

An Improved Scale of Solvent Nucleophilicity Based on the Solvolysis of the *S*-Methyldibenzothiophenium Ion^{†,1}

Dennis N. Kevill* and Steven W. Anderson

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received September 24, 1990

A scale of solvent nucleophilicity (N_T values) based upon the specific rates of solvolysis of the *S*-methyldibenzothiophenium ion is presented. A comparison of this scale with the originally developed solvent nucleophilicity scale based upon methyl *p*-toluenesulfonate solvolysis (N_{OTs} values) strongly suggests that the appropriate m value for methyl *p*-toluenesulfonate solvolysis for incorporation into the extended (two-term) Grunwald-Winstein equation is 0.55. Revised N_{OTs} values (termed N'_{OTs}) are in good agreement with N_T values. Good linear free energy relationships are obtained in comparisons of the specific rates of solvolysis of other RX^+ substrates with N_T values. Suggestions, by Acheson and by Kurz, that the solvolyses of *S*-methyl- and *S*-ethylthiophenium ions involve little charge development at the transition state on the nucleophilic oxygen of the attacking solvent molecules are refuted and conventional S_N2 mechanisms, in which general-base catalysis is an important consideration, are proposed.

Although a scale of solvent ionizing power based upon the specific rates of solvolysis of *tert*-butyl chloride was developed over 40 years ago, progress in developing a parallel scale of solvent nucleophilicity has been both slower and, in some aspects, less secure. In the present paper, we introduce an improved scale of solvent nucleophilicity and show that a simple adjustment of the original methyl *p*-toluenesulfonate (tosylate) scale (N_{OTs} values) brings it into good agreement with the new scale.

The Grunwald-Winstein scale of solvent ionizing power² (Y values) affords an excellent general way of correlating the rates of unimolecular solvolyses and, rather surprisingly,³⁻⁵ frequently the rates of bimolecular solvolyses as the composition of a given binary solvent mixture is varied (eq 1). Within eq 1, k and k_0 are the specific rates of

$$\log(k/k_0) = mY \quad (1)$$

solvolysis in the solvent under consideration and in 80% ethanol, respectively, and m is the sensitivity of the specific rate of solvolysis of the substrate under consideration to changes in Y values. It has been shown⁶ that the *tert*-butyl chloride scale involves a nucleophilic component and Y_X scales for various leaving groups (X) based on the solvolysis of either a 1- or 2-adamantyl derivative have been developed.⁷

In 1951, it was suggested⁸ that for bimolecular solvolyses a second term, governed by the sensitivity l to solvent nucleophilicity N , should be added to eq 1. The resulting equation (eq 2) is often referred to as the extended (or two-term) Grunwald-Winstein equation.

$$\log(k/k_0) = lN + mY \quad (2)$$

Conceptually, the development of a required N scale is considerably more difficult than the development of a Y scale. In principle, for a unimolecular solvolysis, $l = 0$ and eq 2 simplifies to eq 1 and, taking m as unity for the standard substrate, measurement of specific rates can lead directly to a Y scale. For bimolecular solvolyses of an initially neutral substrate (RX), there is no situation where the mY term can be neglected and, in particular, it is essential to have a reasonably good estimate of the m_{RX} value for insertion into eq 3.

$$N_{RX} = \log(k/k_0)_{RX} - m_{RX}Y \quad (3)$$

It was a further 25 years before the first listing of N values of the commonly used pure and binary solvents was

made available.^{9,10} Use was made of the observation that, in liquid sulfur dioxide as solvent, acetic and formic acids at low concentration have essentially the same nucleophilicity.¹¹ Schadt, Bentley, and Schleyer took the bold step of assuming that this correspondence could be extrapolated all the way to the pure acids. By studying the specific rate of solvolysis of their chosen standard (methyl tosylate) at 50 °C in each of the two pure acids of identical N value (assumed) and known Y value, eq 3 could be used to determine a m_{MeOTs} value of 0.3. It was argued that a Y scale based on 2-adamantyl tosylate solvolysis^{7,9,12} (Y_{OTs}) would be the most appropriate, and N_{OTs} values were obtained from eq 4.

$$N_{OTs} = \log(k/k_0)_{MeOTs} - 0.3Y_{OTs} \quad (4)$$

Use of N_{OTs} and Y_{OTs} values^{7,13} within eq 2 has led to very good correlations of the specific rates of solvolysis of alkyl,⁹ allyl,^{14,15} and benzyl^{9,16,17} arenosulfonates. However, the very acceptable correlations obtained cannot be taken as support for the choice of a value of 0.3 for m_{MeOTs} . In the use of N_{OTs} and Y_{OTs} for the correlation of the specific rates of solvolysis of a tosylate ester (ROT_s), it is easy to demonstrate¹⁵ that the magnitudes of l and of the correlation coefficient are independent of the value for m_{MeOTs} .

(1) (a) Abstracted, in part, from the Ph.D. Dissertation of S.W.A., Northern Illinois University, August, 1985. (b) A brief outline of a portion of this work has appeared previously: Kevill, D. N.; Anderson, S. W.; Fujimoto, E. K. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; Advances in Chemistry Series, No. 215, American Chemical Society: Washington, DC, 1987; pp 275-277.

(2) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* 1948, 70, 846.

(3) Wells, P. R. *Linear Free Energy Relationships*, Academic Press: New York, 1968; p 67.

(4) Kaspi, J.; Rappoport, Z. *Tetrahedron Lett.* 1977, 2035.

(5) Kevill, D. N.; Lin, G. M. L. *J. Am. Chem. Soc.* 1979, 101, 3916.

(6) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* 1982, 104, 5741.

(7) For a recent review, with tables of values and leading references, see: Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* 1990, 17, 121. We thank Dr. Bentley for a preprint.

(8) Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* 1951, 73, 2700.

(9) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1976, 98, 7667.

(10) For a review, see: Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* 1977, 14, 1.

(11) Peterson, P. E.; Waller, F. J. *J. Am. Chem. Soc.* 1972, 94, 991.

(12) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1976, 98, 7658.

(13) For additional values, see: Fujio, M.; Goto, M.; Yoshino, T.; Funatsu, K.; Tsuji, Y.; Ouchi, S.; Tsuno, Y. *Mem. Fac. Sci., Kyushu Univ., Ser. C* 1987, 16, 85.

(14) Kevill, D. N.; Rissmann, T. J. *J. Chem. Soc., Perkin Trans. 2* 1984, 717.

(15) Kevill, D. N.; Rissmann, T. J. *J. Org. Chem.* 1985, 50, 3062.

(16) Kevill, D. N.; Rissmann, T. J. *J. Chem. Res., Synop.* 1986, 252.

(17) Kevill, D. N.; Ren, H. *J. Org. Chem.* 1989, 54, 5654.

[†] Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

previously inserted within eq 3; any error in the choice of 0.3 as the value (eq 4) will be reflected entirely in the m_{ROTs} value subsequently obtained. The same argument will, of course, apply to RX substrates with other anionic leaving groups, provided that the study is limited to solvents for which the Y_X values tabulated for a leaving group X mimic Y_{OTs} values. In general, the observed m_{ROTs} value (m_{obs}) will be related to the true value by eq 5.

$$m_{\text{ROTs}} = m_{\text{obs}} + (m_{\text{MeOTs}} - 0.3)l_{\text{ROTs}} \quad (5)$$

Several years ago, being unable to improve upon either the method used to estimate m_{MeOTs} or the choice of the initially neutral standard substrate, we embarked upon a different approach. This approach involves minimizing the mY contribution by choice of a RX^+ substrate. In this substrate, the positive charge is located on the atom adjacent to the α -carbon, such that the leaving group is a neutral molecule. The qualitative Hughes-Ingold theory of solvent effects¹⁸ then predicts a relatively small change in rate with change in solvent polarity for the *dispersal* of charge involved in going from the ground state to the transition state of a solvolytic reaction. For example, the *tert*-butyldimethylsulfonium ion solvolyzes in a variety of solvents¹⁹ in accord with eq 6. This indicates a sensitivity

$$\log(k/k_0)_{t\text{-BuSMe}_2^+} = -0.09Y \quad (6)$$

of the logarithm of the specific rate of solvolysis toward solvent variation of a little less than 1/10 of that for *tert*-butyl chloride, the standard substrate used in obtaining the original Y scale.²

Our initial scale (N_{KL})⁵ involved the use of the triethyloxonium ion as standard ($l = 1$) and Y^+ values either based on *tert*-butyldimethylsulfonium ion specific rates of solvolysis (eq 7) or, when the experimental values were

$$\log(k/k_0)_{t\text{-BuSMe}_2^+} = Y^+ \quad (7)$$

not available, estimated from eq 6. A N_{KL} scale was then developed using eq 8.

$$N_{\text{KL}} = \log(k/k_0)_{\text{Et}_3\text{O}^+} - 0.55Y^+ \quad (8)$$

Subsequently, it was shown^{20,21} that the variation in the specific rate of solvolysis of the *tert*-butyldimethylsulfonium ion with solvent was determined principally by changes in solvent nucleophilicity and not by leaving-group effects. A new Y^+ scale based on 1-adamantyldimethylsulfonium ion solvolysis was developed. However, it was found²¹ that the Y^+ values varied only slightly from 0, and it was suggested that the N scale could be constructed with the very small mY^+ contribution neglected (eq 9). The

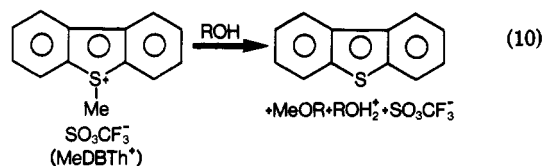
$$\log(k/k_0)_{\text{Et}_3\text{O}^+} = N_{\text{Et}_3\text{O}^+} \quad (9)$$

$N_{\text{Et}_3\text{O}^+}$ scale has been used successfully in the correlations of both neutral¹⁵⁻¹⁷ and positively charged²² substrates.

Comparison, for several substrates, of the pairs of m values obtained from parallel treatments using either N_{OTs} or $N_{\text{Et}_3\text{O}^+}$, together with Y_{OTs} values, has indicated¹⁵ that the m_{MeOTs} value that should be inserted into eq 3 is not 0.3 but 0.55.

Two disadvantages associated with the $N_{\text{Et}_3\text{O}^+}$ scale are that the l values require a scaling factor before they can be directly compared to l values based on solvolysis of a

methyl derivative, such as methyl tosylate, and (for the more nucleophilic solvents) the solvolysis rates are a little too high to be conveniently measured at temperatures close to ambient. The trimethyloxonium ion solvolyzes some 15-40 times faster,⁵ and while it would remove the first disadvantage it would intensify the second. Other simple methyl derivatives of the MeX^+ type, such as sulfonium²³ or quaternary ammonium ions,²⁴ solvolyze too slowly for them to constitute a convenient standard. A survey of the literature suggested that a good standard of the MeX^+ type would be the solvolysis (eq 10) of the *S*-methylthiophenium ion (MeDBTh⁺). This is easy to prepare in the presence of a counterion of low nucleophilicity, and it has been shown to solvolyze in methanol at a convenient rate at ambient temperature.²⁵ The solvolyses in solvents of relatively low nucleophilicity can be conveniently studied at several higher temperatures and values at 25 °C obtained by extrapolation. Thiophenium ions solvolyze at a faster rate than simple sulfonium ions since the aromaticity of the thiophene is perturbed in forming the salt^{25,26} and the restoration of the lost aromaticity provides a driving force for the solvolysis. A new solvent nucleophilicity scale (N_T values) is defined according to eq 11.



thiophenium ion (MeDBTh⁺). This is easy to prepare in the presence of a counterion of low nucleophilicity, and it has been shown to solvolyze in methanol at a convenient rate at ambient temperature.²⁵ The solvolyses in solvents of relatively low nucleophilicity can be conveniently studied at several higher temperatures and values at 25 °C obtained by extrapolation. Thiophenium ions solvolyze at a faster rate than simple sulfonium ions since the aromaticity of the thiophene is perturbed in forming the salt^{25,26} and the restoration of the lost aromaticity provides a driving force for the solvolysis. A new solvent nucleophilicity scale (N_T values) is defined according to eq 11.

$$N_T = \log(k/k_0)_{\text{MeDBTh}^+} \quad (11)$$

Results

Specific rates of solvolysis as a function of temperature, measured in ethanol at temperatures close to ambient and in eight solvents of relatively low nucleophilicity at three or four higher temperatures, are presented in Table I, together with the calculated enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) of activation. The specific rates measured in 29 solvents at 25.1 °C, together with values obtained at 25.1 °C from an extrapolation (using the Arrhenius equation) of eight sets of data at higher temperatures (Table I), are presented in Table II. Also presented in Table II are N_T values (defined by eq 11) and N'_{OTs} values, defined according to eq 12 and calculated by using previously reported^{7,13} N_{OTs} and Y_{OTs} values within eq 13.

$$N'_{\text{OTs}} = \log(k/k_0)_{\text{MeOTs}} - 0.55 Y_{\text{OTs}} \quad (12)$$

$$N'_{\text{OTs}} = N_{\text{OTs}} - 0.25 Y_{\text{OTs}} \quad (13)$$

When Y_{OTs} values are not directly available, they can be estimated from specific rates of solvolysis of 1-adamantyl *p*-toluenesulfonate by using eq 14.²⁷

$$Y_{\text{OTs}} = 0.868 \log(k/k_0)_{1\text{-AdOTs}} + 0.027 \quad (14)$$

Discussion

The specific rates of solvolysis of the *S*-methylthiophenium ion correlate well with the specific rates

(18) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1969; pp 457-463.

(19) Swain, C. G.; Kaiser, L. E.; Knee, T. E. C. *J. Am. Chem. Soc.* **1958**, *80*, 4092.

(20) Kevill, D. N.; Kamil, W. A.; Anderson, S. W. *Tetrahedron Lett.* **1982**, *23*, 4635.

(21) Kevill, D. N.; Anderson, S. W. *J. Am. Chem. Soc.* **1986**, *108*, 1579.

(22) Kevill, D. N.; Anderson, S. W. *J. Heterocycl. Chem.* **1988**, *25*, 399.

(23) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1986**, *51*, 5029.

(24) Thornton, E. R. *Solvolytic Mechanisms*; Ronald Press: New York, 1964; p 165.

(25) Acheson, R. M.; Harrison, D. R. *J. Chem. Soc. C* **1970**, 1764.

(26) Marino, J. P. In *Topics in Sulfur Chemistry*; Senning, A., Ed.; Georg Thieme Publishers: Stuttgart, 1976; Vol. 1, p 82.

(27) (a) Allard, B.; Casadevall, E. *Nouv. J. Chim.* **1985**, *9*, 565. (b) Kevill, D. N.; Hawkinson, D. C. *J. Org. Chem.* **1989**, *54*, 154.

Table I. Solvolysis of the *S*-Methyldibenzothiophenium Ion^a at Temperatures Other Than 25.1 °C: Specific Rates of Solvolysis and Activation Parameters

solvent ^b	temp, °C	10 ⁷ <i>k</i> , s ⁻¹	Δ <i>H</i> ^{‡,c} kcal mol ⁻¹	Δ <i>S</i> ^{‡,c} eu
EtOH	14.9	376 ± 13	19.0	-13.4
	35.5	3580 ± 140	(±0.1) ^d	(±0.3) ^d
	45.2	9510 ± 410		
HCO ₂ H	49.9	23.6 ± 0.6	19.5	-24.2
	60.1	62.1 ± 2.3	(±0.1)	(±0.3)
	70.1	149 ± 6		
CH ₃ CO ₂ H	49.7	144 ± 3	21.9	-13.0
	60.1	454 ± 11	(±0.6)	(±1.9)
	70.1	1160 ± 60		
TFE ^e	60.1	2.84 ± 0.12	21.4	-24.4
	70.6	8.21 ± 0.35	(±0.7)	(±2.0)
	80.4	19.2 ± 1.6		
97% TFE	49.7	6.07 ± 0.16	24.2	-12.3
	60.1	19.6 ± 1.1	(±0.6)	(±1.8)
	70.1	61.0 ± 4.3		
97% HFIP ^f	60.1	0.50 ± 0.04	28.7	-6.1
	70.1	1.69 ± 0.09	(±0.8)	(±2.7)
	80.1	6.11 ± 0.26		
90% HFIP	60.0	11.1 ± 0.6	27.8	-2.7
	68.9	31.5 ± 1.3	(±0.7)	(±2.3)
	80.1	116 ± 9		
70% HFIP	89.5	369 ± 24		
	60.0	82.0 ± 2.6	27.5	+0.5
	70.6	289 ± 10	(±0.5)	(±1.6)
80.4	996 ± 56			
	89.9	2640 ± 140		
	60.0	142 ± 4	24.9	-6.2
50% HFIP	70.3	465 ± 16	(±0.2)	(±0.8)
	80.3	1280 ± 40		
	90.0	3500 ± 250		

^aAs the trifluoromethanesulfonate salt. ^bMixed solvents on a weight-to-weight basis, with other component water. ^cUnless otherwise indicated, calculated (with associated standard error) at 60 °C; estimated specific rates at 25.1 °C are presented in Table II. ^dCalculated at 25.1 °C, with inclusion (from Table II) of the experimental specific rate at 25.1 °C. ^e2,2,2-Trifluoroethanol. ^f1,1,1,3,3,3-Hexafluoro-2-propanol.

of solvolysis of the triethyloxonium ion for those solvents within which both solvolyses have been studied. A plot of the log (*k*/*k*₀)_{Et₃O⁺} values (at 0.0 °C) against the log (*k*/*k*₀)_{MeDBTh⁺} values (at 25.1 °C) for 33 solvents gives a good linear correlation, with a slope (*l* value) of 0.69 ± 0.04, intercept of 0.09 ± 0.05, and correlation coefficient of 0.962. The only point showing appreciable deviation is that for solvolysis in 100% trifluoroethanol (TFE), which lies appreciably above the correlation line.^{1b} When this point is omitted, corresponding values of 0.77 ± 0.03, 0.14 ± 0.04, and 0.971 are obtained.

A possible explanation for the deviation of the 100% TFE point would be if, in this low nucleophilicity solvent, the triethyloxonium ion has a superimposed unimolecular solvolysis component. While one is reluctant to propose unimolecular reactions for ethyl derivatives, it is well known that acid-catalyzed reactions of primary alcohols, proceeding through an oxonium ion, frequently give products strongly suggesting the occurrence of 1,2-shifts of the type associated with carbenium ion formation.²⁸ Indeed, the increased tendency for ethyl derivatives to solvolyze via a carbocationic intermediate gives an additional reason for developing a solvent nucleophilicity scale based upon solvolysis of a methyl derivative.

It is of interest to compare the *N*_T scale values with those of the *N*_{OTs} scale. The *N*_{OTs} values are available for 30 of

Table II. Specific Rates of Solvolysis of the *S*-Methyldibenzothiophenium Ion^a at 25.1 °C and Comparison of Calculated Solvent Nucleophilicity Values (*N*_T) with Revised *N*_{OTs} Values (*N*'_{OTs})

solvent ^b	10 ⁷ <i>k</i> , ^c s ⁻¹	<i>N</i> _T ^d	<i>N</i> ' _{OTs} ^e
100% EtOH	1143 ± 34	+0.37	+0.55 (+0.43) ^f
80% EtOH	484 ± 14	0.00	0.00
60% EtOH	199 ± 10	-0.39	-0.31
40% EtOH	89.1 ± 1.3	-0.74	-0.72
20% EtOH	33.2 ± 1.4	-1.16	-1.17
100% H ₂ O	20.3 ± 1.3	-1.38	-1.47
100% MeOH	723 ± 10	+0.17	+0.19
80% MeOH	418 ± 14	-0.06	-0.17
60% MeOH	140 ± 6	-0.54	-0.51
40% MeOH	65.4 ± 1.5	-0.87	-0.82
20% MeOH	28.7 ± 1.0	-1.23	-1.20
95% acetone	158 ± 6	-0.49	
90% acetone	214 ± 12	-0.35	+0.11 (-0.05) ^f
80% acetone	206 ± 13	-0.37	-0.19 (-0.27) ^f
60% acetone	146 ± 8	-0.52	-0.58
40% acetone	72.1 ± 3.7	-0.83	-0.84
20% acetone	37.6 ± 1.5	-1.11	-1.14
80% dioxane	168 ± 9	-0.46	+0.04 (-0.08) ^f
70% dioxane	205 ± 10	-0.37	(-0.19) ^f
60% dioxane	140 ± 5	-0.54	
40% dioxane	69.8 ± 3.4	-0.84	
20% dioxane	37.0 ± 3.0	-1.12	
100% TFE ^g	0.0566 ± 0.0071 ^h	-3.93	-3.51
97% TFE ⁱ	0.241 ± 0.022 ^h	-3.30	-3.25
90% TFE ⁱ	1.36 ± 0.04	-2.55	-2.87 ⁱ
70% TFE ⁱ	5.11 ± 0.27	-1.98	-1.70
50% TFE ⁱ	8.97 ± 0.15	-1.73	-1.47
80T-20E ^k	8.40 ± 0.25	-1.76	-1.97
60T-40E	55.1 ± 1.4	-0.94	-1.06
40T-60E	220 ± 7	-0.34	-0.44
20T-80E	585 ± 19	+0.08	
97% HFIP ^{i,l}	0.00268 ± 0.00040 ^h	-5.26	-5.17
90% HFIP ⁱ	0.0702 ± 0.0113 ^h	-3.84	
70% HFIP ⁱ	0.562 ± 0.068 ^h	-2.94	
50% HFIP ⁱ	1.56 ± 0.09 ^h	-2.49	-2.41 ^m
HCO ₂ H	1.75 ± 0.02 ^h	-2.44	-3.11
CH ₃ CO ₂ H	8.09 ± 0.83 ^h	-1.78	-2.06

^aAs the trifluoromethanesulfonate salt. ^bUnless otherwise stated on a volume-volume basis, at 25.0 °C, with the other component water. ^cWith associated standard deviation for averaged values and associated standard error for extrapolated values. ^dThe logarithm (base ten) of the specific rate of solvolysis in the solvent relative to that in 80% ethanol. ^eBased on methyl *p*-toluenesulfonate solvolysis (ref 9), but using an *m* value within eq 4 of 0.55 rather than 0.3; easily estimated using the data of ref 7 within eq 13. ^fValues in parentheses are using *Y*_{OTs} values obtained by use of eq 14 (this also modifies the *N*_{OTs} value). ^g2,2,2-Trifluoroethanol. ^hValue obtained by extrapolation, using the data of Table I. ⁱPrepared on a weight-weight basis. ^jFrom interpolated *N*_{OTs} and *Y*_{OTs} values. ^kT-E are 2,2,2-trifluoroethanol-ethanol mixtures. ^l1,1,1,3,3,3-Hexafluoro-2-propanol; preliminary *N*_T values in the HFIP-H₂O mixtures have been reported previously (ref 21). ^mUsing data from ref 13.

the solvent systems for which *N*_T values have been determined. If these *N*_{OTs} values are plotted against the *N*_T values, one obtains a reasonably good correlation with a slope of 0.815, intercept of 0.075, and correlation coefficient of 0.944. The correlation is considerably improved when *N*'_{OTs} values (defined as in eq 12) are substituted for *N*_{OTs} values; the slope is now 1.005, the intercept is 0.020, and the correlation coefficient improves to a value of 0.986.

One can define a scale of *N*'_T values by eq 15, where the *Y*⁺ scale is based on the specific rates of solvolysis of the 1-adamantyldimethylsulfonium ion.²¹ Only small changes

$$N'_T = \log (k/k_0)_{\text{MeDBTh}^+} - 0.55Y^+ \quad (15)$$

in slope, intercept, and correlation coefficient are observed when the *N*'_{OTs} values are plotted against *N*'_T rather than *N*_T values (new values of 0.951, 0.039, and 0.984). This is consistent with the suggestion²¹ that scales of solvent nu-

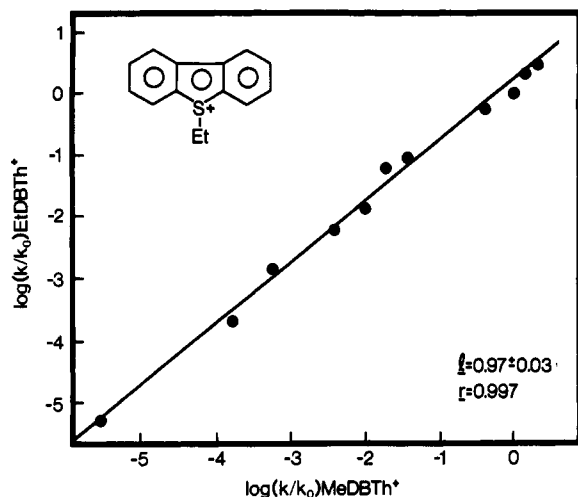


Figure 1. Plot, at 25.1 °C, of $\log(k/k_0)_{\text{EtDBTh}^+}$ against $\log(k/k_0)_{\text{MeDBTh}^+}$ (i.e., N_T values).

cleophilicity based upon solvolysis of a RX^+ substrate can be set up with exclusion of the small mY^+ term.

The previous proposal¹⁵ that the N_{OTs} scale should be set up using a m_{MeOTs} value of 0.55 (to give N'_{OTs} values) rather than the originally chosen⁹ value of 0.30 can be checked by assuming that N_T and N'_{OTs} values should be identical and calculating the value of m_{MeOTs} that best satisfies this requirement. This is conveniently done by the use of eq 16, where x represents the required value for

$$(N_{\text{OTs}} - N_T) = (x - 0.3)Y_{\text{OTs}} \quad (16)$$

m_{MeOTs} . A plot of $(N_{\text{OTs}} - N_T)$ against Y_{OTs} will have a slope of $(x - 0.3)$. Using N_T values, a slope of 0.23, intercept of 0.04, and correlation coefficient of 0.873 is obtained. Using N'_T values, the corresponding values are 0.25, 0.10, and 0.872. The x values obtained are, therefore, 0.53 and 0.55, respectively; these values are in excellent agreement with the previous estimate of 0.55 based on comparisons of correlations using either N_{OTs} or $N_{\text{Et}_3\text{O}^+}$ values.¹⁵ Indeed, for an $\text{S}_{\text{N}}2$ transition state with little charge development on the α -carbon, a m value in the region of 0.55, roughly half the value to be anticipated if the activation process for an ionization was to lead directly to an ion pair, is not unexpected.

We have investigated the utility of the N_T scale by correlating the specific rates of solvolysis of other RX^+ type substrates against the N_T values. The specific rates of solvolysis of the *S*-ethyldibenzothiophenium ion (EtDBTh^+) in 11 solvents²² correlate excellently with N_T values (Figure 1), with a slope of 0.93 ± 0.03 , intercept of 0.15 ± 0.07 , and correlation coefficient of 0.996 when $\log(k/k_0)_{\text{EtDBTh}^+}$ is plotted. Multiple regression analysis against both N_T and Y^+ leads to a l value of 0.97 ± 0.04 , a m value of 0.46 ± 0.30 , an intercept of 0.14 ± 0.07 , and a correlation coefficient of 0.997. The essentially identical values for l , the intercept, and the correlation coefficient irrespective of whether the mY^+ term is included or not, plus the lack of precision in the m value obtained when the term is included, gives strong support to our belief that the specific rates of solvolysis of RX^+ substrates can be adequately correlated by linear regression against solvent nucleophilicity values.

The specific rates of solvolysis of the *S*-methylphenylsulfonium ion have been studied in 26 solvents.²³ Correlation of the specific rates of solvolysis against N_T values (Figure 2) gives a good linear relationship. Considering the relationship between $\log(k/k_0)_{\text{MeSPh}_2^+}$ and N_T values leads to a slope (l value) of 0.80 ± 0.04 , intercept

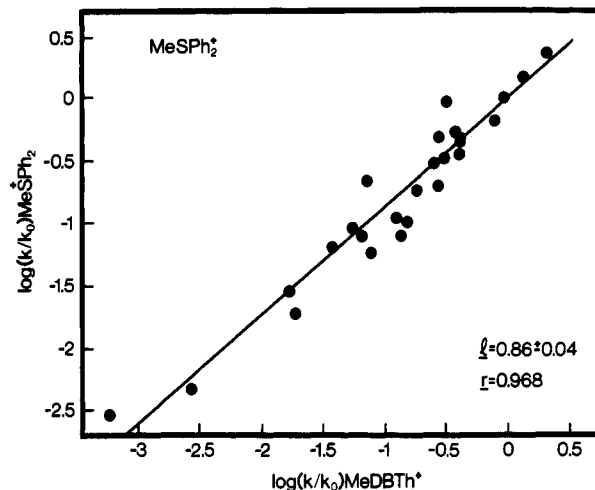


Figure 2. Plot of $\log(k/k_0)_{\text{MeSPh}_2^+}$ values, at 50.0 °C, against $\log(k/k_0)_{\text{MeDBTh}^+}$ values (N_T values) at 25.1 °C.

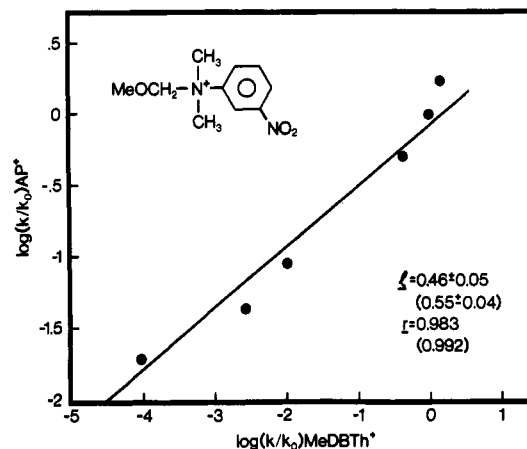


Figure 3. Plot of $\log(k/k_0)$ values for the *N*-(methoxymethyl)-*N,N*-dimethyl-*m*-nitroanilinium ion, at 25.0 °C, against $\log(k/k_0)_{\text{MeDBTh}^+}$ values (N_T values) at 25.1 °C.

of -0.05 ± 0.05 , and correlation coefficient of 0.968. Again, the improvement on introducing the mY^+ term is negligible: l value of 0.78 ± 0.08 , m value of -0.23 ± 0.53 , intercept of -0.04 ± 0.05 , and correlation coefficient of 0.969. The rather low value for l will be, at least, in part due to this substrate being studied at a 25° higher temperature than the temperature at which N_T values were determined.

Knier and Jencks²⁹ have studied the specific rates of solvolysis of the *N*-(methoxymethyl)-*N,N*-dimethyl-*m*-nitroanilinium ion in six solvents. In support of their claim that solvent nucleophilicity determined the relative rates, a logarithmic plot against N_T values gives a reasonably good correlation (Figure 3). When values of $\log(k/k_0)$ for the substrate are correlated against N_T values, a l value of 0.46 ± 0.04 , intercept of 0.04 ± 0.09 , and correlation coefficient of 0.983 are obtained. As in the correlation of the Et_3O^+ specific solvolysis rates, the point for 100% TFE lies appreciably above the best fit line. When this point is omitted, the l value becomes 0.55 ± 0.04 , the intercept becomes 0.03 ± 0.06 , and the correlation coefficient improves to 0.992.

The good correlation against Et_3O^+ , EtDBTh^+ , and MeSPh_2^+ , with slopes of close to unity, supports the belief that the standard substrate for the N_T scale solvolyzes by a conventional $\text{S}_{\text{N}}2$ mechanism.^{30,31} The methoxymethyl

derivative,²⁹ where considerable S_N1 character is to be expected, correlates but with a lower *l* value, consistent with the solvolysis mechanism for the MeDBTh⁺ ion having appreciably more S_N2 character. In their pioneering studies of the preparation and reactions of *S*-alkylthiophenium ions, Acheson and Harrison²⁵ proposed that the methyl and ethyl derivatives solvolyzed by an S_N1 mechanism and Kurz³²⁻³⁴ has proposed that the *S*-methylthiophenium ion, and also several methyl esters, solvolyze in water or methanol by a mechanism in which little charge is developed at the transition state on the nucleophilic oxygen of attacking solvent molecules, and in which the activation process involves predominantly changes in solvation. The methyl transfer to water was considered to be a partly coupled process. We will discuss these proposals of Acheson and Harrison and of Kurz and will suggest that the observations on which they are based can be rationalized equally well, or better, in terms of a conventional S_N2 mechanism.

It is relatively easy to dispose of the two types of evidence put forward by Acheson and Harrison in support of the *S*-methyl- and *S*-ethylthiophenium salts solvolyzing largely by an S_N1 mechanism. The claim²⁵ that, in S_N2 reaction, methyl derivatives always react faster than ethyl derivatives was known to be incorrect as early as 1966. In that year, Heppollette and Robertson,³⁵ in a study of the hydrolyses in water at 50 °C of several pairs of methyl and ethyl derivatives, found the k_{Me}/k_{Et} ratio to be small and frequently less than unity; for the iodide leaving group, a value as low as 0.5 was found. For the methanolysis of benzothiophenium and dibenzothiophenium salts, the k_{Me}/k_{Et} ratio was found to be in the range of 0.25 to 0.5. For an S_N1 reaction, an accelerative influence of up to 10⁸ for replacing an α -hydrogen by methyl has been estimated.³⁶ In practice, values are usually somewhat lower but they do involve several orders of magnitude. The small (20%) increase in the specific rate of reaction of the *S*-ethylbenzothiophenium ion on adding 0.1 M chloride ion to the hydrolysis reaction²⁵ can be considered to be a consequence of the relatively high reactivity of the substrate leading to low selectivity and hence only a small rate increase on addition of a modest concentration of chloride ion. A similar situation was found³⁷ on the addition of various nucleophilic anions to the S_N2 ethanolysis of the triethylxonium ion.

The mechanism proposed by Kurz for the hydrolysis and methanolysis of the *S*-methylthiophenium ion also proposes that there is very little, if any, bonding of the attacking nucleophilic oxygen to the substrate. Indeed, although the mechanism must be considered as (at least) bimolecular, it would appear that if, as suggested, the activation process involves predominantly changes in solvation, then the assignment of mechanism using the Hughes-Ingold concept for the molecularity of an S_N reaction, defined as the number of molecules necessarily undergoing covalency changes in the rate-determining step

of the reaction,³⁸ would require to a first approximation an S_N0 classification.

Kurz based his conclusions on a detailed study of solvent isotope effects in reactions of the *S*-methylthiophenium ion, methyl perchlorate, and methyl trifluoromethanesulfonate over the full composition range of mixtures of water or an alcohol with a dipolar aprotic solvent, most often acetonitrile. In general, he found a first-order dependence on the substrate concentration and terms of zero, first, and second order in water or alcohol. The zero-order term involved background solvolysis to give a nitrilium ion, and the other two terms reflected the involvement of one or two water or alcohol molecules in the activated complex (rate coefficients k_1 and k_2). The role for a second alcohol molecule in alcoholyses of alkyl³⁹ or acyl halides⁴⁰ in a dipolar aprotic solvent was in early studies explained in terms of a "push-pull" mechanism, where one acted as a nucleophile and the second as an electrophile. More recently, this type of kinetic behavior, for both alkyl⁴¹ and acyl⁴² derivatives, has been explained in terms of general-base catalysis by a second molecule to nucleophilic attack by the first. Support for this structure for the activated complex came from a pronounced general-base catalysis on adding salts containing the anionic leaving group and from the absence of catalysis upon adding phenol, which would function better as an electrophile than the second alcohol molecule but worse as a general base.^{41,42}

In his interpretation, Kurz reverts to an electrophilic role for the second alcohol molecule, within the third-order kinetic process. His argument is essentially that the solvent deuterium isotope effect is almost identical for the overall second- and third-order processes (k_1 and k_2 terms). If one involved general-base catalysis and not the other, this would not be expected to be the case. We believe a more probable explanation to be that general-base catalysis is present in both processes but in the k_1 term it is provided by an acetonitrile molecule⁴² and in the k_2 term by a water or alcohol molecule. Indeed, the observation within the study that acetonitrile can compete as a nucleophile (hence the term zero order in hydroxylic species) would suggest that it should also be capable of competing as a general base. This alternative makes suspect the assignment of little or no positive charge to the nucleophilic oxygen at the activated complex. The analysis is based on a model that assumes the association of the second water or alcohol molecule with the activated complex for the term that is first order in methanol. It may well be, however, that the analysis should be carried out in terms of displacing an acetonitrile molecule by the second hydroxylic molecule. In that case, the ratio of the rate coefficients cannot be analyzed in the way presented³⁴ and the relatively low k_2/k_1 would be a consequence of the general-base catalysis by acetonitrile increasing the magnitude of k_1 to well above the uncatalyzed value that is required for the analysis.

Experimental Section

Materials. The purifications of acetone, dioxane, ethanol, and methanol were as previously described.⁴³ The purifications of

(30) Arguments in favor of an S_N2 mechanism for nucleophilic substitution reactions of the triethylxonium ion have been summarized: Perst, H. *Oxonium Ions in Organic Chemistry*; Verlag Chemie: Weinheim, 1971; pp 73-75.

(31) For arguments favoring S_N2 attack in reactions of methylarylsulfonium ions, see: Coward, J. K.; Sweet, W. D. *J. Org. Chem.* 1971, 36, 2337.

(32) Kurz, J. L.; Lee, J. *J. Am. Chem. Soc.* 1980, 102, 5429.

(33) Kurz, J. L.; Lee, J.; Rhodes, S. *J. Am. Chem. Soc.* 1981, 103, 7651.

(34) Kurz, J. L.; Lee, J.; Love, M. E.; Rhodes, S. *J. Am. Chem. Soc.* 1986, 108, 2960.

(35) Heppollette, R. L.; Robertson, R. E. *Can. J. Chem.* 1966, 44, 677.

(36) Fry, J. L.; Harris, J. M.; Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* 1970, 92, 2540.

(37) Kevill, D. N.; Fujimoto, E. K. *J. Chem. Res., Synop.* 1988, 408.

(38) Hughes, E. D. *Q. Rev.* 1951, 5, 245.

(39) (a) Swain, C. G. *J. Am. Chem. Soc.* 1948, 70, 1119. (b) For a brief review, see: Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; pp 62-63.

(40) Gilkerson, W. R. *J. Phys. Chem.* 1956, 60, 1142.

(41) Kevill, D. N.; Posselt, H. S. *J. Chem. Soc., Perkin Trans. 2* 1984, 909.

(42) (a) Kevill, D. N.; Foss, F. D. *J. Am. Chem. Soc.* 1969, 91, 5054.

(b) Kevill, D. N.; Kim, C.-B. *Bull. Soc. Chim. Fr.* 1988, 383. (c) Kevill, D. N.; Kim, C.-B. *J. Chem. Soc., Perkin Trans. 2* 1988, 1353.

(43) Kevill, D. N.; Kolwyck, K. C.; Weitz, F. L. *J. Am. Chem. Soc.* 1970, 92, 7300.

acetic acid,¹⁹ formic acid,⁴⁴ 1,1,1,3,3,3-hexafluoro-2-propanol,⁴⁵ and 2,2,2-trifluoroethanol⁴⁶ were also by use of previously reported procedures. Silver trifluoromethanesulfonate (Aldrich, 99.99%) and dibenzothiophene (Aldrich, 95%) were used as received. Iodomethane was purified as described previously;⁴⁷ it was then stored over copper in a brown glass bottle.

S-Methyldibenzothiophenium Trifluoromethanesulfonate. The synthetic procedure was a modification of that used by Acheson and Harrison²⁵ to prepare the corresponding tetrafluoroborate salt. Protected by a nitrogen atmosphere, 9.25 g (0.036 mol) of silver trifluoromethanesulfonate and 5.06 g (0.027 mol) of dibenzothiophene were added to 40 mL of dry⁴⁸ benzene. Iodomethane (12 mL, 0.19 mol) was then added from a syringe through a rubber septum over a period of 3 min, followed by magnetic stirring for 128 min. A yellow-green precipitate was removed by filtration and washed with 150 mL of acetonitrile. The combined filtrate was concentrated (rotary evaporator) to give a clear brown oil. Upon cooling in an ice bath and scratching, the oil was converted into a white solid. The solid was transferred to a Büchner funnel, washed with 100 mL of ether, and dried overnight (over P₂O₅) in a vacuum dessicator (7.33 g, 77.9%): mp 129–131.5 °C;⁴⁹ IR (KBr disk) includes 1420, 1262, 1162, 1033, 982, 758, 744 cm⁻¹; UV (H₂O) λ_{max} nm (10⁻⁴ ε) 207 (3.12), 228 (2.48), 236 (2.44), 274 (0.983), 312 (0.279); ¹H NMR (CD₃CN) δ 8.35–7.68 (m, 8 H, Ar), 3.31 (s, CH₃, 3H). Anal. Calcd for C₁₄H₁₁F₃O₃S₂: C, 48.27; H, 3.18; S, 18.41. Found: C, 48.25, H, 3.22; S, 18.29.

(44) Winstein, S.; Marshall, H. *J. Am. Chem. Soc.* 1956, 74, 1126.

(45) Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. *F. J. Chem. Soc., Perkin Trans 2* 1980, 1244.

(46) Rappoport, Z.; Kaspi, J. *J. Am. Chem. Soc.* 1974, 96, 4518.

(47) Fieser, L. F. *Experiments in Organic Chemistry*, 3rd rev. ed.; Heath: Boston, 1957.

(48) Loewenthal, H. J. E. *Guide for the Perplexed Organic Experimentalist*; Heyden: Philadelphia, 1978.

(49) Other preparations had melting points differing by up to 4 °C from this range. It has been pointed out previously that, for sulfonium salts, melting points are a poor test of purity. The usually observed decomposition points depend very much upon the rate of heating: Saunders, W. H.; Asperger, S. *J. Am. Chem. Soc.* 1957, 79, 1612.

The spectral data for the cation were in good agreement with those reported for the corresponding tetrafluoroborate salt.²⁵ Complete ethanolysis of a tared sample, at 60 °C for 2 h, led to a titration against NaOMe in MeOH corresponding to 101.8% of the theoretical value.

On evaporation to dryness, the filtrate from the ether washing of the precipitate yielded a small amount of unreacted dibenzothiophene, identified by mp⁵⁰ and C, H analysis.

Kinetic Procedures. The majority of the runs were carried out by withdrawal of 1–5 mL aliquots from tightly stoppered volumetric flasks. For very slow runs, or for runs at temperatures approaching the boiling point of the solvent, the aliquots were initially sealed within Kimble Neutraglas ampules. For runs in water, alcohols, and aqueous–organic mixtures, the aliquots were removed from the constant temperature bath at suitable time intervals and added to 25 mL of acetone containing Lacmoid (resorcinol blue) indicator (cooled within a solid CO₂–acetone slush bath), and the acid developed was titrated against a standardized solution of sodium methoxide in methanol. The titration procedures for runs in acetic and formic acids and the calculation of the specific rates of solvolysis were as previously described.⁵

For runs in water and aqueous–organic mixtures with high water content, a fluffy white precipitate appeared when the solubility of dibenzothiophene was exceeded. This precipitate did not perturb the solvolysis kinetics. For example, for solvolysis of 0.0062 M substrate in 40% ethanol at 25.1 °C, a precipitate was first observed at about 40% reaction, mp 95–97 °C (lit.⁵⁰ 99–100 °C).

Acknowledgment. This research was supported, in part, by a Doctoral Research Fellowship to S.W.A. by the NIU Graduate School. D.N.K. thanks Professor R. Gompper, Institut für Organische Chemie der Universität München, for hospitality during the time that this paper was being prepared.

(50) Weast, R. C., Ed. *Handbook of Chemistry and Physics*, 69th ed.; CRC Press: Boca Raton, FL, 1988; p C-242.