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Correlation of the specific rates of solvolysis of trimethylsilylmethyl trifluoromethanesulfonate using a two-term Grunwald–Winstein equation

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The specific rates of solvolysis of trimethylsilylmethyl trifluoromethanesulfonate have been measured at 25.0 °C in ethanol, methanol, and 2,2,2-trifluoroethanol (TFE) and their mixtures with water. Determinations were also made in aqueous acetone and in TFE–ethanol mixtures. An extended (two-term) Grunwald–Winstein equation correlation gave sensitivities towards changes in solvent nucleophilicity and solvent ionising power as expected for an S_N2 pathway, consistent with a previous proposal. For four solvents specific rates were determined at three or four additional temperatures and appreciably negative entropies of activation were observed, consistent with the proposed mechanism. At –20 °C, the specific rate of methanolysis is almost identical to that for methyl trifluoromethanesulfonate, suggesting a fortuitous balance between steric hindrance effects and a favourable electronic effect upon the introduction of the trimethylsilyl group.

Keywords: solvolysis, trimethylsilylmethyl, trifluoromethanesulfonate, Grunwald–Winstein equation

There has been a brief report[1] of the kinetics and products involved in the solvolyses of trimethylsilylmethyl trifluoromethanesulfonate (triflate, **1**). It was found, at –20 °C, that the ethanolysis led only to the unrearranged ethyl trimethylsilylmethyl ether (equation (1)), in contrast to the 92% rearranged product observed[2] in the ethanolysis of neopentyl *p*-toluenesulfonate (tosylate), containing the carbon-for-silicon-substituted alkyl group.

$$(CH_3)_3SiCH_2OTf \xrightarrow{EtOH} (CH_3)_3SiCH_2OEt + EtOH_2^+ + OTf^- \quad (1)$$

The solvolysis of **1** in 97% 2,2,2-trifluoroethanol (TFE), a solvent of low nucleophilicity,[3] was found to be considerably slower than the solvolysis in ethanol or aqueous ethanol. This solvent effect upon the rate, coupled with the absence of rearrangement, was discussed in terms of an S_N2 pathway. Calculations suggested[1] that the S_N2 pathway for solvolysis is favoured for **1**, relative to neopentyl derivatives, because the C–Si bond at the reaction centre is longer than a C–C bond. The reduction of steric crowding at the transition state leads to the barrier to S_N2 reaction being lowered by as much as 20 kcal mol^{-1}.

The previous report[1] also compared the results from correlations using the one-parameter Grunwald–Winstein equation[4,5] (equation (2)). In equation (2), k and k_0 are the specific rates of solvolysis of RX in a given solvent and in the standard solvent (80% ethanol), respectively; m is the sensitivity to changes in solvent ionising power[4] (Y_X for a leaving group X[5]); c is a constant (residual) term.

$$\log (k/k_0)_{RX} = mY_X + c \quad (2)$$

It was concluded, from a consideration of the m values obtained in correlations against either the original Y scale[4] or the Y_{OTs} scale,[5,6] that the observation of lower m values for **1** than for neopentyl triflate (**2**) indicates a higher degree of nucleophilic assistance to the solvolyses of **1**. While this is almost certainly a consideration, one must exercise caution because of the 45 °C difference between the two studies and, especially, because of the different ranges of aqueous-ethanol composition involved in the two studies: 100–90% ethanol for solvolyses of **1** and 80–60% ethanol for solvolyses of **2**. Subsequent studies of the solvolyses of 2-adamantyl triflate have established scales of Y_{OTf} values at 25.0 °C[7] and at –20.0 °C[8] and the two sets of values have been tabulated.[5]

An improved approach toward assessing the extent of nucleophilic participation during solvolyses of **1** is to apply the extended (two-term) Grunwald–Winstein equation,[3,6,9,10] equation (3). In equation (3), the additional term involves the sensitivity l to changes in solvent nucleophilicity (N).

$$\log (k/k_0) = lN + mY_X + c \quad (3)$$

In the present study, we determine specific rates of solvolysis of **1** in a wide variety of solvents and carry out correlation analyses using equation (3), with the incorporation of N_T values[3,10] and of Y_{OTf} values, using the more extensive listing[5,8] based on the measurements made at –20.0 °C.

Results

The specific rates of solvolysis of **1** have been measured at –20.0 °C in ethanol and methanol and in aqueous ethanol, aqueous methanol, and aqueous acetone mixtures with at least 80% (by volume) organic solvent component. At 25.0 °C, increased solubility allowed the range of solvent composition to be extended to 50–60% organic solvent component. Specific rates were also obtained at 25.0 °C in 100–50% TFE (by weight) and over the full range of TFE–ethanol compositions. The specific rates of solvolysis, together with N_T[3,10] and Y_{OTf}[5,8] values, are reported in Table 1.

The specific rates of solvolysis in 100% and 80% ethanol, 100% methanol, and 97% TFE were also measured at three additional temperatures. These values, together with activation parameters calculated using the data at –20.0 °C and 25.0 °C from Table 1 as well, are reported in Table 2.

Discussion

At –20.0 °C and with 20% or more water present in aqueous ethanol or aqueous methanol, solubility problems led to erratic results, both within each run and also from run to run. The eight determinations made at –20.0 °C by sampling and titration of the produced acid include values for 100 and 90% ethanol which are in good agreement with previously reported values.[1] In the previous report, presented only as a preliminary communication, there is no mention of solubility problems. Since we are not told either the concentration of substrate or the technique used to determine the reported specific rates of solvolysis, it is difficult to estimate the possible influence of low solubility and/or low rate of dissolution of substrate upon the reported values. We might mention that, while it is tempting to assume that essentially constant rate coefficient values during a run indicate the absence of solubility problems, Bentley *et al.*[11,12] have shown that it is quite a

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Table 1 Specific rates of solvolysis of trimethylsilylmethyl trifluoromethanesulfonate in several solvents and the corresponding solvent nucleophilicity (N_T) and solvent ionising power (Y_{OTf}) values

	10^3 k/s^{-1} [b]	10^4 k/s^{-1} [b]		
Solvent[a]	(25.0 °C)	(–20.0 °C)	N_T[c]	Y_{OTf}[d]
100% EtOH	20.6 ± 0.2	1.96 ± 0.10[e]	0.37	–1.84
90% EtOH	38.0 ± 0.3	4.23 ± 0.10[f]	0.16	–0.65
80% EtOH	55.8 ± 0.4[g]	(5.35 ± 0.30)[h]	0.00	0.00
70% EtOH	60.9 ± 0.3		–0.20	0.53
60% EtOH	65.3 ± 0.2		–0.39	0.94
50% EtOH	(36.2 ± 0.2)		–0.58	
100% MeOH	34.3 ± 0.3	3.00 ± 0.14	0.17	–0.88
90% MeOH	46.9 ± 0.2	4.33 ± 0.16	–0.01	–0.10
80% MeOH	64.9 ± 0.2	(5.81 ± 0.38)[h]	–0.06	0.71
70% MeOH	73.0 ± 0.4		–0.40	1.26
60% MeOH	(53.5 ± 0.6)[i]		–0.54	2.04
50% MeOH	(25.9 ± 0.3)		–0.75	
90% Acetone	25.1 ± 0.1	3.98 ± 0.10	–0.35	–0.35
80% Acetone	44.1 ± 0.2	6.22 ± 0.22	–0.37	0.24
70% Acetone	58.6 ± 0.2		–0.42	0.78
60% Acetone	71.3 ± 0.2		–0.52	1.30
100% TFE	0.0282 ± 0.0003		–3.93	1.23
97% TFE	0.114 ± 0.001		–3.30	1.36
90% TFE	0.378 ± 0.002		–2.55	1.61
80% TFE	0.984 ± 0.002		–2.19	
70% TFE	1.81 ± 0.01		–1.98	
50% TFE	4.35 ± 0.01		–1.73	
80T–20E[j]	0.437 ± 0.002		–1.76	0.26
60T–40E[j]	1.44 ± 0.01		–0.94	–0.31
40T–60E[j]	3.83 ± 0.03		–0.34	–1.02
20T–80E[j]	8.87 ± 0.05		0.08	–1.48

[a]On a volume–volume basis at 25.0 °C, except for TFE–H_2O mixtures, which are on a weight–weight basis. [b]With associated standard deviations. [c]From ref. 3. [d]From ref. 5. [e]Ref. 1 gives a value of 2.02 ± 0.09 at –20.3 °C. [f]Ref. 1 gives a value of 5.05 ± 0.03 at –20.3 °C. [g]Ref. 1 gives a value (extrapolated from measurements at lower temperatures) of 95.9. [h]Integrated values vary erratically, both within each run and from run to run. [i]Not included in the Grunwald–Winstein equation correlations, due to problems involving substrate solubility and/or rate of entering into solution. [j]T–E solvents are mixtures of 2,2,2-trifluoroethanol (TFE) and ethanol, in the proportions stated.

common occurrence for essentially constant (but erroneous) specific rates of solvolysis to be accompanied by pronounced solubility problems.

The temperature at which the specific rates of solvolysis were measured was increased to 25 °C. The resulting increases in solubility and rate of dissolution allowed a determination, in terms of changes in conductivity, of specific rates in solvents with up to 50% water in combination with TFE, 40% water in combination with ethanol or acetone, and 30% water in combination with methanol. With higher water contents in aqueous ethanol and aqueous methanol, the specific rates, as experimentally determined, showed fairly good precision but the values were lower than anticipated.

The values given in Table 1 were, except where exclusion is indicated, used within an extended Grunwald–Winstein treatment (equation (3)) involving all solvents for which both N_T and Y_{OTf} value are listed. For the 20 data points available, values were obtained of 1.06 ± 0.05 for l, 0.51 ± 0.05 for m, and –0.05 ± 0.05 for c. The multiple correlation coefficient (R) had a value of 0.984, the F-test value was 254, and the standard error of the estimate was 0.20. It is frequently found, especially when steric factors can be important, that the points for TFE–ethanol mixtures lie somewhat below the correlation line.[13] In the present study, the deviations are only minor, but omission of the four points for solvolyses in TFE–ethanol mixtures does lead to a slightly improved correlation. The values for the resultant 16-point correlation are 1.00 ± 0.03 for l, 0.41 ± 0.04 for m, and 0.01 ± 0.04 for c. The goodness-of-fit parameters improve to 0.994 for R, 559 for the F-test value, and 0.13 for the standard error of the estimate. In the Fig. the 16-point correlation is presented and the TFE–ethanol points are added to show their modest deviation from the correlation.

The l value is identical to that (by definition) for the solvolyses of the *S*-methyldibenzothiophenium ion,[10] and essentially identical to that for the solvolyses of methyl tosylate, 0.96 ± 0.04.[14] The m value is similar to but lower than the value of 0.53 ± 0.04 for the solvolyses of methyl

Table 2 Specific rates of solvolysis of trimethylsilylmethyl trifluoromethanesulfonate at various temperatures and the enthalpies ($\Delta H^{\ddagger}$/kcal mol^{-1}) and entropies ($\Delta S^{\ddagger}$/cal mol^{-1} K^{-1}) of activation

	10^3 k, s^{-1}[a]					
Solvent	15.0 °C	35.0 °C	45.0 °C	55.0 °C	$\Delta H^{\ddagger}_{298}$[b]	$\Delta S^{\ddagger}_{298}$[b]
100% EtOH[c,d]	8.01 ± 0.08	40.1 ± 0.2	80.2 ± 0.9		14.3 ± 0.3	–18.2 ± 1.1
80% EtOH[e,f]	21.1 ± 0.1	106 ± 1	216 ± 1		13.3 ± 0.7	–19.6 ± 2.6
100% MeOH[c]	13.2 ± 0.1	63.9 ± 0.6	125 ± 1		14.4 ± 0.4	–16.9 ± 1.5
97% TFE[e,g,h]		0.234 ± 0.002[i]	0.513 ± 0.004	1.12 ± 0.01	14.3 ± 0.5	–28.8 ± 2.0

[a]With associated standard deviations. [b]With associated standard errors. [c]Activations parameters calculated also using values at –20.00 °C and 25.00 °C (Table 1). [d]Literature values (two temperatures) of 13.7 kcal mol^{-1} for $\Delta H^{\ddagger}$ and –23.0 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$ (ref. 1). [e]Activation parameters calculated also using value at 25.00 °C. (Table 1). [f]Volume–volume basis at 25.0 °C. [g]Weight–weight basis. [h]Literature values (two temperatures) of 16.4 kcal mol^{-1} for $\Delta H^{\ddagger}$ and –24.4 cal mol^{-1} K^{-1} for $\Delta S^{\ddagger}$ (ref. 1.) [i]Ref. 1 gives a value of 0.183 ± 0.004.

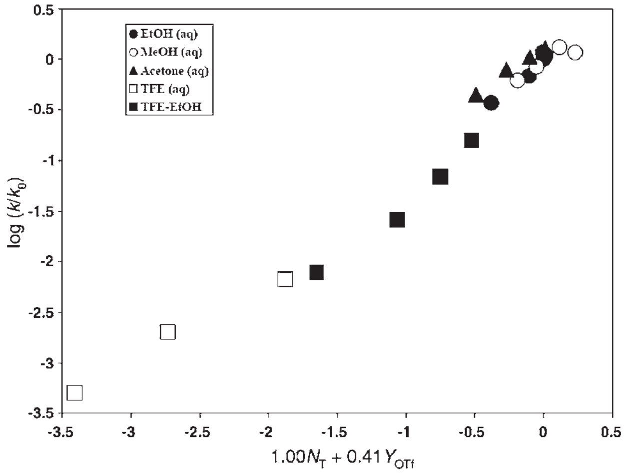

Fig.1 Plot of log (k/k_0) for solvolyses of trimethylsilylmethyl trifluoromethanesulfonate at 25.0 °C against ($1.00\ N_T + 0.41 Y_{OTf}$). The four points (filled squares) for TFE–ethanol mixtures are not included in the correlation; they are added to the figure to show the magnitude of their deviation from the plot.

tosylate.[14] The decrease in the m value might be associated, in part, with different Y_X scales being used in the two correlations, with a better internal dispersion of negative charge in a leaving triflate ion relative to that in a leaving tosylate ion, leading to a reduced demand for charge dispersion into the solvating molecules. The l and m values are typical for an S_N2 mechanism. This operates across the full range of the studied solvents, and strong support is given to the conclusions of the earlier study.[1] The modest activation energies and rather large negative entropies of activation (Table 2) are consistent with the proposed mechanism.[15]

Differences are observed between our directly measured values at 25.0 °C and the values which have been obtained by extrapolation (presumably using unreported values at –20.3 °C and –10.2 °C, although this is not explicitly stated) for the solvolyses in 80% and 60% ethanol. The extrapolated values[1] of 9.59×10^{-2} s^{-1} in 80% ethanol and 0.214 in 60% ethanol are 72% and 228% higher, respectively, than our values. Although *directly determined* values tend to be lower in the presence of solubility problems, the higher *extrapolated* values can be easily rationalised. In the measurements at reduced temperatures,[1] the lower the temperature the more severe will be both solubility problems and the concomitant lowering of the apparent specific rate value. In Arrhenius-plot extrapolations to get specific rates at higher temperatures, the resulting influence on the slope will lead, other than for very modest extrapolations, to erroneously high values. Since solubility problems are shown (Table 1) to appear, and then become more severe, as increasing amounts of water are added to the organic component, the much larger discrepancy between the directly measured and the extrapolated values in 60% ethanol than in 80% ethanol is as expected.

It is possible, for methanolysis, to study the influence on the specific rate of the introduction of the trimethylsilyl group. The specific rate of methanolysis of methyl triflate was determined[16] at 0.3 °C and at –23.4 °C, allowing the estimation of a value of 3.66×10^{-4} s^{-1} at –20.0 °C. This value is remarkably similar to the value (Table 1) of 3.00×10^{-4} s^{-1} at this temperature for trimethylsilylmethyl triflate. Since the trimethylsilyl group will give an appreciable steric hindrance relative to hydrogen, it appears that this must be counterbalanced by favourable electronic effects. Such an electronic effect is consistent with calculations which show that, for hydride exchange reaction at carbon, there is a dramatic lowering of the energy barrier on changing the substrate from methane or ethane to methylsilane.[1]

In conclusion, the specific rates of solvolysis of trimethylsilylmethyl triflate (**1**) correlate very well (equation (3)) with a combination of solvent nucleophilicity and ionising power values, with the l and m values strongly indicating an S_N2 reaction. For methanolysis at –20.0 °C, the specific rate of solvolysis is almost identical to that for methyl triflate. Even at ambient temperatures, the available range of water content within binary mixtures is severely limited by a low solubility and/or a low rate of dissolution of **1**.

Experimental

The trimethylsilylmethyl trifluoromethanesulfonate (Aldrich, 99%) was used without further purification. Solvents were purified and the titrimetric runs (those at –20 °C) carried out as previously described.[10] The procedure for following the extent of solvolysis conductometrically has also been reported previously.[17] The 5×10^{-3} M solution in 25 ml of solvent required the introduction of 25 μL of the substrate.

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