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Kinetic solvent isotope effects and correlations of rates of solvolyses for α-methylthio and other substituted acetyl chlorides†

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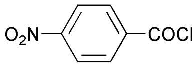
Kinetic data for solvolyses of α-methylthioacetyl chloride, phenylthioacetyl chloride and thiophene-2-acetyl chloride in at least 33 aqueous solvent systems including 2,2,2-trifluoroethanol–ethanol solvent were determined at 10 °C by a conductimetric method, and their rates of solvolyses were correlated using Grunwald–Winstein type equations with the ionizing power parameter (Y_{Cl}: based on the solvolyses of 1-adamantyl chloride) and the nucleophilicity parameter (N_T). Kinetic solvent isotope effects (KSIEs) in water and methanol were investigated for the above compounds and in methanol also for phenyl, diphenyl, and trimethylacetyl and isobutyryl chlorides. The results show similar absolute rate constants, similar large amounts of nucleophilic solvent assistance, but different KSIE values (explained by general base catalysis).

Kinetic solvent isotope effects (KSIEs) for solvolyses have most often been determined from rate ratios for solvolyses in water and D_2O, and *KSIE results (when expressed as* k_H/k_D*) for many* S_N1 *and* S_N2 *reactions at saturated carbon are generally between 1.0 and 1.3.*[1] Less extensive studies in methanol and MeOD have shown that the KSIE values are similar to those for corresponding reactions in water,[2,3] but measurements in methanol are easier to obtain because rates are lower than for water (particularly important for studies of highly reactive acid halides) and solubilities of organic compounds are much greater. The low KSIE results in MeOH of 0.97–1.18 for solvolyses of various diphenylmethyl chlorides[4] and of 1.22 for *p*-methoxybenzoyl and *p*-methoxybenzyl chlorides[5] (S_N1 reactions), and 1.11 for methyl toluene-*p*-sulfonate[6] (S_N2 reaction) indicate that the above generalisation also applies to solvolyses in MeOH.

A second generalisation is *that higher KSIE values (> 2.0) are usually obtained for general base catalysed hydrolyses*, (*e.g.* see ref. 7, Table 7). In solvolyses under neutral or acidic conditions, the solvent could act both as a general base catalyst and as a nucleophile, and for acetic anhydride, KSIE values of 2.8 in water and in MeOH are observed.[2] Solvolyses of four acid chlorides [*p*-nitrobenzoyl chloride (**1**),[8] *p*-nitrobenzenesulfonyl chloride (**2**),[9] *p*-nitrophenyl chloroformate (**3**),[10] and diphenyl phosphorochloridate (**4**)[11]] provide a subset of this second generalisation—all show KSIE values > 2.0 in MeOH,[8–11] and rates and products of these solvolyses in ethanol– and methanol–water mixtures have been explained quantitatively by competing third order reactions in which one molecule of solvent acts as a nucleophile and a second molecule acts as a general base catalyst.[8–11]



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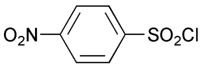

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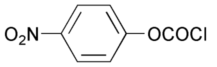

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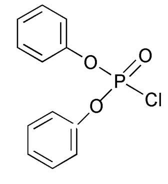

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Published KSIE work on solvolyses of acid halides in methanol has been concerned mainly with aromatic (aroyl) systems ($ArCOCl$[3a,5,12] and $ArSO_2Cl$[3a,13]) and chloroformates;[10,14] all show results in the range 1.2 to 2.5. Of the non-aromatic acyl systems, only two solvolyses have been studied: *p*-nitrobenzyl chloroformate gives a value of 2.42,[15] within the range of other chloroformates,[10,14] but for acetyl chloride the KSIE result is low (1.29).[16] Introduction of sulfur atoms adjacent to a reaction centre, studied for chloroformates, caused a partial shift away from general base catalysed addition–elimination (S_AN) through competing, dual reaction channels (DC) to the ionization channel (IC) [*i.e.*: PhOCOCl[17] (S_AN) ⟶ PhSCOCl[18,19] ≈ PhOCSCl[20] (DC) ⟶ PhSCSCl[20] (IC)].

We now report additional studies of solvent effects on the reactivity of three more acyl chlorides, each containing a sulfur atom (**5**–**7**), and KSIE data in methanol for additional acyl chlorides, phenylacetyl chloride (**8**), diphenylacetyl chloride (**9**), trimethylacetyl chloride and isobutyryl chloride (**10**). The results provide new insights into mechanistic classifications for solvolyses having KSIE values within the range 1.2 to 2.0, and allow further investigation of solvation effects adjacent to the reaction site.[5,21–23]

Results

Kinetic data for solvolyses in 80% ethanol–water at 10 °C are as follows: α-methylthioacetyl chloride (**5**), $k_0/s^{-1} = 1.65 \times 10^{-1}$; phenylthioacetyl chloride (**6**), $k_0/s^{-1} = 1.32 \times 10^{-1}$; thiophene-2-acetyl chloride (**7**), $k_0/s^{-1} = 1.44 \times 10^{-1}$; other results at 10 °C are given in Tables S1–S3.† KSIE data for chlorides **5**–**10** and other acyl chlorides are given in Table 1. Additional KSIE data in water for **5**–**7** are given in Table 2. Reactions were initiated by injecting a few µL of a dilute solution of the substrate into the

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† Electronic supplementary information (ESI) available: Tables S1–S3. See http://www.rsc.org/suppdata/p2/b2/b202664n/

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Table 1 First order rate constants (k/s^{-1}) in methanol, kinetic solvent isotope effects (KSIEs) and values of solvolysis rate ratios in 40% (v/v) ethanol–water compared with 97% (w/w) trifluoroethanol–water[a]

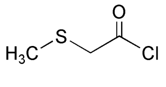
Compound	MeOH	MeOD[b]	(k_H/k_D)[c]	$[k_{40E}/k_{97T}]_Y$[d]
5 (10 °C)	$(1.64 \pm 0.04) \times 10^{-1}$	$(1.10 \pm 0.05) \times 10^{-1}$	1.49	240
6 (10 °C)	$(1.57 \pm 0.03) \times 10^{-1}$	$(9.36 \pm 0.01) \times 10^{-2}$	1.68	215
7 (10 °C)	$(1.98 \pm 0.06) \times 10^{-1}$	$(1.10 \pm 0.02) \times 10^{-1}$	1.80	254
8 (10 °C)	$(1.44 \pm 0.05) \times 10^{-1}$	$(1.03 \pm 0.02) \times 10^{-1}$	1.40	
MeCOCl (0 °C)	$(1.09 \pm 0.03) \times 10^{-1}$	$(8.21 \pm 0.08) \times 10^{-2}$	1.32[e]	320[e]
Bu^{t}COCl (0 °C)	$(1.78 \pm 0.03) \times 10^{-1}$	$(1.22 \pm 0.02) \times 10^{-1}$	1.46	88 (10 °C)[f]
9 (10 °C)	$(6.83 \pm 0.01) \times 10^{-2}$	$(4.25 \pm 0.02) \times 10^{-2}$	1.61	
10 (10 °C)	$(1.67 \pm 0.04) \times 10^{-1}$	$(1.22 \pm 0.01) \times 10^{-1}$	1.37	

[a] Determined conductimetrically at least in duplicate. [b] MeOD was Aldrich (> 99.5% D). [c] Kinetic solvent isotope effect. [d] Subscript Y symbol means very similar ionizing power (Y_{Cl}), ref. 24, but different nucleophilicity (N_T), refs. 25 and 26—Y_{Cl} of 2.75, N_T of −0.75 for 40% (v/v) ethanol–water and Y_{Cl} of 2.85, N_T of −3.30 for 97% (w/w) trifluoroethanol–water. [e] Ref. 16 reports a value of 1.29 ± 0.03. [f] The value calculated at 10 °C for the ratio of rate constants $[k_{40E}/k_{97T}]_Y$; in 40% (v/v) ethanol–water k_{calc} is 1.82 s^{-1} from an Arrhenius plot using observed rate constants at −10, −5 and 0 °C 0.226 ± 0.003, 0.389 ± 0.006 and 0.667 s^{-1} (ref. 27), respectively; an Arrhenius plot using three observed rate constants (−10, −5 and 0 °C) gives $\Delta H^\ddagger$ 14.9 kcal mol^{-1}, $\Delta S^\ddagger = -4.5$ cal K^{-1} mol^{-1} ($r = 0.99994$); for 97% (w/w) TFE–water, the rate constant (k_{obs}) observed at 10 °C is 0.0207 ± 0.0002 s^{-1}.

Table 2 First order rate constants (k/s^{-1}) in water for kinetic solvent isotope effects (KSIEs)[a]

Compound	H_2O	D_2O[b]	(k_{H_2O}/k_{D_2O})
5 (5 °C)	1.53 ± 0.03	1.01 ± 0.06	1.51
6 (5 °C)	0.413 ± 0.03	0.213[c]	1.94
7 (5 °C)	0.698 ± 0.07	0.35 ± 0.06	1.99

[a] Determined under the same conditions as shown in footnote *a* in Table S1 except for the amount injected, 4 μL of 1% (w/w) substrate in dry acetonitrile. [b] Triple injected and a turbo-stirrer continued to be used to solve the problem of solubility for kinetic runs (mp of D_2O: 3.5 °C). [c] Observed kinetic data for three half lives, because of unsatisfactory variations of conductivity values with time towards the end of the reaction.



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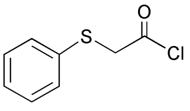

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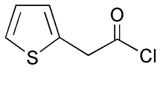

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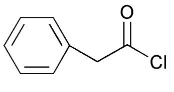

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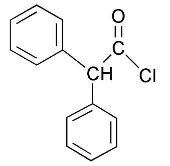

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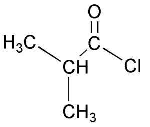

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rapidly-stirred thermostatted solvent, and were monitored by the change in conductance due to liberated HCl and organic acid. Many of the reactions were relatively rapid, and in addition to determining each rate constant at least in duplicate, some rate constants at 10 °C were checked by extrapolating data from −10 and 0 °C (see Table S2, footnote *e*, and Table S3, footnote *d*). KSIE values were determined by monitoring two reactions (*e.g.* MeOH and MeOD) simultaneously.

Discussion

The substituted-acetyl chloride substrates (**5**–**7**) react at about the same rate as the parent acetyl chloride in pure ethanol (at 10 °C, we observe $k = 5.02 \times 10^{-2}$ s^{-1}; lit:[28] 4.65×10^{-2} s^{-1}), but are less reactive than acetyl chloride in more aqueous media. Consequently, it has now been possible to obtain solvolysis rate constants over the full range of acetone– and ethanol–water mixtures (Tables S1–S3). In contrast, more strongly electron-withdrawing groups (*e.g.* changing Me, $\sigma_I = -0.01$ to CH_2Cl, $\sigma_I = 0.17$)[29] increase rates and available solvolysis rate data are restricted to solvents of relatively low ionising power (for solvolyses of $CH_2ClCOCl$, see Table 7 of ref. 30). Mechanistic differences can be seen from methanolyses of acetyl chloride in acetonitrile, which are accelerated by added phenol (electrophilic assistance to formation of a cationic intermediate[30]), whereas phenolysis of chloroacetyl chloride in acetonitrile is retarded.[30]

The kinetic results can be explained by competing reaction channels[17–20,31–37] and/or by variations in transition state structure; the presence of an electron-withdrawing group, such as Cl in chloroacetyl chloride or PhO in phenoxyacetyl chloride, favours solvolyses *via* an addition–elimination (S_AN mechanism) or tighter S_N2 transition state,[30,31] whereas alkyl groups capable of electron donation favour a looser S_N2 mechanism in which positive charge develops on the carbonyl group.[16,30] If solvolyses of $MeSCH_2COCl$ (**5**) occurred *via* a cationic transition state, rates would be disfavoured by the inductive effect ($\sigma_I = 0.12$ for $MeSCH_2$)[29] and/or by a steric effect of the SR group;[31,38] alternatively, if reaction occurred by a mechanism similar to that of $ClCH_2COCl$, **5** would be less reactive because the inductive effect of $MeSCH_2$ is less than that of $ClCH_2$.[29]

Rates of solvolyses can be correlated by a modified Grunwald–Winstein equation (1), where k and k_0 refer to the rate constants for solvolyses in a given solvent and in 80% v/v ethanol–water, respectively; m is the susceptibility to changes in solvent ionizing power (Y_{Cl}) and c is the intercept.[24] Good linear correlations are obtained using eqn. (1) for solvolyses of **5**–**7** in a range of solvents from 100% ethanol to pure water ($n = 11$ solvents and solvent mixtures, Table 3), whereas in previous work on acetyl chloride only data from 100–60% v/v ethanol–water were available.[16]

The KSIE values for **5**–**7** are similar in both MeOH (Table 1) and water (Table 2), consistent with similar reaction mechanisms in the two solvents. Also, the satisfactory linear correlations (Table 3) for solvolyses of **5**–**7** in ethanol–water mixtures are consistent with reactions *via* single reaction channels throughout the range of solvent compositions. In contrast, solvolyses of trimethylacetyl chloride gave a non-linear plot *vs.* Y (explained by competing, dual reaction channels[27]), and a plot *vs.* Y_{Cl} is also non-linear (Table 3). The slopes of correlations (m, Table 3) are about 0.3 lower for solvolyses of **5**–**7** than acetyl chloride in ethanol–water mixtures. Closely-similar trends to those discussed above for ethanol–water mixtures are observed for solvolyses in acetone–water mixtures (Table 3).

$$\log (k/k_0) = mY_{Cl} + c \qquad (1)$$

Table 3 Correlation analyses of log (k/k_0) for solvolyses of **5**–**7** and acetyl chlorides with single or dual parameter Grunwald–Winstein equations [(1) and (2)][a]

Compound	Parameter	Solvent	n^b	r^c	m^d	l^d	c^e
5 (10 °C)	Y_{Cl}	Ethanol	11	0.995	0.18		−0.027
		Acetone	9	0.994	0.33		−0.665
		All	34	0.273	0.12		−0.461
	Y_{Cl}, N_T	All[f]	33	0.964	0.46	1.02	−0.016
6 (10 °C)	Y_{Cl}	Ethanol	11	0.980	0.27		−0.035
		Acetone	9	0.993	0.27		−0.705
		All	36	0.144	0.06		−0.400
	Y_{Cl}, N_T	All	35	0.963	0.39	1.02	0.032
7 (10 °C)	Y_{Cl}	Ethanol	11	0.982	0.16		−0.019
		Acetone	9	0.991	0.31		−0.668
		All	34	0.195	0.08		−0.435
	Y_{Cl}, N_T	All	33	0.959	0.42	1.03	0.031
MeCOCl (0 °C)[g]	Y_{Cl}	Ethanol	5	0.999	0.51		0.014
		Acetone	5	0.999	0.67		0.238
Bu^{t}COCl (0 °C)[h]	Y_{Cl}	Ethanol	8	0.971	0.50		0.193
		100–80[i]	3	0.9991	0.29		−0.004
		60–30[i]	4	0.9997	0.76		−0.412
		Acetone	7	0.990	0.64		−0.258
		90–70[i]	3	0.999	0.45		−0.455
		60–30[i]	4	0.998	0.79		−0.565

[a] Origin 6.0 program was used for the multiple regression analysis. [b] Number of solvents. [c] Correlation coefficient. [d] Sensitivity to each solvent parameter chosen. [e] Value of intercept obtained from correlation. [f] See Fig. 3. [g] Data from ref. 16. [h] Data from ref. 27. [i] Correlations for two limited ranges of ethanol–water or acetone–water solvent compositions.

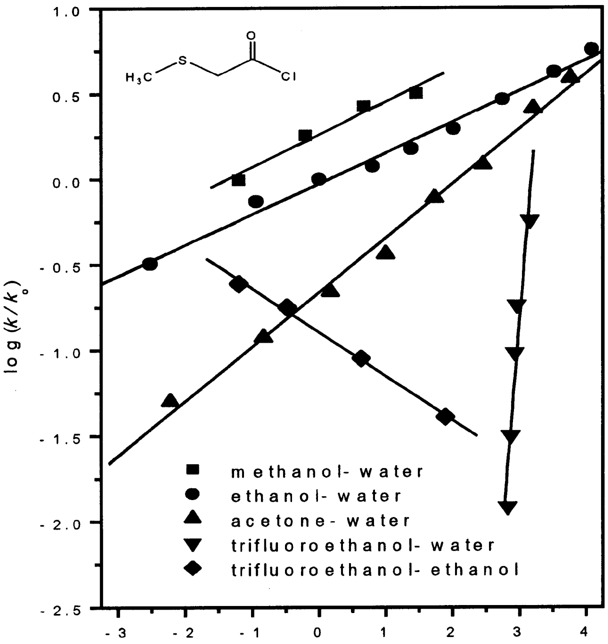

Fig. 1 Correlation of logarithms of rate constants for solvolyses of **5** with Y_{Cl}.

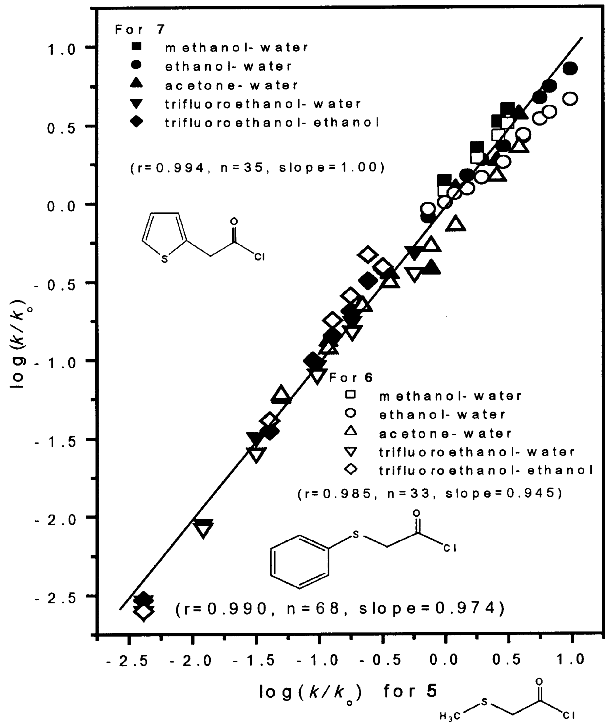

Fig. 2 Correlation of logarithms of rate constants for solvolyses of **5** *versus* rates for **6** and **7** at 10 °C.

The results for eqn. (1) evaluated for all solvent systems (n = 33–35) give very dispersed plots for the various binary mixtures (typically shown in Fig. 1 for solvolyses of **5**), including a negative slope (m = −0.26–0.39) for the 2,2,2-trifluoroethanol (TFE)–EtOH system. However, rate–rate profiles for solvolyses of **5**, **6** and **7** (Fig. 2) show to only a small extent the phenomena of dispersion (the tendency towards separate correlation lines for different binary solvent mixtures) caused by differences in solvation adjacent to the reaction site (C=O);[5,21–23] there is a good linear correlation (correlation coefficient, r = 0.990, n = 68), and slopes are close to unity. In particular, a rate–rate correlation of **5** against **7**, in which the S-atom is in different positions with respect to the carbonyl group, led to excellent linearity with slope = 1.00 and r = 0.994. These results (Fig. 2) also provide important evidence that rates of solvolyses of thioacetyl chlorides (**5** and **6**) are not affected by the electron lone pair of the S-atom, separated by one carbon from the reaction site (*i.e.* no neighboring group effect), and support the above arguments that **5**, **6** and **7** solvolyse by very similar reaction pathways.

Inspection of Fig. 1 shows that for a Y_{Cl} value of −1, the rate constant in methanol is about 10-fold faster than in acetone–water. These and similar dispersion phenomena were analyzed using the extended Grunwald–Winstein equation (2), considering also the solvent nucleophilicity term, lN_T, where l is the susceptibility to change in solvent nucleophilicity, N_T (based on the solvolyses of S-methyldibenzothiophenium ion[25,26]). The

$$\log (k/k_0) = lN_T + mY_{Cl} + c \qquad (2)$$

results (Table 3) show very similar m-values (0.39–0.45, error ±0.03) and l-values (1.02–1.03, error ±0.05), with an acceptable r value (≥ 0.956) for dual linear regression analysis with 33–35 aqueous solvent systems, including the TFE–EtOH solvent system which showed major deviations from eqn. (1) (*e.g.* see Fig. 1).

Although eqn. (2) is primarily applied to correlations involving solvents of widely different nucleophilicities (*e.g.* ethanol, $N_T = 0.37$; TFE, $N_T = -3.93$),[26] more subtle effects can also be explained. According to the N_T scale, methanol and methanol–water mixtures are slightly more nucleophilic than corresponding acetone–water mixtures (*e.g.* 100% methanol, $N_T = 0.17$; 80% acetone–water, $N_T = -0.37$),[26] so a difference in l value of 1.00 will account for dispersion corresponding to a factor of 3.5 in rate. However, even using eqn. (2), a significant dispersion can be seen from the separation between methanol–water and acetone–water correlation lines (*e.g.* see Fig. 3), probably caused at least in part by inadequacies of Y_{Cl} as a model for solvolyses of acid chlorides.[39]

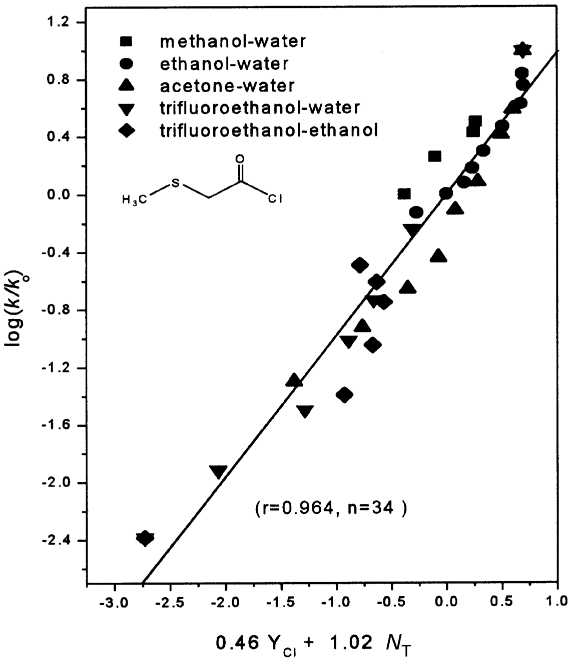

Fig. 3 Correlation of logarithms of rate constants for solvolyses of **5** at 10 °C.

The results for solvolyses of **5**–**7** (Table 3) can be explained by the same mechanism with the same structure of transition state, controlled by the contribution from strong nucleophilic participation by the molecule of solvent as well as weak solvent polarity (ionization), regardless of the different adjacent groups containing an S-atom (even if these are not attached directly to the reaction centre). The rate ratio k_{40E}/k_{97T}, a measure of nucleophilic solvent assistance,[24] shows similar ratios (range 215–320) for solvolyses of **5**–**7** and also of acetyl chloride (Table 1).

Nucleophilic participation by solvent may also be assisted by general base catalysis by a second solvent molecule, which could explain why the KSIE results (Table 1) in the range 1.46–1.80 are significantly greater than for typical S_N1/S_N2 solvolyses[1,4–6] and for acetyl chloride (1.32, Table 1); such catalysis might also account for the lower m values for solvolyses of **5**–**7**, compared with acetyl chloride (Table 3), because any positive charge on the attacking solvent nucleophile will be more highly dispersed if assisted by a general base catalyst. Solvolyses of **8**–**10** (lacking a sulfur atom) have similar KSIE values (range 1.37–1.61) to **5**–**7**, but subtle differences are also detectable (*e.g.* 2-thiophenylacetyl chloride (**7**) has a KSIE value of 1.8, whereas phenylacetyl chloride (**8**) has a lower KSIE of 1.4). The relatively low KSIE of 1.46 for solvolyses of Bu^{t}COCl is probably due (at least in part) to competing reaction channels.[16,27]

Conclusions

Solvolyses of the substituted acetyl chlorides **5**–**7** are the first solvolyses of acyl chlorides for which kinetic data have been obtained for the full range of solvents from ethanol to water (spanning seven orders of magnitude of S_N1 reactivity[24]). The main effect of the sulfur atom is to deactivate these acyl solvolyses (by inductive and/or steric effects[30,31,38]), and only very subtle solvation effects adjacent to the reaction site were detectable. Unlike solvolyses of many acid chlorides,[8,11,13,27,32–34,40] linear mY correlations for a given binary mixture [eqn. (1)] are obtained (Table 3), and the results can be explained by reactions *via* a single reaction channel; m values are unusually low and the extended Grunwald–Winstein equation (2) reveals a high sensitivity to solvent nucleophilicity ($l = 1.0$, Table 3).

Whilst kinetic solvent isotope effects (KSIEs, Tables 1 and 2) vary from 1.3 to 2.0, covering the intermediate range between S_N1/S_N2 reactions (KSIE 1.0–1.3)[1,4–6] and well established, general base catalysed reactions (KSIE > 2.0),[8–11] measures of nucleophilic solvent assistance (*e.g.* k_{40E}/k_{97T} ratios, Table 1 or l values, Table 3) are very similar (*ca.* 250 for k_{40E}/k_{97T} ratios). In contrast for S_N1/S_N2 reactions, there is a narrower range of KSIE values but l values [eqn. (2)] vary throughout the whole range from 0 to 1.[41] A rationalization of these observations is that the KSIE values of 1.5–2.0 for solvolyses of **5**–**7** in methanol and water may indicate increasing amounts of general base catalysis.

Experimental

Materials

α-Methylthioacetyl chloride (**5**) was prepared from the reaction of α-methylthioacetic acid (5 g, 0.047 mol) in two drops of DMF with thionyl chloride (3.42 mL, 0.047 mol) at 55 °C during 1.5 hours and then the product was purified by distillation under reduced pressure as described elsewhere;[42] bp 49–50 °C/14 mmHg (lit.:[42] 45 °C/13 mmHg; ^{1}H NMR: $\delta = 2.26$ (3H, s, SMe), 3.24 (2H, s, CH_2). α-Phenylthioacetyl chloride (**6**) and thiophene-2-acetyl chloride (**7**) were Aldrich reagents, acid chlorides **8**–**10**, acetyl chloride and trimethylacetyl chloride were Aldrich reagents (AR: 99.6%), used without distillation and/or recrystallization. All solvents used for the kinetics in this work were dried and distilled by standard methods.

Kinetic methods

Conductimetric measurements were made by the rapid-injection conductimetric method,[8] and calculations of rate constants were carried out by the Origin 6.0 program using the Guggenheim equation[43] from data monitored automatically. KSIE measurements were made by simultaneous measurements (using a conductimeter with a multiple channel converter). We tried switching H and D measurements to show that the two cells gave the same results.

Analytical methods

^{1}H NMR measurements were made on a Hitachi FT/NMR R-1500 (60 Hz) spectrometer, Karl Fischer titrations were determined on a Model:ORION AF8 instrument using Karl Fischer reagent (Hydranal composit 5K, precision: 0.3% at 1 mg H_2O) and conductimetric measurements were made using a digital multiple converter, which was set up under computer control (MS-Pentium: A/D converter interface program) collecting up to 1000 readings from a stirred conductivity cell to solve the problems of fast reactions ($t_{1/2} < 4$ min) and of low solubilities of substrates in highly aqueous media.

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