Solvent and substituent effects in solvolyses of benzoyl chlorides. Variation of mechanisms from Grunwald–Winstein correlation analyses with Y_{BnCl} scales †

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Received (in Cambridge, UK) 25th June 1999, Accepted 20th December 1999

The solvolysis of seven aromatic acid chlorides, namely 2,6-dimethyl- (**1**), 2-methyl- (**2**), 4-methoxy- (**3**), 4-methyl- (**4**), 4-chloro-(**6**), 4-nitro- (**7**), and unsubstituted benzoyl chloride (**5**), in a variety of solvents was studied. The observation of a linear correlation of log *k* against solvent ionizing power Y_{BnCl} using the single-parameter Grunwald–Winstein equation indicates a limiting S_N1 mechanism for the solvolysis of **1**. An S_N1 mechanism with significant nucleophilic solvent participation was found in the solvolysis of **2**–**4**, based on the apparent splitting of lines in log *k vs.* Y_{BnCl} plots. Different types of non-S_N1 reactions are probably involved in the solvolysis of **5**–**7**, and are likely solvent dependent. Hammett-type plots against σ^+ constants indicated a linear relationship for **3**–**6** only in solvents of high water content (60% aqueous methanol, 50% aqueous acetone and 50% aqueous ethanol) or with high ionising power (100% trifluoroethanol and 80% trifluoroethanol–20% ethanol), but for **3**–**5** in some solvents containing lower amounts of water or trifluoroethanol. Plots of log *k* in different solvents against ΔE_{iso} for the isodesmic reaction also suggested a solvent dependence of mechanisms. The advantage of using Y_{BnCl} rather than a combination of Y_{Cl} and aromatic ring parameter *I* in the correlation analysis is discussed.

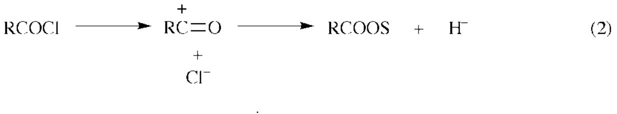
Introduction

Acyl chlorides are among the most reactive of organic substrates versatile to a large number of transformations, and thus are attractive for mechanistic studies.[1,2] A pioneering kinetic study of the solvolysis of aromatic acyl chlorides was performed by Berger and Olivier some seventy years ago.[3] Early workers suggested the dependence of the mechanism on solvent composition,[4] but indicated the failure of employing the single-parameter Grunwald–Winstein equation (1)[5] to the solvolysis

$$\log(k/k_o) = mY \qquad (1)$$

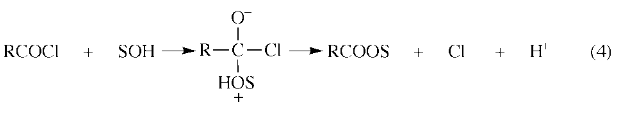
of 4-nitrobenzoyl chloride,[6] or acetyl and benzoyl chlorides[7] in hydroxylic solvents. On the other hand, the variation between S_N1 and S_N2 mechanisms for the hydrolysis of aromatic acyl chlorides with substituents, and thus Hammett σ constants, was also realised.[8] Those and later studies by many authors led to a conclusion of three possible mechanisms of solvolysis,[9] namely the unimolecular dissociation [eqn. (2)], the bimolecular synchronous S_N2-type [eqn. (3)] and the addition-elimination [eqn. (4)] mechanisms.

Mechanistic study of the solvolysis of benzoyl chlorides has advanced since the 1980s.[10] Based on the proposal of a limiting S_N1 mechanism for the solvolysis of 4-methoxybenzyl chloride, the observation of a linear correlation between logarithms of rate constants in a number of solvents for 4-methoxybenzyl chloride and those for 4-methoxylbenzoyl chloride led to the conclusion of similarity in mechanism for the two systems.[11] Different mechanisms of solvolysis for aromatic acyl chlorides containing different substituents were suggested from rate–product selectivity studies.[10c,d,12–14] Non-linear log *k vs.* mY_{Cl} plots were observed.[12] Both 2,6-dimethylbenzoyl chloride (**1**) and 4-methoxybenzoyl chloride (**3**) were considered to solvolyse by the S_N1 mechanism from a selectivity study, but the dispersion in log *k*(**1**) *vs.* log *k*(**3**) plots suggested weak solvent assistance in the solvolysis of **3**.[15]

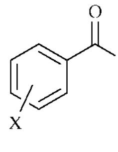


$$\mathrm{RCOCl} \longrightarrow \mathrm{R\overset{+}{C}{=}O} + \mathrm{Cl^-} \longrightarrow \mathrm{RCOOS} + \mathrm{H^-} \qquad (2)$$

$$\mathrm{RCOCl} + \mathrm{SOH} \longrightarrow [\mathrm{TS}]^{\ddagger} \longrightarrow \mathrm{RCOOS} + \mathrm{Cl} + \mathrm{H^{\prime}} \qquad (3)$$



$$\mathrm{RCOCl} + \mathrm{SOH} \longrightarrow \mathrm{R{-}\overset{\overset{\textstyle O^-}{|}}{\underset{\underset{\textstyle H\overset{+}{O}S}{|}}{C}}{-}Cl} \longrightarrow \mathrm{RCOOS} + \mathrm{Cl} + \mathrm{H^{\prime}} \qquad (4)$$



1: 2,6-$(CH_3)_2$
2: 2-CH_3
3: 4-CH_3O
4: 4-CH_3
5: 4-H
6: 4-Cl
7: 4-NO_2

However, the presence of a significant nucleophilic solvent intervention in the solvolysis of 4-methoxybenzyl chloride was recently demonstrated.[16] A downward deviation of data points in log *k vs.* Y_{BnCl}[17] plots for those measured in trifluoroethanol–ethanol solvents, and the observation of a linear regression of log *k* with Y_{BnCl} and N_{OTs}[18] or N_T[19] scales in the dual-parameter

$$\log(k/k_o) = mY + lN \qquad (5)$$

equation[20] [eqn. (5)], were considered as evidence, among others, leading to such a conclusion. Moreover, the weakly nucleophilic trifluoroethanol–ethanol systems were not employed in the previous work,[11–15] which made the conclusion about S_N1 mechanism for compound **1** and solvent participation for others less convincing. Owing to the small variation of rate data reported by different research groups, the results of correlation analysis will be more meaningful if all data from

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† Electronic supplementary information (ESI) available: solvolysis rate constants. See http://www.rsc.org/suppdata/p2/a9/a905125b

DOI: 10.1039/a905125b

Table 1 Solvolysis rate constants (×10^2) for compounds **1** and **2** at 25 °C

Solvent [a]	**1**	**2**	Solvent [a]	**1**	**2**
100E	4.94	0.370	60A	646 [b]	10.4
90E	49.2 [b]	1.42	100M	97.1 [b]	2.96
80E	162 [b]	4.23	90M	457 [b]	8.10
70E	505 [b]	13.3	80T20E		20.2
90A	0.843	0.108	60T40E	1120 [b]	5.71
80A	14.6	0.581	40T60E	174 [b]	1.99
70A	141 [b]	2.68			

[a] A = Acetone, E = ethanol, M = methanol, T = 2,2,2-trifluoroethanol. Figures shown are volume percentages in water, and that with *w* denotes weight percent; 80T20E indicates T-E of 80:20 v/v and likewise for 60T40E and 40T60E. [b] Extrapolated from data at other temperatures.

Table 2 Correlation analyses using eqn. (1) against Y_{BnCl}

Substrate	n [a] (solvent)	R	m (s.d.) [b]
1	12 (All)	0.991	0.921 (0.039)
2	13 (All)	0.930	0.504 (0.060)
	10 (AEM)	0.995	0.698 (0.025)
3	19 (All)	0.916	0.588 (0.063)
	15 (AEM)	0.994	0.766 (0.024)
4	19 (All)	0.835	0.434 (0.070)
	15 (AEM)	0.990	0.622 (0.025)
5	19 (All)	0.505	0.212 (0.088)
	15 (AEM)	0.952	0.447 (0.040)
6	19 (All)	0.127	0.054 (0.103)
	15 (AEM)	0.864	0.307 (0.050)
7	19 (All)	0.149	−0.0871 (0.141)
	15 (AEM)	0.855	0.233 (0.039)

[a] Numbers of data points. [b] Standard deviation.

one group are used. Consequently, it would be desirable to redetermine the rate constants in both nucleophilic and poorly nucleophilic solvents for **1**, **3**–**7** and the hitherto unmeasured **2**, and to examine the applicability of the Y_{BnCl} scale and the possibility of solvent intervention in the solvolysis of benzoyl chlorides **1**–**7**. We confirmed that only 2,6-dimethylbenzoyl chloride (**1**) solvolysed with limiting S_N1 mechanism, whereas the solvolysis for others involved nucleophilic solvent participation or even a different mechanistic route.

Results

2,6-Dimethylbenzoyl chloride (**1**), 2-methylbenzoyl chloride (**2**), 4-methoxybenzoyl chloride (**3**), 4-methylbenzoyl chloride (**4**), benzoyl chloride (**5**), 4-chlorobenzoyl chloride (**6**), and 4-nitrobenzoyl chloride (**7**) were solvolysed in twelve to nineteen different solvents, and the rate constants measured by a conductimetric method as described.[17a] Unlike those reported by Bentley and co-workers,[10c,d,11–15] in the present study most of the substituted benzoyl chlorides were found not completely soluble in binary solvent systems containing 50 (aqueous methanol) or 60% (aqueous acetone and ethanol) of water by volume, even at concentrations of about 10^{-4} to 10^{-5} M. Hence, rate constants measured in those and other high water-containing solvents were considered somewhat unreliable and were discarded. In addition, the rate of solvolysis in 70% aqueous trifluoroethanol[12] was too fast to be measured accurately in many cases. Pertinent data at 25 °C for **1** and **2** are listed in Table 1. Others are available as Supplementary material. The agreement of our data for **1**, **3**–**7** is within 5 to 20% of those reported.[10–15]

Regression analyses of log *k* values in Table 1 against Y_{Cl}[21] using eqn. (1) showed poor correlation with scattered data points in each case. Table 2 shows the correlation with Y_{BnCl}.[17] A good linear relationship, correlation coefficient $R = 0.991$, was found for all log *k* values *vs.* Y_{BnCl} in the case of compound **1** (Fig. 1). On the other hand, for acid chlorides **2**, **3** and **4**, two lines, one in nucleophilic solvents (aqueous acetone, ethanol and methanol) and the other in trifluoroethanol–ethanol, were observed against Y_{BnCl} (Fig. 2 for **3** as an example). Widely dispersed log *k* *vs.* Y_{BnCl} plots were found for **5**, **6** and **7** (Fig. 3 for **5** and Fig. 4 for **7** as examples). Consequently, correlation analyses against Y_{BnCl} and N_{OTs}[18] or N_T[19] using eqn. (5) for only **2**, **3** and **4** were carried out. The results are shown in Table 3.

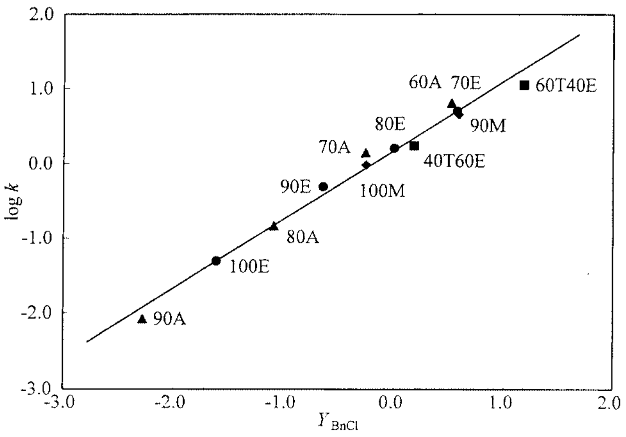


Fig. 1 Plots of log *k* for compound **1** against Y_{BnCl}.

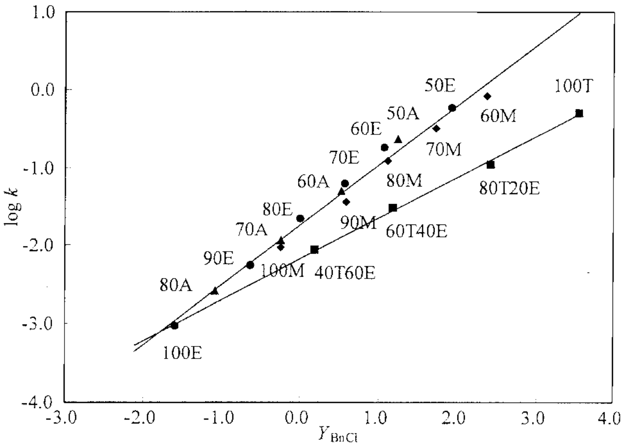


Fig. 2 Plots of log *k* for compound **3** against Y_{BnCl}.

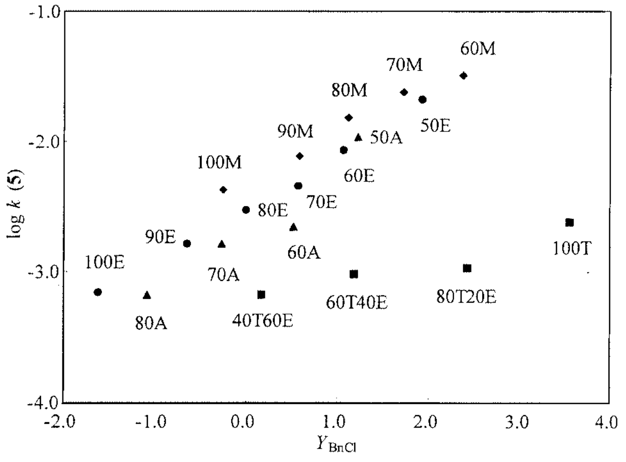


Fig. 3 Plots of log *k* for compound **5** against Y_{BnCl}.

Hammett-type correlation analyses of log *k* values for compound **3**–**7** in individual solvent systems, namely, aqueous acetone, aqueous ethanol, aqueous methanol, and trifluoroethanol–ethanol, respectively, against σ^+ constants,[22] eqn. (6),

$$\log(k/k_o) = \sigma^+\rho \quad (6)$$

Table 3 Correlation analyses using dual-parameter eqn. (5)

Substrate	Parameters	n^a	R	m (s.d.)^b	l (s.d.)^b
2	Y_{BnCl}, N_{OTs}	11	0.978	0.692 (0.060)	0.639 (0.122)
	Y_{BnCl}, N_T	13	0.966	0.635 (0.060)	0.424 (0.133)
3	Y_{BnCl}, N_{OTs}	17	0.981	0.768 (0.043)	0.506 (0.073)
	Y_{BnCl}, N_T	17	0.955	0.773 (0.078)	0.360 (0.103)
4	Y_{BnCl}, N_{OTs}	17	0.967	0.631 (0.045)	0.558 (0.077)
	Y_{BnCl}, N_T	17	0.923	0.654 (0.080)	0.426 (0.106)

[a] Numbers of data points. [b] Standard deviation.

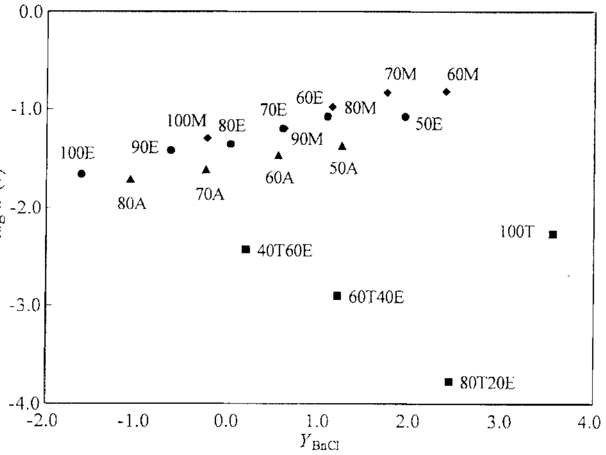


Fig. 4 Plots of log k for compound **7** against Y_{BnCl}.

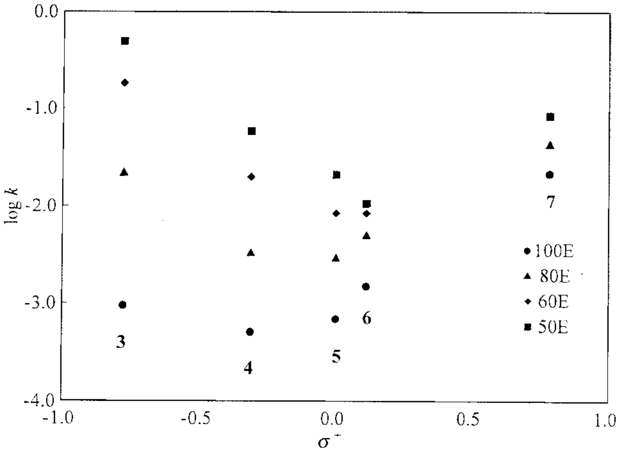


Fig. 5 Correlation analysis using Brown-Okamoto treatment for the solvolysis of compounds **3**–**7** in aqueous ethanol.

were carried out. Representative plots in nucleophilic and poorly nucleophilic solvents, respectively, are displayed in Figs. 5 and 6. Selected data are listed in Table 4.

To estimate the charge distribution in acylium ions, *ab initio* calculations using the SPARTAN program version 4.1.1 (Wavefunction Inc., Irvine, CA, 1996) were carried out. The results of Mulliken population analyses[23] at the RHF/6-31G*//RHF/6-31G* level are presented in Table 5. The energies of isodesmic reactions (7) were also obtained at this level of calculation.

$$\mathrm{RCOCl} + \mathrm{CH_3CO^+} \longrightarrow \mathrm{RCO^+} + \mathrm{CH_3COCl} \qquad (7)$$

The total energies for **1**–**7** and for **1a**–**7a** and ΔE_{iso}[24] are given in Table 6.

The rate data for compounds **1**–**7** were also analysed by using multi-parameter eqns. (8) and (9) including aromatic ring parameter I,[25] and the results are shown in Table 7.

$$\log(k/k_o) = mY_{Cl} + hI \qquad (8)$$

$$\log(k/k_o) = mY_{Cl} + lN_T + hI \qquad (9)$$

Table 4 Hammett plots of selective log k values against σ^+ constants

Solvent	n^a	ρ	R	s.d.^{b}
50E	4	−1.95	0.998	0.081
60E	4	−1.54	0.980	0.222
60E	3	−1.73	0.991	0.236
50A	4	−1.85	0.999	0.048
60A	4	−1.43	0.959	0.298
60A	3	−1.70	0.988	0.264
60M	4	−1.70	0.996	0.103
70M	3	−1.57	0.988	0.246
100T	4	−3.02	0.998	0.117
80T20E	4	−2.67	0.999	0.098
60T40E	4	−1.97	0.997	0.114

[a] Numbers of data points: $n = 4$ for compounds **3**–**6**; $n = 3$ for **3**–**5** [b] Standard deviation.

Table 5 Calculated atomic charges for acylium ions **2a**–**7a** derived from acyl chlorides **2**–**7**

Atoms	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
Carbonyl O	−0.233	−0.250	−0.232	−0.221	−0.221	−0.198
Carbonyl C	0.649	0.633	0.654	0.664	0.662	0.683
Aryl ring^a	0.584	0.617	0.579	0.557	0.559	0.515

[a] Total charge on the aryl or phenyl ring.

Table 6 Calculated *ab initio* energies for acylium ions **1a**–**7a** and acyl chlorides **1**–**7**

Substrate	E(ArCOCl)/ hartree^a	E(ArCO$^+$)/ hartree^a	ΔE_{iso}^{b}/kcal mol^{-1}
1	−880.406 99	−420.682 10	−29.50
2	−841.376 34	−381.639 41	−21.95
3	−916.227 20	−456.493 01	−23.67
4	−841.382 19	−381.641 04	−19.30
5	−802.343 71	−342.596 39	−15.43
6	−1261.242 02	−801.487 96	−11.20
7	−1005.809.11	−546.037 07	0.09

[a] 1 hartree = 627.5 kcal mol^{-1}. [b] Derived from eqn. (7) with $E(\mathrm{CH_3CO^+}) = -152.05930$ hartree and $E(\mathrm{CH_3COCl}) = -611.83120$ hartree.

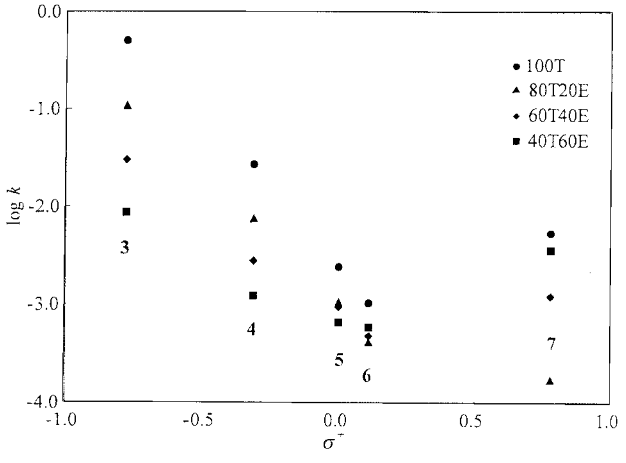


Fig. 6 Correlation analysis using Brown-Okamoto treatment for the solvolysis of compounds **3**–**7** in trifluoroethanol–ethanol.

Discussion

In recent studies of the solvent effect on solvolysis of benzylic substrates by using correlation analyses of the Grunwald–Winstein type, eqns. (1) and (5), we found it necessary to establish new scales of solvent ionising power, Y_{BnX}, to obtain better understanding of mechanisms.[26] To extend the applicability of

Table 7 Correlation analyses against Y_X, N_T and I

Substrate	Parameters	n	R	m (s.d.)[a]	l (s.d.)[a]	h (s.d.)[a]
1	Y_{Cl}, I	11	0.969	0.790 (0.074)		1.18 (0.269)
2	Y_{Cl}, I	12	0.912	0.463 (0.073)		0.395 (0.287)
3	Y_{Cl}, I	16	0.937	0.551 (0.057)		0.057 (0.252)
4	Y_{Cl}, I	16	0.821	0.385 (0.075)		−0.047 (0.329)
1	Y_{Cl}, N_T, I	11	0.989	0.909 (0.058)	0.654 (0.186)	1.17 (0.173)
2	Y_{Cl}, N_T, I	12	0.984	0.666 (0.048)	0.671 (0.113)	0.601 (0.136)
3	Y_{Cl}, N_T, I	16	0.963	0.704 (0.070)	0.281 (0.098)	0.374 (0.230)
4	Y_{Cl}, N_T, I	16	0.882	0.562 (0.098)	0.326 (0.137)	0.321 (0.322)

[a] Standard deviation.

this approach to other categories of substrates, we undertook to examine the solvolysis of aromatic acyl chlorides. Although much solvolytic rate data have been measured by Lee *et al.* and by Bentley *et al.*,[10] a complete coverage of different types of solvents is wanting. Moreover, the use of isodielectric trifluoroethanol–ethanol mixtures[27] has been shown to be a diagnostic tool for examining nucleophilic solvent intervention in solvolysis of benzylic[16,17b,28] and aliphatic[29] substrates. Therefore, both highly nucleophilic solvents (aqueous acetone, ethanol and methanol) and weakly nucleophilic solvents (trifluoroethanol–ethanol) with large differences in solvent ionising power (ΔY_{BnCl} = 3.5–5.2) were employed for solvolyses of acyl chlorides **1**–**7**.

Table 2 indicates an excellent linear relationship (R = 0.991) in the log k *vs.* Y_{BnCl} plot for compound **1** (Fig. 1), and thus confirms the solvolysis to proceed *via* the S_N1 mechanism as proposed earlier.[11] The limiting S_N1 process for the solvolysis of **1** is in line with the $A_{AC}1$ mechanism suggested for the hydrolysis of methyl mesitoylate (2,4,6-trimethylbenzoate).[30]

On the other hand, in the log k *vs.* Y_{BnCl} plots for compounds **2**–**4**, the data points measured in nucleophilic solvents (aqueous acetone, ethanol and methanol) and those measured in poorly nucleophilic trifluoroethanol-ethanol mixtures fall on two separate lines, as in Fig. 2. This indicates the presence of nucleophilic solvent intervention in these solvolyses. Obviously, the steric hindrance of only one *ortho*-methyl group in **2** is not large enough to prevent the carbonyl carbon from nucleophilic attack, but its bulkiness may contribute significantly to the higher reactivity of **2** than **4**. The poor regression (Table 1) for **2**–**4** with respect to all solvents by using the single-parameter eqn. (1) could be improved if the dual-parameter eqn. (5) was employed, but not to excellent linear correlation ($R \geq 0.99$[31]) no matter whether N_{OTs}[18] or N_T[19] was used (Table 3). Nevertheless, the low m value and the high l value obtained in each case suggested significant nucleophilic solvent participation in the solvolysis of **2**–**4**. The downward splitting of the line for data points obtained in trifluoroethanol–ethanol from that in nucleophilic solvents (aqueous acetone, ethanol and methanol) in the log k *vs.* Y_{BnCl} plots (*e.g.* Fig. 2) is thus essential for the presence of nucleophilic solvent participation in solvolyses, as has been illustrated in several other cases.[16,17b,28,32]

The behavior of benzoyl chlorides **5**–**7** in solvolysis is different from that of **1**–**4**. Table 2 suggests non-linear relationships for **5**–**7** with Y_{BnCl} using the single-parameter eqn. (1). Plots of log k *vs.* Y_{BnCl} show scattered data points, as in Fig. 3 for **5** and Fig. 4 for **7**, and those for **6** are similar to the latter. The results show some similarity with those found for benzoyl chloride **5**.[10c] The distinct difference between the plot of log k *vs.* Y_{BnCl} in trifluoroethanol–ethanol and those in nucleophilic solvents for **7** (and also for **6**), and the variation of linear relationships for data points corresponding to different solvent systems (Figs. 3 and 4), probably suggest a changing mechanism in different media, as previously proposed.[10]

Hammett-type plots against σ^+ constants for the solvolysis of substituted benzoyl chlorides gave linear relations in 97[10c] and 90%[33] trifluoroethanol. Linear regression was observed for compounds **3**–**6** in 40% methanol, but only a concave curve was found in methanol.[10c] Similarly, log k *vs.* σ^+ plots for **3**–**7** exhibit linear relationships for **3**–**6** only in solvents containing a high percentage of water (50A, 50E and 60M) or a high percentage of trifluoroethanol (100T and 80T20E), for **3**–**5** in solvents containing less water (60A, 60E and 70M) or less trifluoroethanol (60T40E). Pertinent data are listed in Table 4, and representative figures are given in Figs. 5 (aqueous ethanol) and 6 (trifluoroethanol-ethanol). The observation of small negative ρ values in most solvents, but the more negative ones in high ionising and low nucleophilic solvents, 100T and 80T20E, can be considered as an indication of less charge development at the transition state of solvolysis in nucleophilic solvents. From the significant deviation displayed in Figs. 5 and 6, it is obvious that the solvolysis of 4-nitrobenzoyl chloride (**7**), and probably 4-chlorobenzoyl chloride (**6**) too, proceeds *via* a different mechanism from others, as has been discussed.[10d,12]

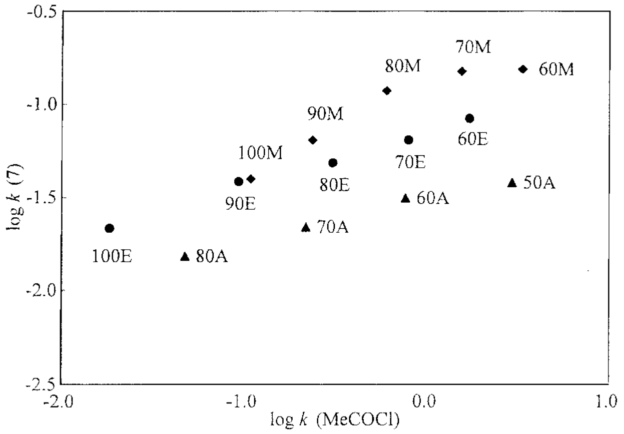


Fig. 7 Plots of log k for 4-nitrobenzoyl chloride (**7**) against log k for acetyl chloride.

Acetyl chloride was considered to solvolyse with an S_N2 mechanism[2b] [eqn. (3)]. Logarithm plots of rate data for 4-nitrobenzoyl chloride (**7**) in the present study against those for acetyl chloride in the literature[2b] are shown in Fig. 7. Similar to those observed in Fig. 4, the data points obtained in aqueous acetone exhibited a good linear relationship, but those obtained in aqueous ethanol or methanol indicated some distortion. Therefore, the solvolysis of **7** in nucleophilic solvents might also involve S_N2 mechanisms with a variable transition state in different solvent systems. Similar results were also found for 4-chlorobenzoyl chloride (**6**), but not for benzoyl chloride **5** (Fig. 8), which suggested a similarity in solvolytic behavior between **6** and **7**, in harmony with the conclusion reached previously. In poorly nucleophilic trifluoroethanol–ethanol, **6** and **7** might take different routes, probably the addition-elimination mechanism eqn. (4). It may then be concluded that Grunwald-Winstein type correlation analysis, eqns. (1) and (5), using appropriate Y and N scales, provides a better understanding of solvolytic mechanisms for benzoyl chlorides. Hammett type correlation analysis is less sensitive to solvent change, especially

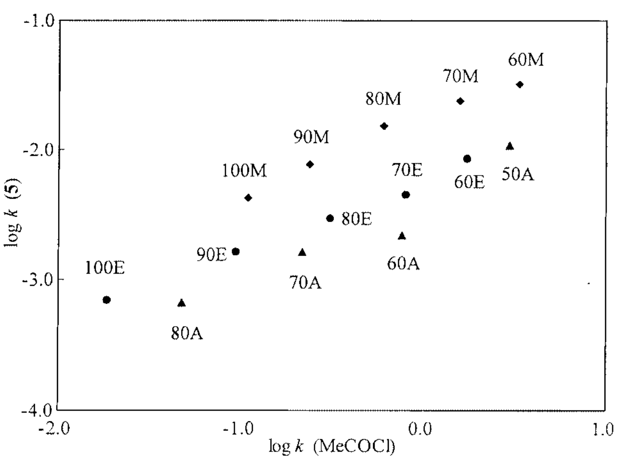
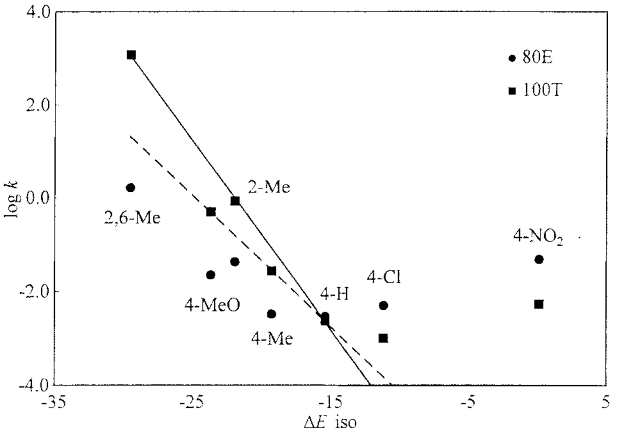


Fig. 8 Plots of log *k* for benzoyl chloride (**5**) against log *k* for acetyl chloride.



$$\mathrm{RCOCl} + \mathrm{CH_3CO^+} \longrightarrow \mathrm{RCO^+} + \mathrm{CH_3COCl} \qquad (7)$$

Fig. 9 Plots of log *k* in 80E and in 100T for compounds **1**–**7** against ΔE_{iso}/ kcal mol^{-1}.

for those reactions without intensive charge development at the transition state, such as the solvolysis of benzoyl chlorides.

On the other hand, the charge distribution in acylium ions **2a**–**7a** derived from **2**–**7** was estimated by *ab initio* calculations. Mulliken population analyses[23] at the RHF/6-31G*//RHF/6-31G* level are given in Table 5, in which charges on hydrogens and on ring carbons are summed. The small difference of the charge distribution on carbonyl carbons, and likewise on aryl rings, among acylium ions **2a**–**6a** is in agreement with the small ρ values mentioned previously (Table 4). Similar results are obtained also using charges derived from the molecular electrostatic potential[34] and from natural population analysis.[35]

By using acetyl chloride as the reference in eqn. (7),[36] the energies of the isodesmic reactions (ΔE_{iso}) were calculated at the RHF/6-31G* level of geometry optimisation, and are listed in Table 6. Randomly dispersed plots of ΔE_{iso} *vs.* the logarithms of rate constants measured in nucleophilic 80% ethanol (closed circles in Fig. 9) reveal the importance of solvent intervention in the solvolysis. Since the rates of solvolysis for most of the acyl chlorides **1**–**7** were too fast in hexafluoropropan-2-ol to be measured accurately, trifluoroethanol was the least nucleophilic solvent employed in this work. In this medium, nucleophilic solvent intervention may be considered insignificant. Indeed, excellent linear relationships for 2,6-dimethyl- (**1**), 2-methyl- (**2**) and unsubstituted benzoyl chloride (**5**) (solid line in Fig. 9), and also for 4-methoxy- (**3**) and 4-methyl-benzoyl chloride (**4**) and **5** (broken line in Fig. 9) can be observed. The more negative slope in the former case probably indicates that steric effects have a greater influence than electronic effects in enhancing solvolytic reactivity for substituted benzoyl chlorides. The observed linearity in the log *k* *vs.* ΔE_{iso} plots for **3**, **4** and **5** accords with the results of Hammett-type plots for data obtained in solvents containing high percentages of water or trifluoroethanol (see above). However, there were differences between **5** and other benzoyl chlorides in single-parameter Grunwald–Winstein plots (Table 2), and between **5** and **6** or **7** in log *k* *vs.* log *k* (acetyl chloride) plots (Figs. 7 and 8). It might be concluded that solvolysis of **5** takes a different route from those of other analogues, probably at the borderline of unimolecular dissociation, eqn. (2), and the addition-elimination mechanism, eqn. (4).

Thus, for solvolyses of benzoyl chlorides, the results from Grunwald–Winstein type correlation analysis, eqns. (1) and (5), using the Y_{BnCl} scale as the solvent parameter are in coherence with the results from Hammett type correlation analysis using σ^+ constants, eqn. (6), and also with the outcome of *ab initio* calculations. It may be concluded that Y_{BnCl} parameters are also useful in the correlation analysis for the solvolytic reactivity not only benzylic chlorides,[17] but also benzoyl chlorides. Since Kevill *et al.* have proposed the use of the aromatic ring parameter *I*, together with Y_{X} to substitute Y_{BnX} for studying the solvolytic behavior of benzylic substrates,[25] it is thus desirable to compare these two approaches to benzoyl chlorides. A comparison of Table 7 with Tables 2 and 3 clearly illustrates the superiority of using Y_{BnCl} in the single-parameter eqn. (1) and the dual-parameter eqn. (5) to the use of a combination of Y_{Cl} and aromatic ring parameter *I* in the multi-parameter eqns. (8) and (9). Therefore, in addition to the drawbacks already mentioned,[32*e*,37,38] the less satisfactory application to the solvolysis of benzoyl chlorides is another cause for concern.

Conclusion

Solvolytic mechanisms for benzoyl chlorides may be understood by means of Grunwald–Winstein type correlation analysis, eqns. (1) and (5), using Y_{BnCl} scales[17] for a sufficiently large variety of solvents, in association with the results of Hammett type study and *ab initio* calculations. 2,6-Dimethylbenzoyl chloride (**1**) solvolyses with limiting $\mathrm{S_N}1$ mechanism, eqn. (2), whereas the solvolysis of 2-methyl- (**2**), 4-methoxy- (**3**) and 4-methyl-benzoyl chloride (**4**) proceeds with nucleophilic solvent participation. The solvolytic mechanism of benzoyl chloride (**5**) is probably at the borderline of unimolecular dissociation, eqn. (2), and the addition-elimination (eqn. 4) mechanisms. In the solvolysis of 4-chloro- (**6**) and 4-nitro-benzoyl chloride (**7**) an $\mathrm{S_N}2$ mechanism, eqn. (3), is likely to be involved in nucleophilic solvents, and an addition-elimination mechanism in trifluoroethanol–ethanol. However, slight variation of mechanism in different solvents cannot be excluded.

Experimental

General

Proton and carbon-13 NMR spectra were recorded on a Bruker Model DMX-300 instrument, IR spectra on a Perkin-Elmer Model 983G spectrometer.

Materials

Spectral-grade or reagent-grade solvents (E. Merck) were purified following conventional methods[39] for kinetic studies. Doubly deionised water was used to prepare aqueous solvent mixtures for solvolytic studies. Commercially available acid chlorides (**2** and **6** from Aldrich Chemical company, and **2**, **3**, **5** and **7** from Acros Chemical Company) were used or purified if needed. 2,6-Dimethylbenzoyl chloride (**1**) was prepared from the corresponding acid (Aldrich) with thionyl chloride. The IR and NMR spectra were found to be in accord with the assigned structure.

Kinetic measurements

Rate constants were measured by a conductimetric method at least in duplicate. The conductivity cells containing solution of 1×10^{-4} to 1×10^{-5} M were placed in a thermostat with a temperature variation of ±0.02 °C. The maximum error for the measurement of k is ±2%.

Rate constants monitored at other temperatures were extrapolated to those at 25 °C by the use of an Arrhenius plot. The results for compounds **1** and **2** at 25 °C are given in Table 1. The data for **3**–**7** at 25 °C, and for **1** and **3** at low temperature are included in Table S1 and Table S2, respectively (see Supplementary material).

Calculations

The SPARTAN version 4.1.1 program on a Dec Alpha 3000 system was used.

Acknowledgements

We are indebted to the National Science Council, Republic of China, for financial support (Grants NSC87-2113-M-002-007 and NSC88-2113-M-002-014).

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Paper a905125b