Rate and product studies in the solvolyses of *N*,*N*-dimethylsulfamoyl and 2-propanesulfonyl chlorides

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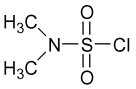
Contrary to earlier suggestions of an S_N1 pathway for solvolyses of *N*,*N*-dimethylsulfamoyl chloride (**1**), an extended Grunwald–Winstein equation treatment of the specific rates of solvolysis in 32 solvents shows an appreciable sensitivity towards changes in *both* solvent nucleophilicity and solvent ionizing power. The actual values are very similar to those obtained in earlier studies of the solvolyses of sulfonyl and phosphoryl chlorides, solvolyses which are believed to proceed by an S_N2 pathway. The observation of similar selectivities in aqueous-alcohol solvents further supports this assignment. In a recent report, an addition–elimination (association–dissociation) pathway was proposed for solvolyses of 2-propanesulfonyl chloride (**2**). A severe multicollinearity problem has been removed by the addition of several specific rates of solvolysis in fluoroalcohol-containing solvents. The new analyses using the extended Grunwald–Winstein equation lead to sensitivities similar to those for **1** and the previously studied related compounds, and these solvolyses are also best described as following an S_N2 pathway.

The mechanism of solvolysis of *N*,*N*-dimethylsulfamoyl chloride (**1**) has been described[1] as controversial, and, indeed, both S_N1[2–4] and S_N2[5,6] mechanisms have been proposed.



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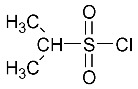

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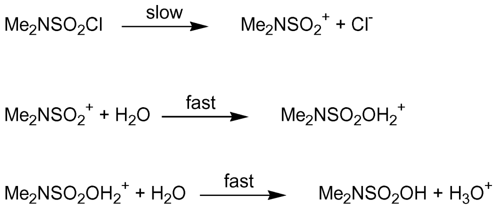
Hall[2] studied solvolyses in 86% water–14% dioxane and found the rate to be unaffected by moderate additions of hydroxide ion or pyridine. A claim that addition of pyridine led to large amounts of *N*,*N*-dimethylsulfamoylpyridine without any rate increase was subsequently withdrawn[3] and a bimolecular pathway to this product was proposed. The underlying solvolysis was, however, assigned as S_N1 in both publications.[2,3] Competitive reaction with azide ion was also considered to be bimolecular and this was also observed, in water, by Rogne.[5] Rogne reported a Grunwald–Winstein *m* value of 0.69 for solvolyses in aqueous-acetone mixtures when the one-term equation[7] [eqn (1)] was applied.

$$\log (k/k_0) = mY + c \tag{1}$$

In eqn (1), k and k_0 are the specific rates of solvolysis in a given solvent and in 80% ethanol, respectively; m is the sensitivity to changes in solvent ionizing power (Y); and c is a constant (residual) term. This m value was higher than that obtained in corresponding analyses of alkanesulfonyl and arenesulfonyl chlorides[8] but somewhat lower than what would have been anticipated for an S_N1 reaction.[7] An S_N2 mechanism with a loose transition state and some ionic character was proposed for the solvolyses.

Ko and Robertson[4] proposed an S_N1 mechanism for the hydrolyses of **1** (Scheme 1). They accepted the bimolecular nature of the superimposed reaction with azide ion[5] but, reasonably, argued that the underlying hydrolysis could be S_N1 in character. The observation that the heat capacity of activation ($\Delta C_p^\ddagger$, a measure of the temperature dependence of the enthalpy of activation) for the hydrolysis was very close in value to that measured for *tert*-butyl chloride[9] was considered to support this assignment. An extension to the hydrolyses of other *N*,*N*-disubstituted-sulfamoyl chlorides gave substantially less negative values for $\Delta C_p^\ddagger$, but these were also considered as proceeding by the S_N1 pathway.[10] The interpretation of $\Delta C_p^\ddagger$ values can be considerably more complicated than originally proposed.[11]



Scheme 1

Lee and Lee[6] measured the specific rates of solvolysis of **1** in mixtures of water with methanol, ethanol, acetone and acetonitrile. On the basis of solvent-effect correlations against dielectric constant and Y values,[7] they proposed (in accord with the conclusion of Rogne[5]) that the solvolyses were S_N2 in character (Scheme 2), but with bond breaking running ahead of bond making. An S_N2 reaction with ionic character was also proposed

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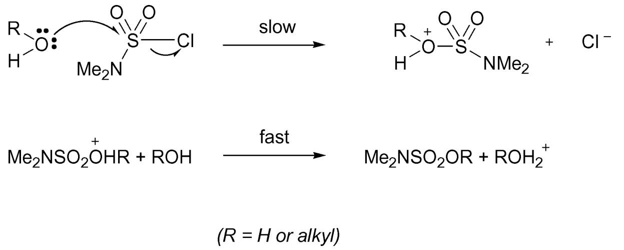


Scheme 2

based upon salt effects upon the specific rate of solvolysis in 50% acetone.[12]

A powerful tool for the study of the mechanism of a solvolysis reaction is to apply an extended two-term form of the Grunwald–Winstein equation (eqn 2).

$$\log(k/k_0) = lN_T + mY_X + c \tag{2}$$

In eqn 2, k and k_0 are defined as for eqn 1; l is the sensitivity to changes in solvent nucleophilicity values (N_T, when based on specific rates of solvolyses of the *S*-methyldibenzothiophenium ion[13,14]); m is the sensitivity to changes in solvent ionizing power (Y_X for a leaving group X and based on specific rates of solvolysis of adamantyl derivatives[15,16]); c is a constant (residual) term. As the mechanism moves from unimolecular to bimolecular, the l value should increase and the m value should decrease. Although initially developed for substitution at carbon, it has been demonstrated that the equation can effectively be used to study solvolytic displacements at phosphorus[17–19] and sulfur.[20] The correlations carried out[18–20] were consistent with an S_N2 mechanism for both arenesulfonyl chloride and chlorophosphate solvolyses. In view of the previous proposals for solvolyses of **1** of either S_N1 character or of S_N2 character with bond breaking running ahead, it will be of interest to see how the l and m values for solvolyses of **1** compare with the values established earlier for solvolyses of related substrates and with the values from kinetic studies of the solvolyses of an alkanesulfonyl chloride [2-propanesulfonyl chloride (**2**)], which was previously studied[21] in aqueous ethanol, methanol, and acetone, but not in aqueous-2,2,2-trifluoroethanol (TFE) or aqueous-1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).

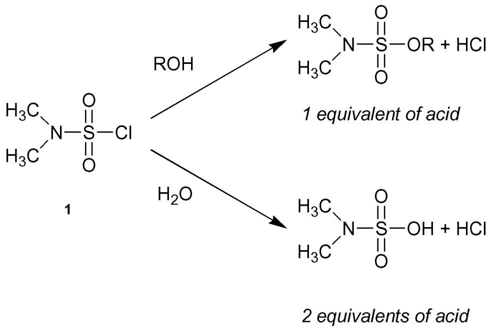
Selectivity ratios in aqueous-alcohol solvents [eqn (3)] can give useful mechanistic information. In eqn (3), the selectivity ratio (*S*)[22,23] is the ratio of second-order rate coefficients for reaction of an acid chloride (AX) to give ester (AOR; by reaction with alcohol, ROH) or acid (AOH; by reaction with water). Trends observed as the binary composition is altered can be compared with those observed for similar substrates, whose solvolysis mechanism has previously been studied.[24–26] Also, if a marked alteration of a trend is observed as one passes through a concentration region, especially if a reversal is observed, this can be tentatively taken as indicating a change in mechanism.[22,27–29] Such a consideration is strengthened if a change also occurs in Grunwald–Winstein plots in the same solvent composition region.[22,27–30]

$$S = k_2^{\text{Ester}}/k_2^{\text{Acid}} = \frac{[\text{AOR}]_{\text{prod}}}{[\text{AOH}]_{\text{prod}}} \times \frac{[\text{H}_2\text{O}]_{\text{solvent}}}{[\text{ROH}]_{\text{solvent}}} \tag{3}$$

In the present study we measure additional specific rates of solvolysis of **1**, already available for water and water–acetone mixtures,[5] and we also determine the product partitioning in mixtures of water with methanol, ethanol, or 2,2,2-trifluoroethanol (TFE). Mechanistic conclusions are then drawn from a consideration of the analyses using the extended Grunwald–Winstein equation, including a comparison with the l and m values determined from a combination of published[21] and new kinetic data for solvolyses of **2**. Use is also made of selectivity values and activation parameters.

Results

The specific rates of solvolysis of **1** at 25.0 °C and of **2** at 45.0 °C are reported in Tables 1 and 2, respectively. Several of the values are, as indicated, from the literature[4,5,21] or, in one instance, extrapolated from literature values at other temperatures.[21] Also reported in Table 1 are N_T[13,14] and Y_{Cl}[15,16,31] values and, for several of the solvolyses, activation parameters calculated using the specific rates of the table together with those from the literature[6] at 35, 40, and 45 °C. The specific rates from the tables are used, together with the N_T and Y_{Cl} values from Table 1, to carry out correlations using eqn (2). The l, m, and c values obtained, together with the multiple correlation coefficient and *F*-test value, are reported, together with the corresponding values from the solvolyses of related substrates, in Table 3. In Table 4 are given selectivity values (*S*) for the solvolyses of **1** in binary mixtures of water and alcohol (eqn 4).



(4)

These values are readily obtained from the infinity titer for the solvolyses which reflects the extent to which one or two equivalents acid are being produced,[19,32] with solvolyses in 100% ethanol or methanol (1 equiv.) and aqueous acetone (2 equiv.) being used as reference points. After determination of the percentage of the overall reaction which is with water (Table 4), one can calculate [eqn (3)] the *S* value for that particular solvent composition.

Discussion

Sulfonyl chlorides react with appropriate nucleophiles to make sulfonamides, sulfonic acid esters, and other derivatives. In turn, these products can be utilized in the production of medicinals, pesticides, and herbicides. The synthesis of derivatives of sulfamoyl chloride, of which **1** is a disubstituted example, and their conversion to biologically active compounds has been reviewed.[33] Sulfonyl transfer reactions have also been reviewed from a mechanistic viewpoint.[34]

A wide variety of mechanisms for the reactions of nucleophilic reagents with sulfonyl halides have been proposed. A direct replacement, as in eqn 4, can involve a direct one-step substitution (S_N2),[5,6,34–36] possibly involving a variable transition state

Table 1 Specific rates of solvolysis (k) of N,N-dimethylsulfamoyl chloride (**1**)[a] at 25.0 °C and N_T and Y_{Cl} values for the solvents

Solvent[b]	$10^6k/s^{-1}$ [c]	N_T [d]	Y_{Cl} [e]	$\Delta H^{\ddagger}_{298.2}$/kcal mol^{-1} [f]	$\Delta S^{\ddagger}_{298.2}$/eu[g]
100% EtOH	5.16 ± 0.08	0.37	−2.50		
90% EtOH	22.8 ± 0.08	0.16	−0.90	19.0 ±1.3	−16.2 ± 4.4
80% EtOH	49.4 ± 1.8	0.00	0.00	19.0 ± 0.6	−14.4 ± 2.1
70% EtOH	93.3 ± 3.7	−0.20	0.80	18.9 ± 0.6	−13.7 ± 2.0
60% EtOH	169 ± 4	−0.39	1.38	18.4 ± 1.1	−14.0 ± 3.9
50% EtOH	327 ± 7	−0.58	2.02	17.8 ± 0.7	−14.8 ± 2.3
100% MeOH	25.0 ± 0.2	0.17	−1.20		
90% MeOH	67.7 ± 1.0	−0.01	−0.20	18.1 ± 0.3	−17.0 ± 1.0
80% MeOH	139 ± 1	−0.06	0.67	17.8 ± 0.4	−16.5 ± 1.6
70% MeOH	261 ± 5	−0.40	1.46	17.6 ± 0.4	−16.1 ± 1.6
60% MeOH	388 ± 7	−0.54	2.07	19.0 ± 1.1	−10.3 ± 3.6
50% MeOH	656 ± 18	−0.75	2.70		
80% Acetone	6.0[g]	−0.37	−0.83	16.6 ± 0.5	−26.9 ± 1.7
70% Acetone	20.4[g]	−0.42	0.17	15.1 ± 0.1	−29.3 ± 0.2
60% Acetone	55.3[g]	−0.52	1.00	15.3 ± 0.4	−26.7 ± 1.3
50% Acetone	149[g]	−0.70	1.73	15.3 ± 0.4	−24.7 ± 1.5
40% Acetone	378[g]	−0.83	2.46	14.8 ± 0.1	−24.7 ± 0.2
30% Acetone	856[g]	−0.96	3.21	15.5 ± 0.6	−20.7 ± 2.1
20% Acetone	1690[g]	−1.11	3.77		
10% Acetone	2740[g]	−1.23	4.28	16.2 ± 0.5	−16.1 ± 1.8
100% H_2O	3980 ± 40[g,h]	−1.38	4.57	16.4 ± 0.4[i]	−14.5 ± 1.3[i]
97% TFE[j]	2.04 ± 0.06	−3.30	2.83		
90% TFE[j]	6.15 ± 0.14	−2.55	2.85		
70% TFE[j]	37.5 ± 0.5	−1.98	2.96		
50% TFE[j]	151 ± 2	−1.73	3.16		
80T–20E[k]	6.71 ± 0.02	−1.76	1.89		
60T–40E[k]	9.70 ± 0.19	−0.94	0.63		
40T–60E[k]	8.10 ± 0.31	−0.34	−0.48		
20T–80E[k]	6.57 ± 0.20	0.08	−1.42		
97% HFIP[j]	0.0671 ± 0.0035	−5.26	5.08		
70% HFIP[j]	22.1 ± 0.4	−2.94	3.83		
50% HFIP[j]	66.1 ± 1.7	−2.49	3.80		

[a] Substrate concentration of 0.004 M. [b] Unless otherwise indicated, the binary solvents are on a volume–volume basis at 25.0 °C, with the other component being water. [c] With associated standard deviations; average of all integrated first-order rate coefficients from duplicate runs. [d] From refs. 13 and 14. [e] From refs. 15, 16, and 31. [f] Using specific rate value of the table plus those at 35, 40, 45 °C from ref. 6 (with standard errors). [g] Values from ref. 5. [h] A value of 3913 has been reported at 25.14 °C (ref. 4). [i] Using the five specific rates at 15–35 °C from ref. 5. [j] On a weight-weight basis. [k] T–E are TFE-ethanol mixtures.

Table 2 Specific rates of solvolysis (k) of 2-propanesulfonyl chloride (**2**)[a] at 45.0 °C

Solvent[b]	$10^6k/s^{-1}$ [c]	Solvent[b]	$10^6k/s^{-1}$ [c]
100% EtOH	1.69 ± 0.06	90% TFE[f]	0.683 ± 0.048
90% EtOH	8.51 ± 0.14	80% TFE[f]	2.98 ± 0.19
80% EtOH	13.6 ± 0.9	70% TFE[f]	5.09 ± 0.36
50% EtOH	70.2[d]	50% TFE[f]	13.1 ± 0.7
30% EtOH	154[d]	80T–20E[g]	0.278 ± 0.016
100% H_2O	287[e]	60T–40E[g]	0.979 ± 0.055
100% MeOH	7.24 ± 0.38	40T–60E[g]	1.61 ± 0.06
50% MeOH	143[d]	20T–80E[g]	1.82 ± 0.06
30% MeOH	194[d]	97% HFIP[f]	[2.1 (±0.5) × 10^{-2}][h]
80% Acetone	2.58 ± 0.13	90% HFIP[f]	9.53 (±0.64) × 10^{-2}
70% Acetone	7.06 ± 0.19	70% HFIP[f]	2.16 ± 0.12
97% TFE[f]	3.87 (±0.23) × 10^{-2}	50% HFIP[f]	7.52 ± 0.30

[a] Substrate concentration of 0.05 M. [b] Unless otherwise indicated, the binary solvents are on a volume–volume basis at 25.0 °C, with the other component being water. [c] With associated standard deviations and average of all integrated first-order rate coefficients from duplicate runs; infinity titers for alcohol-containing solvents obtained from a Guggenheim treatment of the data (see Experimental section). [d] Value from ref. 21. [e] Extrapolated value using values from ref. 21 at 25.0 and 35.0 °C. [f] On a weight–weight basis. [g] T–E are TFE–ethanol mixtures. [h] Approximate value, not included in the correlations.

structure,[36c] an addition–elimination (association–dissociation) pathway,[21,37,38] a hybrid of these two pathways,[39] or an ionization (S_N1) pathway.[2–4] The *solvolyses* have been considered to involve a general-base catalysis to the nucleophilic attack by a second solvent molecule.[23,40] When a hydrogen atom is situated on the α-carbon of an alkanesulfonyl halide, elimination reaction to a sulfene can occur, which can then be followed by addition of hydroxylic solvent to give the formal substitution product.[34,41,42] Such behavior can be detected by isotopic substitution in solvent or substrate. When a relatively stable alkyl group can result, the ionization pathway can be accompanied by decomposition, to give what can be termed a solvolysis–decomposition[43] reaction. Such a reaction has also been detected with, for example, loss of CO_2 from chloroformates,[43] of N_2O from azoxytosylate esters,[44] or of SO_2 from chlorosulfinate esters.[45] For solvolysis in 100% water, it was found[40] that the products from 2-methyl-2-propanesulfonyl chloride (t-$BuSO_2Cl$) are formed *via* the *tert*-butyl cation. It would be of interest to compare the observed product ratios with those from the parallel solvolysis–decomposition reactions of the isomeric *tert*-butyl chlorosulfinate (t-BuOSOCl).

Application of the extended Grunwald–Winstein equation [eqn (2)] affords a powerful way of assessing both the importance of

Table 3 Coefficients from extended Grunwald–Winstein treatments (eqn 2) of the solvolyses of *N*,*N*-dimethylsulfamoyl chloride (**1**) and 2-propanesulfonyl chloride (**2**) and a comparison with coefficients from previous correlations involving solvolyses with attack at sulfur or phosphorus

Substrate	*n*[a]	*l*[b]	*m*[b]	*c*[b]	*R*[c]	*F*[d]
1	32[e]	1.20 ± 0.04	0.72 ± 0.03	0.11 ± 0.04	0.985	478
	30[f]	1.21 ± 0.04	0.75 ± 0.03	0.06 ± 0.04	0.988	537
	28[g]	1.18 ± 0.04	0.70 ± 0.03	0.15 ± 0.05	0.986	428
	7[h]	1.25 ± 0.15	0.58 ± 0.21	0.86 ± 0.48	0.982	54
	19[i]	1.10 ± 0.07	0.70 ± 0.04	0.08 ± 0.06	0.980	194
2	23[j]	1.32 ± 0.08	0.68 ± 0.04	0.08 ± 0.08	0.969	152
	19[g]	1.28 ± 0.05	0.64 ± 0.03	0.18 ± 0.06	0.988	333
p-$MeC_6H_4SO_2Cl$[k]	33	1.25 ± 0.15	0.62 ± 0.04	0.21 ± 0.20[l]	0.967	216
p-$MeOC_6H_4SO_2Cl$[k]	37	1.10 ± 0.17	0.61 ± 0.04	0.22 ± 0.23[l]	0.959	194
$(Me_2N)_2POCl$[m]	31	1.14 ± 0.05	0.63 ± 0.04	0.17 ± 0.21[l]	0.982	320
$(MeO)_2POCl$[n]	18	1.24 ± 0.14	0.45 ± 0.08	0.18 ± 0.11[l]	0.941	54
$(MeO)_2PSCl$[n]	28	1.16 ± 0.08	0.55 ± 0.03	0.30 ± 0.06[l]	0.966	154

[a] Number of data points. [b] With associated standard errors. [c] Multiple correlation coefficient. [d] F-test value. [e] Using all the specific rates listed in Table 1. [f] With 100% EtOH and 100% MeOH removed. [g] With the four T–E solvents removed. [h] In the seven TFE–H_2O and HFIP–H_2O solvents. [i] In those solvents for which specific rates are available for both **1** and **2**. [j] Using all the specific rates listed in Table 2, except the approximate value for 97% HFIP. [k] Values from ref. 20. [l] For literature values, the *c* value is associated with the standard error of the estimate. [m] Values from ref. 18. [n] Values from ref. 19.

Table 4 Selectivity values (*S*)[a] for solvolyses of *N*,*N*-dimethylsulfamoyl chloride (**1**) at 25.0 °C in binary mixtures of water with ethanol, methanol, or 2,2,2-trifluoroethanol and a comparison with values for two solvolyses of *p*-substituted-benzenesulfonyl chlorides

Solvent[b]	% $(CH_3)_2NSO_3H$	*S*	$S_{p\text{-MeO}}$[c]	$S_{p\text{-NO}_2}$[d]
90% EtOH	20.8	1.4	1.6	0.40
80% EtOH	33.2	1.6	2.3	0.68
70% EtOH	44.3	1.7		0.94
60% EtOH	55.3	1.7	3.8	1.2
50% EtOH	61.8	2.0	3.9	1.5
40% EtOH	75.1	1.6	4.2	1.7
30% EtOH	77.5	2.2	3.9	1.9
20% EtOH	84.7	2.4	3.6	2.0
10% EtOH	92.7	2.3	3.4	2.0
90% MeOH	9.2	2.5	2.5	0.88
80% MeOH	19.7	2.3	4.2	1.2
70% MeOH	27.1	2.6		1.6
60% MeOH	35.9	2.7	4.4	1.9
50% MeOH	45.9	2.7		2.3
40% MeOH	59.4	2.3	6.0	2.6
30% MeOH	68.4	2.4		2.9
20% MeOH	79.8	2.3	5.9	3.2
10% MeOH	88.7	2.6	5.2	3.4
90% TFE	82.1	0.14		
70% TFE	94.2	0.15		
50% TFE	97.9	0.12		

[a] As defined in eqn (3). [b] Aqueous ethanol and methanol on volume–volume basis at 25.0 °C and aqueous TFE on weight–weight basis. [c] Values for *p*-$MeOC_6H_4SO_2Cl$ from ref. 22. [d] Values for *p*-$NO_2C_6H_4SO_2Cl$ from ref. 23.

nucleophilic participation by solvent in the rate-determining step and the extent of negative charge development at the leaving group in the activated complex. It will be especially useful in studying the mechanism for solvolyses of **1**, since reference values for *l* and *m* are available for similar solvolyses occurring at sulfur or phosphorus, which are believed to proceed by an S_N2 pathway.

The specific rates of solvolysis at 25.0 °C reported in Table 1 for solvolyses of **1** involve 23 new values and nine values (for water and aqueous-acetone mixtures) from the literature.[5] the solvolyses of **2** are slower and values were determined at 45.0 °C. For example, at 25.0 °C, the solvolysis of **2**[21] in 100% ethanol is 8 times slower than that of **1**, in 50% ethanol it is 29 times slower, and the ratio rises to 110 in water. The specific rates of solvolysis of **2**, as reported in Table 2, involve 19 new measurements and five from the literature. Due to very slow reaction in 97% HFIP, half life of about one year at 45.0 °C, the value for this solvent is only approximate. The specific rates from Table 1 and from Table 2 are analyzed in terms of eqn (2) and the sensitivity values *l* and *m*, residual (constant) term *c*, and goodness of fit parameters are reported in Table 3.

The correlations for solvolyses of **1** are found to be very robust and to give values closely related to those reported earlier[18–20] for attack at sulfur or phosphorus of sulfonyl or phosphonyl chlorides (Fig. 1). When the one extreme of methanol and ethanol, where a changeover to addition–elimination might be observed,[22] was removed, the correlation was essentially unchanged. Similarly when TFE–ethanol mixtures were removed, solvents which frequently deviate from the plot,[18] very little change in the correlation occurred. Very striking was that from a correlation which involved only the nine aqueous-fluoroalcohol solvents, those of highest ionizing power and lowest nucleophilicity, very similar sensitivities and correlation coefficient were obtained to those from the correlation using all 32 solvents. All indications are that a bimolecular solvolysis with an appreciable sensitivity towards changes in solvent nucleophilicity is operating across the full range of solvents, based largely on the similarity of the *l* and *m* values to those previously determined for similar substrates believed to solvolyze by a concerted S_N2 process. The enthalpies and entropies of activation, determined in seventeen of the solvents (Table 1), are consistent with the proposed bimolecular pathway.[46]

As was pointed out in conjunction with earlier correlations[20] of the specific rates of sulfonyl chloride solvolyses, there has been a shortage of solvents containing a fluoroalcohol component, probably, in part, due to the very slow reaction in fluoroalcohol-rich solvents. In the recent very thorough study[21] of the solvolyses of **2** across the full range of ethanol–H_2O and methanol–H_2O mixtures and in 80–10% aqueous acetone, a correlation in terms of eqn (2) was carried out. A very good correlation was obtained with an *l* value of 0.96 and *m* value of 0.30, lower than the values obtained previously[20] for solvolyses of arenesulfonyl chlorides.

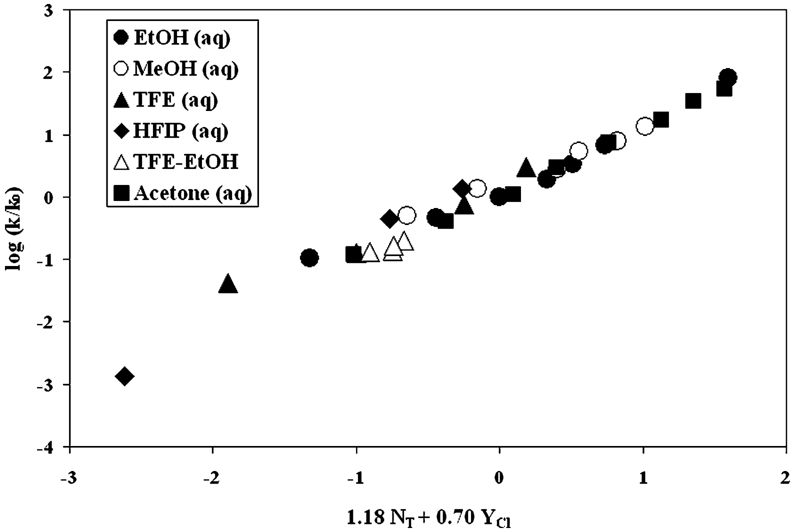


Fig. 1 Plot of log (k/k_0) for solvolyses of N,N-dimethylsulfamoyl chloride against ($1.18N_T + 0.70Y_{Cl}$).

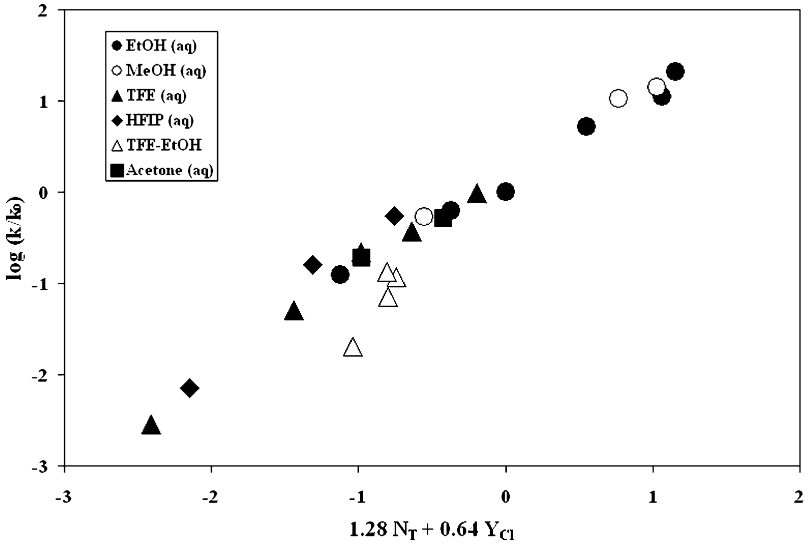


Fig. 2 Plot of log (k/k_0) for solvolyses of 2-propanesulfonyl chloride against ($1.28N_T + 0.64Y_{Cl}$). The data points for TFE–EtOH mixtures are not included in the correlation.

The reduced values could be a feature of the change to an alkanesulfonyl chloride or, more likely, it could be related to a high degree of multicollinearity when the solvents are restricted to these three binary mixtures. Indeed, when we carried out the correlation using all 29 values of Table 1 of the publication,[21] we arrived at values of 0.92 ± 0.10 for l and 0.48 ± 0.02 for m (R = 0.992), together with a warning that multicollinearity was present among the independent variables. Indeed, a direct correlation of N_T against Y_{Cl} values for the 29 solvents had a slope of −0.25 ± 0.01, intercept of −0.15 ± 0.04, and a correlation coefficient of 0.964.

To see the effect of including fluoroalcohol-containing solvents in the correlation of the specific rates of solvolysis of **2**, we have raised the temperature and (Table 2) have included 13 solvents with a fluoroalcohol (TFE or HFIP) component. As can be seen in Table 3, the l and m values and the goodness-of-fit parameters are now similar to those for **1** and the earlier studied substrates. For solvolyses of **2**, omission from the correlation of the four TFE–ethanol solvents (Fig. 2) leads to an improvement in the goodness-of-fit parameters but the l and m values are only slightly changed.

To probe further the similarity between solvent effects upon the specific rates of solvolysis of **1** and **2**, we have carried out a direct comparison of the log (k/k_0) values for **2** against those for **1** for the 19 solvents for which data is available for both substrates. A fairly good linear plot was obtained, with a slope of 1.02 ± 0.10, intercept of 0.25 ± 0.09, correlation coefficient of 0.921, and F-test value of 96.

Proposals of an S_N2 mechanism for the solvolyses of sulfonyl chlorides have frequently incorporated the suggestion[5,6,12] that bond-breaking is running ahead of bond making. In contrast, it has been proposed that the bimolecular solvolyses of **2** proceed by an addition–elimination process.[21] The main argument put forward in support of this proposal is, however, suspect. It was suggested that the rather small rate variation over the full range of aqueous-ethanol or aqueous-methanol mixtures results from a low dependence on solvent ionizing power, which was considered to argue against an S_N2 mechanism and in favor of addition–elimination. In fact, such a relatively small rate variation is frequently a feature of S_N2 reactions in these mixed solvents because, for these systems, as solvent nucleophilicity increases, the solvent ionizing power decreases. Indeed, for an appropriate l/m ratio, the effect of solvent variation within a given binary solvent on the specific rate of an S_N2 reaction can be extremely small.[47]

Although at the current state of knowledge of solvolysis reactions one must be cautious as regards the detailed interpretation of selectivity values (S), the magnitude of values and trends as the composition of a binary mixture is varied can be a useful component of evidence used to assess the mechanism.[22,28–30] Selectivity values for the solvolyses of **1** in aqueous ethanol, aqueous methanol and aqueous TFE are presented in Table 4.

In aqueous ethanol, S values initially rise as increasing amounts of water are added to the ethanol, they then level off at an essentially constant value of 2.0 ± 0.3 for the 70%–10% ethanol range. In aqueous methanol, the S value is essentially constant over the full range of composition (90%–10% methanol) studied, at a value of 2.5 ± 0.2. The values are not very different to those reported earlier for *p*-methoxybenzenesulfonyl chloride and, except for the solvent mixtures with very high alcohol content, they are very similar to the values reported for *p*-nitrobenzenesulfonyl chloride. The similarity for the three sets of values can be considered to support a common mechanism, consistent with the similarities in the l and m values.

In 90%–50% TFE, an essentially constant and low value of 0.14 ± 0.02 is observed. While low, this value is higher than might have been anticipated from the N_T difference of 2.64 between the two pure solvents.[13,14] This may well reflect the favored mixed hydrogen-bond interaction between the more acidic hydrogen of TFE and the more basic oxygen of the water [eqn (5)].

(5)

Such an interaction simultaneously ties up the nucleophilic oxygen of the water and leads to general-base catalysis to attack by the oxygen of the TFE, factors favoring an increase in the S value.

Conclusions

Application of the extended Grunwald–Winstein equation [eqn (2)] indicates that the solvolyses of *N*,*N*-dimethylsulfamoyl chloride (**1**) have responses to changes in solvent nucleophilicity and solvent ionizing power which are essentially identical to those observed in previously studied solvolyses of sulfonyl chlorides. The analyses are strengthened by the availability of specific rates in eleven fluoroalcohol-containing solvents, as opposed to a maximum of two in previous[20] analyses of the specific rates of solvolysis of arenesulfonyl chlorides. Selectivity values in water–ethanol and water–methanol mixtures, except in the solvents of highest ethanol content, are remarkably constant and similar in value to those for *p*-methoxybenzenesulfonyl chloride and, especially, *p*-nitrobenzenesulfonyl chloride. The analyses of both the kinetic and product studies for the solvolyses of **1** are consistent with the proposed S_N2 mechanism. No evidence is found which suggests[5,6,12] that within the mechanism bond breaking is running appreciably ahead of bond making.

A previous study of the specific rates of solvolysis of 2-propanesulfonyl chloride at 25 °C was limited to ethanol and methanol and their mixtures with water, 100% water, and aqueous acetone mixtures. An analysis in terms of eqn (2) was carried out[21] and this gave lower sensitivity values (l and m) than had earlier been observed[20] for arenesulfonyl chloride solvolysis. We have included the important fluoroalcohol-containing solvents in a study at 45 °C. Of the thirteen solvents of this type studied, twelve are included in the correlation (solvolysis in 97% HFIP was so slow that only an approximate value could be obtained). With the extended mix of solvent types available for the correlation, the l and m values are now found to be essentially identical to those for **1** and for the previously analyzed[20] solvolyses of arenesulfonyl chlorides.

Indications are that *N*,*N*-dialkylsulfamoyl, alkanesulfonyl (except those containing a *tert*-alkyl group[4,5]), and arenesulfonyl chlorides all solvolyze by a common mechanism, which is believed to be S_N2 in character.

Experimental

Materials

The *N*,*N*-dimethylsulfamoyl chloride (Aldrich, 99%) and 2-propanesulfonyl chloride (Aldrich, 97%) were used as received. The solvents were purified as previously described.[14a]

Kinetic methods

The kinetic runs were carried out as previously described.[14a] For the solvolyses of **1**, infinity titers were obtained at ten half-lives and used in the calculation of the first-order rate coefficients (specific rates).

For the solvolyses of **2**, the specific rates of solvolysis at 25.0 °C are one to two orders of magnitude lower than those for the corresponding solvolysis of **1**. In the later stages of these solvolyses, there is a perturbation due to additional acid being formed in an S_N2 attack at the alkyl group of the alkyl 2-propanesulfonate ($ROSO_2i$-Pr), formed by reaction with alcohol (ROH).[23,48] Accordingly, for solvolyses of **2** in solvents containing alcohol, the titer at ten half-lives is found to be somewhat higher than the value needed for the kinetic analysis. This type of situation can be handled by an application of the Guggenheim method of kinetic analysis,[49] provided that the perturbation is negligible in the first 75%–80% of reaction. We have applied the equation, as previously,[50] so as to calculate the required infinity titer for the solvolysis of **2**, and then we have calculated the specific rates in the conventional manner, using titers obtained during the first 60% of reaction. For the very slowest reactions (97%, 90% HFIP; 97% TFE), it was not practical to follow the progress of reaction to in excess of 50% and the Guggenheim treatment could not be applied. The infinity titers were estimated by extrapolation of the values calculated for the more aqueous binary mixtures.

The regression analyses were carried out using commercially available statistical packages.

Product studies

For the solvolyses of **1**, the infinity titers could be used to obtain the fractions of reaction proceeding to ester and to acid in water–alcohol mixtures.[32] To maximize the accuracy, the values were determined by preparing a 0.40 M stock solution of **1** in acetone and adding 0.500 mL to 20.0 mL of solvent at 25.0 °C. Titers of the acid produced were carried out in duplicate at ten, fifteen, and twenty half-lives. To standardize the measurements, each series of compositions of an aqueous alcohol mixture was accompanied by solvolyses in 60% and 50% acetone (2 equivalents of acid produced). For solvolyses in aqueous-ethanol and aqueous-TFE mixtures, no upward trend in the values was observed and all six values were averaged to arrive at the percentages of *N*,*N*-dimethylsulfamic acid reported in Table 4. In methanol and aqueous methanol mixtures a very slight upward trend was observed, with the increase in the acid titer in progressing from ten half lives to twenty half lives decreasing steadily from 3.8% in 100% methanol to 0.4% in 50% methanol. For these solvents the average of the two values at ten half lives was used to determine the product ratio.

A corollary of the need to apply the Guggenheim approach to analyze the kinetics of solvolysis of **2** in alcohol-containing solvents is that the approach outlined above for obtaining product ratios for solvolyses of **1** cannot be applied to the solvolyses of **2**.

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