

Correlation of the rates of solvolysis of 2-thiophenecarbonyl chloride[†]

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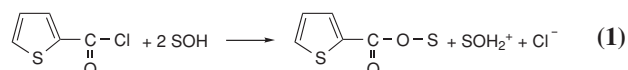
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The specific rates of solvolysis of 2-thiophenecarbonyl chloride are very well correlated by the extended Grunwald-Winstein equation over a wide range of solvents; contrary to previous claims of an S_N2 mechanism, the solvolyses are predominantly by an ionisation mechanism aided by nucleophilic solvation.

Keywords: solvolysis, Grunwald–Winstein equation, nucleophilic participation

There have been two previous reaction mechanism studies^{1,2} of the solvolyses of 2-thiophenecarbonyl (2-thienoyl) chloride (Eqn. 1). In both publications, it was concluded that the reaction proceeded by a dissociative S_N2 mechanism, with



bond-breaking running ahead of bond-making. One might anticipate that the mechanisms for these solvolyses will be similar to those for benzoyl chloride and, indeed, in 70% acetone it was found¹ that the solvolysis rate was one-third that of benzoyl chloride, with the reduction reasonably ascribed to the electron-withdrawing influence of the introduced sulfur atom. There may well also be a contribution from ground-state stabilisation of the substrate, involving an electron-donating resonance effect of the sulfur. However, in our recent analyses³ of the specific rates of solvolysis of benzoyl chloride and several ring-substituted derivatives, we rationalised the overall behaviour in terms of the concurrent operation of addition-elimination (tetrahedral intermediate) and ionisation pathways. In particular, we found no evidence for S_N2 pathways. Accordingly, we felt it appropriate to revisit the proposed^{1,2} S_N2 pathway for 2-thiophenecarbonyl chloride solvolyses.

Results and discussion

The earlier studies were in ethanol, methanol, and water, and in binary mixtures of ethanol, methanol, and acetone with water. A subsequent study² covered a wider range of composition and it also included a value in 97% (by volume) 2,2,2-trifluoroethanol (TFE). We have added (Table 1) additional values in aqueous-TFE mixtures, values over the full range of TFE–ethanol mixtures, and a value in 90% (by weight) 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). We have calculated, from values previously reported¹ in the 30–40°C range, a value for 90% acetone at 25.0°C and have redetermined four of the earlier values. In two instances, our value was in better agreement with the initially reported¹ value and in another it was almost exactly at the mean of the two previously reported values. Since the important value for

Table 1 Specific rates of solvolysis (*k*) of 2-thiophenecarbonyl chloride at 25.0°C

Solvent ^a	10 ³ k/s ^{-1b}	Solvent ^a	10 ³ k/s ^{-1b}
100% EtOH	0.0762 ± 0.0018 ^c	90% TFE	2.90 ± 0.09
90% EtOH	0.273 ± 0.013 ^d	80% TFE	5.45 ± 0.17
80% EtOH	0.435 ± 0.020 ^e	80T–20E ^h	0.464 ± 0.013
90% Acetone	0.0217 ^f	60T–40E ^h	0.188 ± 0.011
70% Acetone	0.368 ± 0.026 ^g	40T–60E ^h	0.102 ± 0.003
90% HFIP	3.91 ± 0.20	20T–80E ^h	0.0882 ± 0.0018
97% TFE	1.72 ± 0.05		

^aVolume/volume basis at 25.0°C, except for TFE–H₂O and HFIP–H₂O mixtures, which are on a weight/weight basis.

^bUsing all integrated values from duplicate runs, with associated standard deviation. ^cPrevious value (ref. 2) of 0.100 × 10⁻³ s⁻¹. ^dPrevious values of 0.230 × 10⁻³ s⁻¹ (ref. 1) and 0.291 × 10⁻³ s⁻¹ (ref. 2). ^ePrevious values of 0.44, × 10⁻³ s⁻¹ (ref. 1) and 0.491 × 10⁻³ s⁻¹ (ref. 2). ^fFrom extrapolation of values (ref. 1) measured in the 30–40 °C range. ^gPrevious values of 0.335 × 10⁻³ s⁻¹ (ref. 1) and 0.216 × 10⁻³ s⁻¹ (ref. 2). ^hT–E are TFE–ethanol mixtures.

100% ethanol was available only in the second publication,² we redetermined it in duplicate and found a value 24% lower than that previously reported.

The earlier studies^{1,2} also included the corresponding oxygen-containing 2-furancarboxyl chloride. Initially, it was proposed¹ that this also solvolysed by a dissociative S_N2 mechanism, but later² an addition–elimination (tetrahedral intermediate) mechanism was proposed. Inspection of the more recent kinetic data² shows a similarity of behaviour for the two carbonyl chlorides in solvents of high alcohol content and increasingly divergent behaviour as the water content is increased. If one assumes that both react by the addition–elimination pathway in 100% ethanol, one can see that (using the 2-thiophenecarbonyl chloride specific rate value from Table 1) the 2-furancarboxyl chloride reacts 2.1 times faster. Since it has been demonstrated that the Grunwald–Winstein parameters are usually similar for different systems reacting by addition–elimination,³ we have further assumed that this ratio remains essentially constant as the solvent is varied and have estimated the specific rates of addition–elimination reaction by dividing the corresponding 2-furancarboxyl chloride value by 2.1. The conclusions are reported in Table 2 as the percentage of overall reaction proceeding by addition–elimination. If the ethanolysis of 2-thiophenecarbonyl chloride does not proceed entirely by addition–elimination, these values must then be considered as upper limits. It can be seen that the fall-off of the percentages

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 2 Estimated percentages of reaction by addition–elimination (%A–E) in the solvolyses of 2-thiophenecarbonyl chloride at 25.0°C^a

Solvent ^b	%A–E	Solvent ^b	%A–E	Solvent ^b	%A–E
100% EtOH	(100) ^{c,d}	100% MeOH	75		
90% EtOH	60 ^d	90% MeOH	66		
80% EtOH	49 ^d	80% MeOH	43	80% Acetone	49
70% EtOH	23	70% MeOH	24	70% Acetone	18 ^d
60% EtOH	11	60% MeOH	13	60% Acetone	12
50% EtOH	S	50% MeOH	6	50% Acetone	5
40% EtOH	2	40% MeOH	2	40% Acetone	2
30% EtOH	1	30% MeOH	1	30% Acetone	0.8
20% EtOH	0.3	20% MeOH	0.5	20% Acetone	0.4
10% EtOH	0.2	10% MeOH	0.2	10% Acetone	0.2
100% H ₂ O	0.1				

^aEstimated (see text) from comparison with 2-furancarboxyl chloride specific rates of solvolysis (ref. 2). ^bVolume/volume basis at 25.0°C, with other component water. ^cBy definition. ^dUsing the specific rate values for 2-thiophenecarbonyl chloride from Table 1.

with increasing water content is very pronounced, and very similar for each of the three binary systems studied.

The extended Grunwald–Winstein equation⁴ (Eqn 2) affords a powerful way of studying the mechanism

$$\log(k/k_0)_{\text{RX}} = lN_{\text{T}} + mY_{\text{X}} + c \quad (2)$$

of solvolysis reactions. In (Eqn 2), k and k_0 are the specific rates of solvolysis of a substrate (RX) in a given solvent and in 80% ethanol, respectively; l is the sensitivity towards changes in solvent nucleophilicity (N_{T})^{5–7}; m is the sensitivity towards changes in solvent ionising power (Y_{X})⁸; and c is a constant (residual) term. Typical values for the operation of an addition–elimination pathway would be those observed for phenyl chloroformate ($l = 1.68$; $m = 0.57$)⁹ or for *p*-nitrobenzoyl chloride ($l = 1.78$; $m = 0.54$)³ and, for ionisation reactions with nucleophilic solvation of a developing acylium ion, typical values would be those observed in the more ionising solvents for ethyl chlorothioformate ($l = 0.66$; $m = 0.93$)¹⁰ or for benzoyl chloride ($l = 0.47$; $m = 0.79$)³. In the above correlations, Y_{Cl} values^{8,11} were used as the solvent ionising power scale.

Specific rates of solvolysis of 2-thiophenecarbonyl chloride are available in 40 solvents. These consist of the 32 reported earlier,² with our values (Table 1) being substituted for 100%, 90%, and 80% ethanol and for 70% acetone (appreciable changes in value only for 100% ethanol and 70% acetone). The value in Table 1 for 97% TFE; of $1.72 \times 10^{-3} \text{ s}^{-1}$ is for a weight–weight solvent composition and it is similar to the value of $1.44 \times 10^{-3} \text{ s}^{-1}$ for a volume–volume composition.² Both values are included in the correlations.

The slight curvature for the least reactive substrates can be considerably reduced by dissecting the rates into values for the two channels, using the data from Table 2. At the extreme, the overall specific rate values for 80% organic solvent content, which lie in this region, have a 40–50% contribution from the addition–elimination pathway. If this were to be subtracted, the points would be lowered by 0.25–0.3 logarithmic units. The l and m values are not appreciably modified when these corrections are made.

The l value of 0.65 is a little over the upper limit which has been documented for those solvolyses at sp^3 -hybridised carbon which are well established as involving ionisation.¹² However, similar values have been observed for other solvolyses at sp^2 -hybridised carbon, consistent with the movement toward a linear acylium ion leading to reduced steric hindrance to solvation.

Use of the simple (one-variable) Grunwald–Winstein correlation for all 40 solvents (Eqn. 2) without the lN_{T} term leads to a poor correlation: $m = 0.57 \pm 0.04$; $c = 0.03 \pm 0.56$; r (correlation coefficient) = 0.9045; F -test value = 171. There is a considerable improvement when the full Eqn. 2 is used: $l = 0.64 \pm 0.06$; $m = 0.77 \pm 0.03$; $c = 0.28 \pm 0.29$; $R = 0.9765$; $F = 379$. Examination of the plot shows that, as with benzoyl chloride,³ the values for solvents with high methanol, ethanol, or acetone content lie somewhat above the plot, consistent with a superimposed addition–elimination pathway. Elimination of 100% and 90% methanol, 100% and 90% ethanol, and 90% acetone leads to a considerably improved plot when Eqn. 2 is used for the remaining 35 solvents: $l = 0.65 \pm 0.04$; $m = 0.86 \pm 0.02$; $c = 0.04 \pm 0.18$; $R = 0.9896$; $F = 754$. This plot of these data is presented in Fig. 1.

Another useful correlation technique is to carry out a direct correlation against the specific rates of solvolysis of a substrate for which the mechanism is believed to be well understood.^{13,14} Since benzoyl chloride has been shown to undergo a solvent-induced change in mechanism,³ a linear plot for $\log(k/k_0)$ for the present substrate against $\log(k/k_0)$ for benzoyl chloride could be taken to indicate the operation of the same two mechanisms with a similar solvent composition range for the changeover region. The plot (Fig. 2) is slightly curved but does give a very good overall linear correlation: slope = 1.21 ± 0.03 ; intercept = 0.19 ± 0.17 ; $r = 0.9923$; $F = 2183$; n (number of data points) = 36. Specific rate values were not available for benzoyl chloride in 98%, 90%, and 80% TFE: or in 90% HFIP.

For a good linear relationship of this type, an algebraic comparison with analyses in terms of Eqn (2) indicates that the l/m ratio obtained for the two series of solvolyses must be very similar (ideally identical). For the 35 solvents believed to favour the ionisation pathway assisted by appreciable nucleophilic solvation, the l/m ratio is 0.76 and, for benzoyl

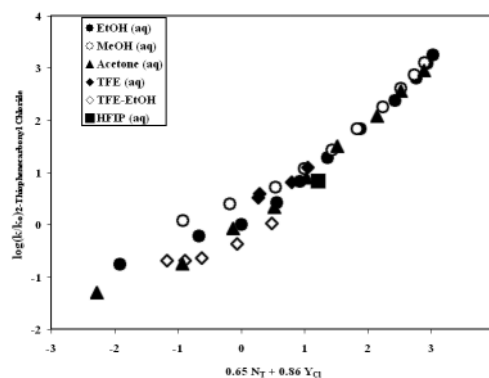


Fig. 1 Plot of $\log(k/k_0)$ for solvolyses of 2-thiophenecarbonyl chloride against $(0.65 N_{\text{T}} + 0.86 Y_{\text{Cl}})$.

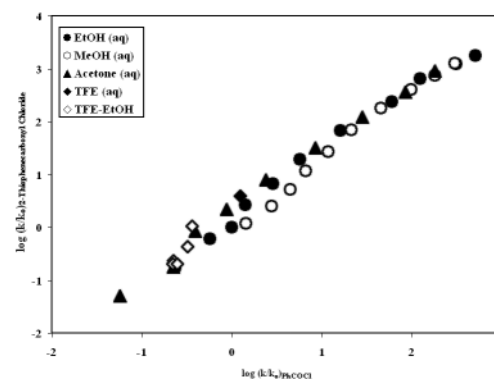


Fig. 2 Plot of $\log(k/k_0)$ for solvolyses of 2-thiophenecarbonyl chloride against $\log(k/k_0)$ for solvolyses of benzoyl chloride.

chloride in its ionisation range, the corresponding value is 0.60. For the overall 40 solvents, the value for the ratio is 0.83 and, for benzoyl chloride in 47 solvents,³ the value is 0.78. Especially over the full range of solvents, the ratios are very similar in value, leading to the near linear plot (Fig. 2). The slope of the plot will then be given by m_Y/m_X (or l_Y/l_X). In this case, these ratios are 1.18 and 1.25, respectively, consistent with the value of 1.21 ± 0.03 obtained directly from the correlation.

Another substrate showing a similar region for the solvent-induced change in mechanism is ethyl chlorothioformate (EtSCOC1). For the full 22 solvents for which specific rates are available,¹⁰ the l/m ratio is 0.58/0.76, or 0.76, again very similar to the value of 0.83 of the present study and a very good linear free energy correlation is obtained, with a slope of 0.94 ± 0.04 and correlation coefficient of 0.9860 for the 16 solvents common to 2-thiophenecarbonyl chloride and ethyl chlorothioformate solvolyses.

Experimental

The 2-thiophenecarbonyl chloride (Aldrich, 97%) was used without further purification. Solvents were purified and the kinetic runs carried out as previously described.⁶ The simple and multiple regression analyses were performed using the ABSTAT statistical package (Anderson-Bell, Arvada, Colorado, USA).

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