidic samples, the separation of carboxylic acids from the injected solvents becomes less distinct (and amine signals become very broad), but regeneration can be repeated. An important advantage of the chosen chromatographic conditions is that buffer salts are not required in the eluent, so fewer pumping problems arise. (We use an old pump to regenerate columns with the pH 7 aqueous buffer.)

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* S. J. Norman (Swansea) was the first in our laboratory to observe this phenomenon.

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