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# Rate and product studies in the solvolyses of methanesulfonic anhydride and a comparison with methanesulfonyl chloride solvolyses†

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ABSTRACT: The specific rates of solvolysis of methanesulfonic anhydride have been measured conductometrically at $-10\,^{\circ}$C in 41 solvents. Use of the extended Grunwald–Winstein equation, with the $N_T$ scale of solvent nucleophilicity and the $Y_{OTs}$ scale of solvent ionizing power, leads to sensitivity to changes in solvent nucleophilicity ($\ell$ value) of 0.95 and a sensitivity to changes in solvent ionizing power ($m$ value) of 0.61, with a multiple correlation coefficient ($R$) of 0.973. Product selectivity values ($S$) in binary hydroxylic solvents favor alcohol attack in EtOH–$H_2O$ (a value of 1.2 in 90% EtOH rising to 4.0 in 40% EtOH) and in MeOH–$H_2O$ (a value of 3.7 in 90% MeOH rising to 6.0 in 50% MeOH). In 2,2,2,-trifluoroethanol–$H_2O$, the $S$ values are much lower at about 0.1. Entropy of activation values are appreciably negative. Literature values for the specific rates of solvolysis of methanesulfonyl chloride have been extended to fluoroalcohol-containing solvents (titrimetric method) and, at 45.0 °C, for an overall 43 solvents values are obtained (using $N_T$ and $Y_{Cl}$ scales) of 1.20 for $\ell$ and of 0.52 for $m$ ($R = 0.969$). It is proposed that both substrates solvolyze by an $S_N2$ pathway. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: methanesulfonic anhydride; methanesulfonyl chloride; solvolysis; extended Grunwald–Winstein equation; product selectivity; $S_N2$ mechanism

## INTRODUCTION

While there have been an appreciable number of kinetic studies of the solvolyses of sulfonyl chlorides,[1–3] there have been only a few of the solvolyses of the closely related sulfonic anhydrides. Christensen[4] studied the hydrolyses of the parent and several ring-substituted benzenesulfonic anhydrides in aqueous acetone and aqueous dioxane. It was concluded that the solvolyses were $S_N2$ in character across the full ranges of solvent composition. The rather fast reactions were followed by a stopped flow technique. The specific rates of reaction were 100- to 400-fold higher than for corresponding solvolyses of arenesulfonyl chlorides and this was found to be primarily associated with a less negative entropy of activation.

Studies[5] of the kinetic solvent isotope effect (KSIE) for the $m$-$NO_2$, $p$-Br, and $p$-Me derivatives led, at 25.0 °C, to $k_{H_2O}/k_{D_2O}$ values of 1.2–1.35. These values were appreciably lower than values of 1.5–1.75, which had previously been reported for arene- and alkanesulfonyl chlorides in water[6] and for alkanesulfonyl chlorides in aqueous acetone[7] or aqueous tetrahydrofuran.[7] It was concluded that the KSIE value was not likely to be of much help in establishing mechanism because for earlier studied systems,[6,8] it had been found to be essentially independent of the detailed mechanism. Rather weak evidence based on changes in the $m$ value, obtained from a simple (one-term) Grunwald–Winstein equation[9] Eqn (1) treatment, at high water

$$\log\frac{k}{k_0} = mY + c$$

content was presented for a change to an ionization ($S_N1$) pathway for the solvolyses of the $p$-methyl derivative ($p$-toluenesulfonic anhydride). In Eqn (1), $k$ and $k_o$ represent the specific rates of solvolysis of the substrate in the solvent under consideration and in the standard solvent (80% ethanol), $m$ is the sensitivity towards changes in solvent ionizing power $Y$ (originally obtained using *tert*-butyl chloride as the standard substrate), and $c$ is a constant (residual) term.

Laird and Spence[10–12] have studied the solvolyses of cyclic and acyclic[12] sulfonic anhydrides in alcohols

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(containing 6.7% ether) and in aqueous-dioxane mixtures containing at least 80% dioxane. A study of solvolyses of methanesulfonic anhydride [$(CH_3SO_2)_2O$, **1**] in the 270–280 K temperature range was included.[12]

In the present investigation, we study the kinetics of solvolysis of **1** in a wide range of solvents, including 2,2,2-trifluoroethanol (TFE) and its mixtures with water and ethanol and aqueous-1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) solvents. Determinations of specific rates at several temperatures, for nine of the solvents, allow calculation of the activation parameters. Product selectivities, involving competition between attack by water or alcohol, are determined for binary mixtures of water with ethanol, methanol, or TFE.

There has been a kinetic study of the solvolyses of methanesulfonyl chloride ($CH_3SO_2C1$, **2**) in mixtures of water with ethanol, methanol, or acetone.[13] We add measurements of the specific rates of solvolysis in TFE–water, HFIP–water, and TFE–ethanol, so that using the combined values a meaningful extended Grunwald–Winstein treatment [Eqn (2)] can be carried out. In Eqn

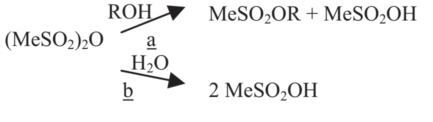
$$\log k/k_0 = \ell N + mY + c \tag{2}$$

(2), for the additional [relative to Eqn (1)] term, the $\ell$ value represents the sensitivity to changes in solvent nucleophilicity (*N*). The $\ell$ and *m* values obtained are compared to those obtained for **1**.

## RESULTS

The specific rates of solvolysis of **1** were determined in 41 solvents at −10.0 °C. The solvents consisted of ethanol and methanol, binary mixtures of TFE with ethanol, and binary mixtures of water with ethanol, methanol, acetone, TFE, and HFIP. The specific rates of solvolysis are reported in Table 1, together with solvent nucleophilicity ($N_T$) values[14,15] and solvent ionizing power ($Y_{OTs}$) values.[16,17] Specific rates measured at other temperatures are reported in Table 2, together with enthalpies and entropies of activation, calculated at 10.0 °C using the data of Table 2 together with, when available, the value at −10.0 °C from Table 1. For six solvents, a value was not directly measured at −10.0 °C and this value could be estimated using the Arrhenius equation; these estimated values are inserted into Table 1 and used within the correlation analysis.

The product ratios in aqueous-alcohol solvents can be arrived at by titration of the acid produced at 10, 15, and 20 half lives. All measurements were in duplicate and since no trends were observed, the six values were averaged. The reaction scheme can be expressed as in Eqn (3).



$$(MeSO_2)_2O \begin{cases} \xrightarrow[\underline{a}]{ROH} MeSO_2OR + MeSO_2OH \\ \xrightarrow[\underline{b}]{H_2O} 2\ MeSO_2OH \end{cases} \tag{3}$$

The percentage of reaction following pathway $\underline{a}$ can be estimated by comparing the observed acid titer with that for reaction in 100% ethanol (all pathway $\underline{a}$) and that for reaction in 60% acetone (all pathway $\underline{b}$).[18,19] The percentages of acid formation resulting from ester formation (Table 3) can then be used to calculate Eqn (4)] the product selectivity values (*S*) for an AX substrate. The calculated

$$S = \frac{[AOR]_{prod} \cdot [H_2O]_{solvent}}{[AOH]_{prod} \cdot [ROH]_{solvent}} \tag{4}$$

*S* values are also in Table 3, where they are compared to some earlier values for solvolyses of arenesulfonyl chlorides.[2e,2h]

The specific rates of solvolysis of **2** have been determined in 13 fluoroalcohol-containing solvents at 45.0 °C. These can be combined with a value for 90% acetone and with literature values at 45.0 °C for 29 other solvents. The literature values at 25.0, 35.0, and 45.0 °C were extrapolated (Arrhenius equation) to give values at −10.0 °C for comparison with those for **1**. These $k_{OMs}/\mathrm{k}_{C1}$ values are listed in Table 1. In some instances, values from Table 2 were extrapolated (or interpolated) to get values for solvolysis of **1** at 45.0 °C. Combination with specific rates from Table 4 leads to additional $k_{OMs}/\mathrm{k}_{C1}$ values.

## DISCUSSION

Anhydride **1** is usually named as methanesulfonic anhydride but an alternative naming as methanesulfonyl methanesulfonate (mesylate) shows better the relationship to methanesulfonyl chloride (**2**). In this manuscript we have throughout used experimental specific rates but in a comparison with **2**, or other substrates with only one reactive site, there should be a statistical correction for the presence of two equivalent sites at which reaction can occur in **1**. Accordingly, in a comparison of reactivities at the sulfur atom of **1** or **2**, the $k_{OMs}/\mathrm{k}_{C1}$ ratios (Table 1) should, for a rigid comparison of the leaving-group effect for loss of mesylate or chloride, be halved.

In the extended Grunwald–Winstein treatment [Eqn (2)] of the specific rates of solvolysis of **1**, ideally the $N_T$ solvent nucleophilicity values should be combined with $Y_{OMs}$ solvent ionizing power values for a mesylate leaving group (based on solvolyses of adamantyl mesylates). These values are available[17,20] but only for a limited number of the solvents used in this investigation. A more comprehensive determination has been made of $Y_{OTs}$ values [based on the solvolyses of adamantyl *p*-toluenesulfonates (tosylates)]. The $Y_{OTs}$ values are available for all of the solvents studied except 65% acetone and that value is readily obtained by interpolation (Table 1). For solvents where the specific rates of solvolysis of an adamantyl derivative have been determined with both mesylate and tosylate as leaving

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**Table 1.** Specific rates of solvolysis ($k_{OMs}$) of methanesulfonic anhydride (**1**)[a] at −10.0 °C, the $N_T$ and $Y_{OTs}$ values for the solvents, and mesylate/chloride rate ratios

| Solvent[b] | $10^4 k_{OMs}$/s$^{-1}$[c] | $n$[d] | $N_T$[e] | $Y_{OTs}$[f] | $10^3 k_{OMs}/k_{C1}$[g] | |
|---|---|---|---|---|---|---|
| 100% EtOH | 4.92 ± 0.08 | 2 | 0.37 | −1.95 | 0.75[h] | (1.5) |
| 90% EtOH | 21.4 ± 1.5 | 3 | 0.16 | −0.77 | 2.4 | |
| 80% EtOH | 40.9 ± 0.9 | 3 | 0.00 | 0.00 | 2.5 | (1.8) |
| 70% EtOH | 65.8 ± 1.4 | 3 | −0.20 | 0.47 | 3.2 | |
| 60% EtOH | 85.8 ± 1.6 | 2 | −0.38 | 0.92 | 3.0 | |
| 50% EtOH[i] | 103 ± 6 | 4 | −0.58 | 1.29 | 2.7 | |
| 40% EtOH[i] | 152 ± 3 | 3 | −0.74 | 1.97 | 3.3 | |
| 30% EtOH[i] | 170 ± 5 | 5 | −0.93 | 2.84 | 3.5 | |
| 20% EtOH[i] | 158 ± 11 | 6 | −1.16 | 3.32 | 3.7 | |
| 100% MeOH | 11.1 ± 0.1[k] | 3 | 0.17 | −0.92 | 2.2 | (1.2) |
| 90% MeOH | 31.4 ± 0.7 | 4 | −0.01 | −0.05 | 2.5 | |
| 80% MeOH | 61.2 ± 0.3 | 4 | −0.06 | 0.47 | 2.6 | |
| 70% MeOH | 96.5 ± 0.3 | 5 | −0.40 | 1.02 | 2.5 | |
| 60% MeOH | 123 ± 6 | 3 | −0.54 | 1.52 | 2.6 | |
| 50% MeOH[i] | 154 ± 3 | 5 | −0.57 | 2.00 | 3.2 | |
| 40% MeOH[i] | 163 ± 7 | 5 | −0.87 | 2.43 | 3.1 | |
| 30% MeOH[j] | 171 ± 5 | 3 | −1.06 | 2.97 | 4.2 | |
| 20% MeOH[j] | 154 ± 7 | 6 | −1.23 | 3.39 | 4.4 | |
| 90% Acetone | 0.704 ± 0.002 | 1 | −0.35 | −1.99 | | |
| 80% Acetone | 2.48 ± 0.01 | 1 | −0.37 | −0.94 | 0.27 | |
| 70% Acetone | 6.57 ± 0.11 | 3 | −0.42 | 0.07 | 0.32 | |
| 65% Acetone | 9.30 ± 0.06 | 1 | −0.48 | 0.36[ℓ] | | |
| 60% Acetone | 13.2 ± 0.1 | 3 | −0.52 | 0.66 | 0.72 | |
| 50% Acetone | 23.7 ± 0.9 | 3 | −0.70 | 1.26 | 0.73 | |
| 40% Acetone[i] | 48.4 ± 2.2 | 4 | −0.83 | 1.85 | 1.7 | |
| 30% Acetone[i] | 82.4 ± 1.4 | 5 | −0.96 | 2.50 | 2.1 | |
| 100% TFE[m] | 0.0295[j] | | −3.93 | 1.77 | | |
| 97% TFE[m,n] | 0.284[j] | | −3.30 | 1.83 | | (3.7) |
| 90% TFE[n] | 1.03 ± 0.01 | 1 | −2.55 | 1.90 | | |
| 80% TFE[n] | 30.8 ± 0.1 | 1 | −2.19 | 1.94 | | |
| 70% TFE[n] | 65.1 ± 0.1 | 1 | −1.98 | 2.00 | | |
| 97% HFIP[m,n] | 0.0358[j] | | −5.26 | 3.61 | | (7.1) |
| 90% HFIP[m,n] | 0.514[j] | | −3.84 | 2.90 | | (14.1) |
| 70% HFIP[m,n] | 4.19[j] | | −2.94 | 2.40 | | (1.7) |
| 50% HFIP[m,n] | 12.5[j] | | −2.63 | 2.26 | | (1.2) |
| 90T-10E[o] | 1.33 ± 0.03 | 2 | −2.62 | 1.32 | | |
| 80T-20E[o] | 2.27 ± 0.01 | 1 | −1.76 | 0.98 | | |
| 60T-40E[o] | 7.37 ± 0.02 | 1 | −0.94 | 0.21 | | |
| 50T-50E[o] | 8.00 ± 0.02 | 2 | −0.64 | 0.14 | | |
| 40T-60E[o] | 8.87 ± 0.04 | 3 | −0.34 | −0.44 | | |
| 20T-80E[o] | 8.10 ± 0.20 | 3 | 0.08 | −1.18 | | |

[a] Substrate concentration of $2.8 \times 10^{-4}$ M.
[b] Unless otherwise indicated, the binary solvents are on a v/v basis at 25.0 °C, with the other component being water (each solvent also contains 0.2% of $CH_3CN$).
[c] With associated standard deviations.
[d] Number of determinations.
[e] From Refs 14 and 15.
[f] From Refs 16 and 17.
[g] Values for $MeSO_2C1$ solvolysis by Arrhenius extrapolation of values (Ref. 13) at higher temperatures. Ratios in parentheses are using the $MeSO_2C1$ value at 45.0 °C (Ref. 13) coupled with an extrapolated value for $(MeSO_2)_2O$ using the data of Table 2.
[h] Extrapolation of the $MeSO_2C1$ values was using a plot with a relatively low correlation coefficient (−0.9956).
[i] Substrate concentration of $5 \times 10^{-5}$ M.
[j] Substrate concentration of $3 \times 10^{-5}$ M.
[k] Also a value of 8.20 ± 0.04 in methanol-d (MeOD) for a $k_{MeOH}/k_{MeOD}$ value of 1.35 ± 0.02.
[l] Obtained by interpolation.
[m] Obtained by extrapolation (Arrhenius plot) of values at higher temperatures.
[n] On a w/w basis.
[o] T-E are TFE–ethanol mixtures.

group, the specific rate ratio $k_{OTs}/k_{OMs}$ varies only from 0.5 to 2.1,[16b.,17] indicating that use of $Y_{OTs}$ values will not lead to any appreciable perturbations. The extended Grunwald–Winstein treatment of **2** uses readily available[17,21] $Y_{C1}$ values in conjunction with the $N_T$ values. The sensitivity values, residual values, and goodness-of-fit parameters from correlations with **1** and **2** as substrates are listed in Table 5 together with earlier values for

**Table 2.** Specific rates of solvolysis of methanesulfonic anhydride[a] at various temperatures and the enthalpies ($\Delta H^{\neq}$/kcal mol$^{-1}$) and entropies ($\Delta S^{\neq}$/cal mol$^{-1}$ K$^{-1}$) of activation

| Solvent[b] | $T$, °C | $10^4 k_{\mathrm{OMs}}$/s$^{-1}$ [c] | $n$[d] | $\Delta H^{\neq}_{283.2}$[e] | $\Delta S^{\neq}_{283.2}$[e] |
|---|---|---|---|---|---|
| 100% EtOH | 0.0 | 15.6 ± 0.1 | 1 | | |
| | 10.0 | 42.7 ± 0.6 | 2 | | |
| | 20.0 | 112 ± 1 | 2 | 15.4 ± 0.1[f] | −14.9 ± 0.4[f] |
| 80% EtOH | −20.0 | 12.5 ± 0.6 | 3 | | |
| | 0.0 | 123 ± 6 | 3 | | |
| | 10.0 | 326 ± 7 | 1 | 14.9 ± 0.1 | −12.3 ± 0.4 |
| 100% MeOH | −20.0 | 3.31 ± 0.04 | 2 | | |
| | 0.0 | 34.3 ± 0.1 | 3 | | |
| | 10.0 | 93.9 ± 0.6 | 3 | 15.3 ± 0.1[g] | −13.4 ± 0.4[g] |
| 100% TFE | 10.0 | 0.207 ± 0.02 | 1 | | |
| | 30.0 | 1.23 ± 0.01 | 1 | | |
| | 50.0 | 5.13 ± 0.02 | 1 | 14.0 ± 0.4 | −30.4 ± 1.4 |
| 97% TFE | 0.0 | 0.663 ± 0.001 | 1 | | |
| | 10.0 | 1.72 ± 0.01 | 1 | | |
| | 20.0 | 4.04 ± 0.02 | 2 | | |
| | 30.0 | 7.98 ± 0.07 | 1 | | |
| | 50.0 | 28.7 ± 0.6 | 1 | 12.6 ± 0.3 | −32.6 ± 1.1 |
| 97% HFIP | 10.0 | 0.292 ± 0.001 | 1 | | |
| | 30.0 | 1.39 ± 0.01 | 1 | | |
| | 50.0 | 5.52 ± 0.02 | 1 | 12.8 ± 0.1 | −34.0 ± 0.2 |
| 90% HFIP | 0.0 | 1.57 ± 0.01 | 1 | | |
| | 10.0 | 4.55 ± 0.01 | 1 | | |
| | 20.0 | 11.8 ± 0.1 | 1 | 15.5 ± 0.2 | −19.1 ± 0. 7 |
| 70% HFIP | 0.0 | 12.5 ± 0.1 | 1 | | |
| | 10.0 | 33.5 ± 0.1 | 1 | | |
| | 20.0 | 87.5 ± 0.3 | 2 | 14.9 ± 0.2 | −17.1 ± 0. 7 |
| 50% HFIP | 0.0 | 36.0 ± 0.1 | 1 | | |
| | 10.0 | 97.6 ± 0.2 | 1 | | |
| | 20.0 | 245 ± 1 | 1 | 14.7 ± 0.1 | −15.8 ± 0.2 |

[a] Substrate concentration of $3 \times 10^{-3}$ M.

[b] 80% EtOH on v/v basis at 25.0 °C and aqueous-fluoroalcohol solvents on w/w basis.

[c] With associated standard deviations.

[d] Number of determinations.

[e] With associated standard errors.

[f] Ref. 12 gives values at 248.2 K (after conversion from E and $\log_{10}A$) of 15.7 kcal mol$^{-1}$ for $\Delta H^{\neq}$ and −13.6 cal mol$^{-1}$ K$^{-1}$ for $\Delta S^{\neq}$ in a solvent consisting of 93.3% EtOH and 6.7% ether.

[g] Ref. 12 gives values at 248.2 K (after conversion from E and $\log_{10}A$) of 14.6 kcal mol$^{-1}$ for $\Delta H^{\neq}$ and −17.3 cal mol$^{-1}$ K$^{-1}$ for $\Delta S^{\neq}$ in a solvent consisting of 93.3% MeOH and 6.7% ether.

solvolyses of arene- and alkanesulfonyl chlorides. The plots of correlations of the specific rates of solvolysis of **1** and **2** are shown in Figs 1 and 2.

The correlation of the specific rates of solvolysis of **2** leads to $\ell$ and $m$ values very similar to those observed previously for the solvolyses of *N*,*N*-dimethylsulfamoyl chloride,[3] 2-propanesulfonyl chloride,[3] and two arenesulfonyl chlorides.[21] As is often the case, discussed elsewhere,[18b] a better correlation is obtained when the specific rates of solvolysis in TFE–ethanol mixtures are omitted. The goodness-of-fit parameters ($R$ and $F$) are also very similar. For the correlation of the specific rates of solvolysis of the anhydride **1**, the $m$ value and the goodness-of-fit parameters are similar to those for **2** and the earlier studied substrates. The $\ell$ value is, however, lower than in the other correlations. This could be a consequence of the mesylate leaving group being appreciably better than chloride, leading to a looser transition state with, in particular, reduced bonding to the attacking nucleophile.

The last column of Table 1 presents the $k_{\mathrm{OMs}}/k_{\mathrm{Cl}}$ ratios, mainly estimated at −10.0 °C but with a few (in parentheses) estimated at 45.0 °C. For solvolyses in aqueous ethanol and aqueous methanol, the values for the ratio at −10.0 °C are in the range of 2200–4400 and those values at 45.0 °C are somewhat lower. The value at −10.0 °C of 750 in ethanol is suspect because of an inferior Arrhenius plot for the literature data[13] for ethanolyses of **2**. Lower values of 270–2100 are observed at −10.0 °C in aqueous acetone. For the three binary systems discussed above, the $k_{\mathrm{OMs}}/k_{\mathrm{Cl}}$ value increased with increasing water content of the solvent. Somewhat higher values were observed, at 45.0 °C for solvolyses in 97% TFE and four aqueous-HFIP solvents (1200–14100).

Literature values exist for the $\mathrm{S_N2}$ reactions in ethanol at 25.0 °C of anionic nucleophiles with alkyl tosylates and chlorides.[22] The *n*-propyl derivatives react with *p*-methylthiophenoxide[23] with a $k_{\mathrm{OTs}}/k_{\mathrm{Cl}}$ ratio of 60 and the ethyl derivatives react with ethoxide ion with a value of about 1500. The values are consistent with attack by

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**Table 3.** Selectivity values ($S$)[a] for solvolyses at −10.0 °C of methanesulfonic anhydride (**1**) in binary mixtures of water with ethanol, methanol, or 2,2,2-trifluoroethanol, and a comparison with solvolyses of *p*-methoxy-and *p*-nitrobenzene sulfonyl chlorides

| Solvent[b] | % Ester ($CH_3SO_2OR$) | $S$ | $S_{p\text{-MeO}}$[c] | $S_{p-NO_2}$[d] |
|---|---|---|---|---|
| 90% EtOH | 76.1 | 1.2 | 1.6 | 0.40 |
| 80% EtOH | 71.0 | 2.0 | 2.3 | 0.68 |
| 70% EtOH | 60.0 | 2.1 | | 0.94 |
| 60% EtOH | 57.5 | 2.9 | 3.8 | 1.2 |
| 50% EtOH | 50.3 | 3.3 | 3.9 | 1.5 |
| 40% EtOH | 44.9 | 4.0 | 4.2 | 1.7 |
| 90% MeOH | 93.7 | 3.7 | 2.5 | 0.88 |
| 80% MeOH | 86.8 | 3.7 | 4.2 | 1.2 |
| 70% MeOH | 81.2 | 4.2 | | 1.6 |
| 60% MeOH | 79.4 | 5.8 | 4.4 | 1.9 |
| 50% MeOH | 72.8 | 6.0 | | 2.3 |
| 40% MeOH | 62.3 | 5.1 | 6.0 | 2.6 |
| 90% TFE | 8.3 | 0.06[e] | | |
| 80% TFE | 7.9 | 0.12[e] | | |

[a] As defined in Eqn (4).

[b] Aqueous ethanol and methanol on v/v basis at 25.0 °C and aqueous TFE on w/w basis.

[c] Values from Ref. 2e.

[d] Values from Ref. 2h.

[e] Ref. 3 gives values of 0.14 and 0.15 in 90% and 70% TFE for the solvolyses of $Me_2NSO_2C1$.

the weaker nucleophile leading to a looser transition state and a larger degree of bond breaking to the leaving group.[22,24] Neutral hydroxylic molecules (water or alcohol) will be even weaker nucleophiles and the larger ratios observed in this study are consistent with the values previously obtained for $S_N2$ attack at carbon. For $S_N1$ solvolyses of adamantyl compounds,[22,25] the $k_{OTs}/k_{C1}$ ratio is about $2 \times 10^5$, at least an order of magnitude higher than the values obtained in this study. As discussed earlier, $k_{OMs}/k_{OTs}$ values are close to unity[16b,,17] and $k_{OTs}/k_{C1}$ values will not be far removed from the corresponding $k_{OMs}/k_{Cl}$ ratios.

The activation parameters for solvolyses of **1** are unremarkable (Table 2). The entropies of activation of from −34 to −12 cal mol$^{-1}$ K$^{-1}$ are consistent with the bimolecular pathway indicated by the magnitudes of the $\ell$ and $m$ values (Table 5).

The KSIE for solvolyses of **1** in either methanol or methanol-d was, at −10 °C, of value 1.35 + 0.02. This is considerably lower than for methanolyses of **2**, which gave values of 1.62 at 25.0 °C and 1.51 at 35.0 °C[13]. A similar lowering effect was observed in the hydrolyses of arenesulfonic anhydrides, where values of 1.2–1.35 were less than the values for the hydrolyses of the corresponding chlorides (1.5–1.75).[5–7] This would suggest, consistent with the lower $\ell$ value, that bond formation to the attacking nucleophile is less advanced for attack on sulfonic anhydrides than on sulfonyl chlorides. For reactions with extensive bond formation, such as alcoholyses of chloroformate esters, KSIE values in the range of 2.1–2.5 have been observed.[26,27]

The product studies for solvolyses of **1** lead to selectivity values ($S$) of the same order of magnitude as those previously obtained for several reactions of sulfonyl chlorides (Table 3). In comparisons with *p*-methoxy-[2e] and *p*-nitrobenzene[2h]sulfonyl chlorides, the values closely resemble those for the *p*-methoxy-derivative, including the tendency for the $S$ value to rise as the water content of ethanol–water or methanol–water mixtures is increased. At high alcohol content, the values are also similar to those for *N*,*N*-dimethylsulfamoyl chloride[3] but the latter compound shows very little variation in $S$ value as the water content is increased. The very low values for $S$ in aqueous-TFE mixtures are consistent with the low nucleophilicity of the TFE component, very similar values were observed in

**Table 4.** Specific rates of solvolysis ($k_{C1}$) of methanesulfonyl chloride (**2**)[a] at 45.0 °C

| Solvent[b] | $10^6 k_{C1}/s^{-1c}$ | Solvent[b] | $10^6 k_{C1}/s^{-1c}$ |
|---|---|---|---|
| 80% EtOH | $264 \pm 13^{d,e}$ | 97% HFIP | $0.056 \pm 0.011^{f}$ |
| 90% Acetone | $15.5 \pm 0.8$ | 90% HFIP | $0.736 \pm 0.028$ |
| 97% TFE | $0.596 \pm 0.052$ | 70% HFIP | $40.6 \pm 0.8$ |
| 90% TFE | $3.86 \pm 0.22$ | 50% HFIP | $166 \pm 5$ |
| 80% TFE | $25.3 \pm 0.9$ | 80T-20E[g] | $4.89 \pm 0.26$ |
| 70% TFE | $62.8 \pm 1.5$ | 60T-40E[g] | $17.6 \pm 1.1$ |
| 50% TFE | $198 \pm 8$ | 50T-50E[g] | $31.3 \pm 1.1$ |
| | | 20T-80E[g] | $48.8 \pm 1.5^{h}$ |

[a] Substrate concentration of $5 \times 10^{-3}$ M.

[b] Aqueous-fluoroalcohol solvents on w/w basis (nine solvents) and others (six solvents) on v/v basis at 25.0 °C.

[c] With associated standard deviations and average of integrated first-order rate coefficients from duplicate runs.

[d] Calculated using a Guggenheim treatment of the data (see Experimental Section).

[e] Also a value of 138 ± 7 at 35.0 °C.

[f] Using an estimated value for the infinity titer.

[g] T-E are TFE–ethanol mixtures.

[h] Also a value of 20.0 ± 0.9 at 35.0 °C.

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**Table 5.** Coefficients from extended Grunwald–Winstein treatments [Eqn (2)] of the solvolyses of methanesulfonic anhydride (**1**) and methanesulfonyl chloride (**2**) and a comparison with coefficients from previous correlations involving solvolyses with displacement at sulfur

| Substrate | $n$[a] | $\ell$[b] | $m$[b] | $c$[b] | $R$[c] | $F$[d] |
|---|---|---|---|---|---|---|
| **1** | 41 | 0.95 ± 0.04 | 0.61 ± 0.03 | −0.10 ± 0.05 | 0.973 | 342 |
| **2** | 43 | 1.20 ± 0.05 | 0.52 ± 0.03 | 0.15 ± 0.06 | 0.969 | 310 |
|  | 39[e] | 1.17 ± 0.04 | 0.49 ± 0.02 | 0.23 ± 0.05 | 0.981 | 454 |
| $(CH_3)_2NSO_2Cl$[f] | 32 | 1.20 ± 0.04 | 0.72 ± 0.03 | 0.11 ± 0.04 | 0.985 | 478 |
| $(CH_3)_2CHSO_2Cl$[f] | 19[e] | 1.28 ± 0.05 | 0.64 ± 0.03 | 0.18 ± 0.06 | 0.988 | 333 |
| *p*-$MeC_6H_4SO_2Cl$[g] | 33 | 1.25 ± 0.15 | 0.62 ± 0.04 | 0.21 ± 0.20[h] | 0.967 | 216 |
| *p*-$MeOC_6H_4SO_2Cl$[g] | 37 | 1.10 ± 0.17 | 0.61 ± 0.04 | 0.22 ± 0.23[h] | 0.959 | 194 |

[a] Number of data points.
[b] With associated standard errors.
[c] Multiple correlation coefficient.
[d] *F*-test value.
[e] With the four T-E solvents removed.
[f] Values from Ref. 3.
[g] Values from Ref. 21.
[h] Associated with the standard error of the estimate.

the solvolyses of *N*,*N*-dimethylsulfamoyl chloride.[3] The change in leaving-group from chloride to methanesulfonate does not appreciably influence the product ratio for attack by alcohol or water in a given binary mixture.

## CONCLUDING REMARKS

Although the solvolyses of **1** proceed, in most solvents, over 1000 times faster than those of **2**, there are only modest changes in sensitivities towards changes in solvent nucleophilicity and solvent ionizing power and in the methanolysis KSIE values. Product selectivity values in alcohol–water mixtures are also similar to those for earlier studied sulfonyl chlorides. The most obvious differences are in a lower $\ell$ value for solvolyses of **1** and a somewhat lower KSIE for solvolyses in methanol and methanol-d. These changes can be rationalized in terms of the better mesylate leaving group leading to a looser transition state for the solvolyses of **1** relative to those for solvolyses of **2** and earlier studied sulfonyl chlorides. Care must be exercised in comparing *m* values since the $Y_{OTs}$ scale values cover a narrower range than the $Y_{Cl}$ values (a variation of 7.6 units for $Y_{Cl}$, but only 5.6 units for $Y_{OTs}$ in going from 100% ethanol to 97% HFIP).[17]

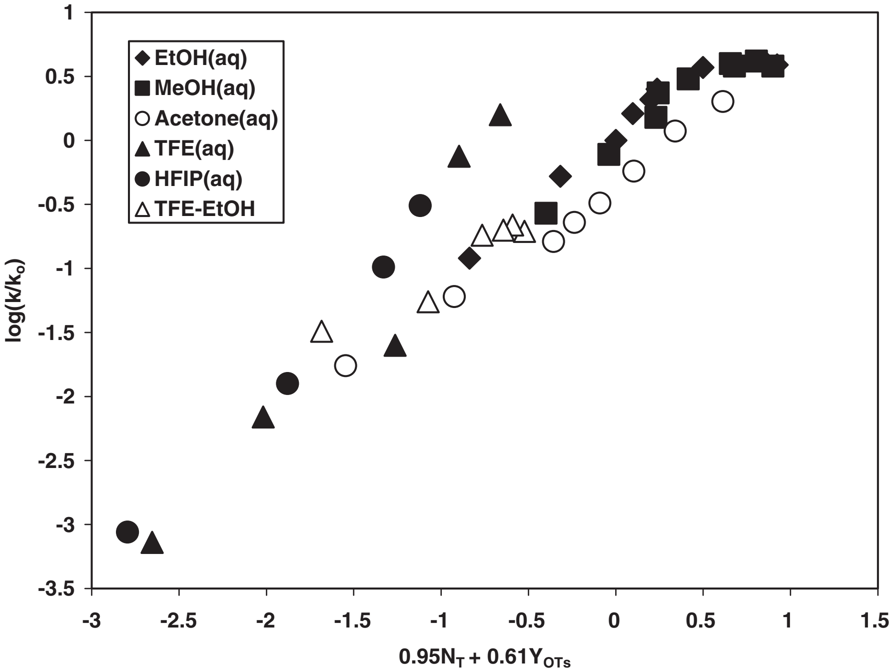

**Figure 1.** Plot of $\log(k/k_0)$ for solvolyses of methanesulfonic anhydride at −10.0 °C against $(0.95N_T + 0.61Y_{OTs})$

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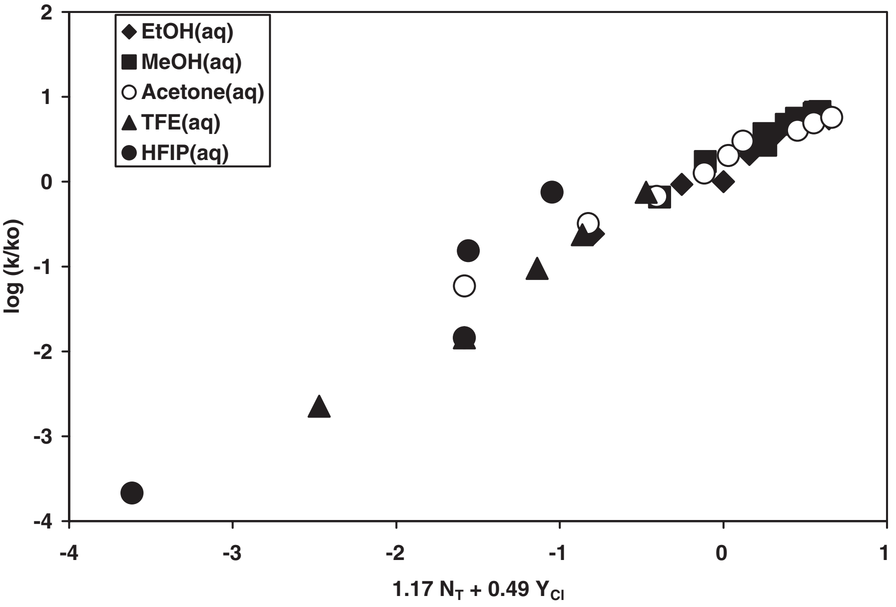

**Figure 2.** Plot of log($k/k_0$) for solvolyses of methanesulfonyl chloride at 45.0 °C against ($1.17N_T + 0.49Y_{C1}$). The data points for TFE–EtOH mixtures are not included in the correlation

## EXPERIMENTAL

The methanesulfonic anhydride (Aldrich 97%, **1**) and methanesulfonyl chloride (Aldrich 99.5%, **2**) were used as received. The solvents were purified as previously described.[14a]

The specific rates of solvolysis of **1** were determined using an apparatus allowing rapid response to changes in conductivity.[28] Details of the apparatus have been previously reported.[29] To promote rapid dissolution of solvent, about 4 μl of a stock solution of **1** in acetonitrile was added to 2 ml of the solvent under study, contained in the conductivity cell at the appropriate temperature. In most instances, the stock solution in acetonitrile was about 3% (w/w) but for the more aqueous solvents this was reduced to 0.5 or 0.3% (w/w), as indicated in the footnotes to Table 1. The changes in conductivity as a function of time were analyzed using the Guggenheim method.[30]

The much slower solvolyses of **2** were followed by a titration method, as previously described.[14a] A recent study of parallel solvolyses of 2-propanesulfonyl chloride required analysis in terms of the Guggenheim method[30] but the approximately 20-fold increase in rate for solvolyses of **1** allowed direct determination of infinity titers at 10 half lives in most instances. Only for the runs in 80% ethanol was the Guggenheim method used. For the very slow reaction in 97% HFIP, the inifinity titer was estimated by extrapolation of the values measured for the more aqueous mixtures.[3]

For the solvolyses of **1**, the infinity acid titers reflect the extents of reaction proceeding to ester and to acid [Eqn (3)].[18,19] To maximize the accuracy, the values were determined by adding 40 μl of a 1.46 M solution of **1** in acetonitrile to 20 ml of solvent, to give a $3 \times 10^{-3}$ M solution. After complete reaction, 5.00-ml portions were removed into 20 ml of acetone containing resorcinol blue (Lacimoid) as indicator and the titration was against $2.4 \times 10^{-3}$ M sodium methoxide in methanol.

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