Correlation of the Rates of Solvolysis of the
S.-Ethyldibenzothiophenium Ion [1]

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Dedicated to Professor Norman H. Cromwell

The specific rates of solvolysis of S-ethyldibenzothiophenium trifluoromethanesulfonate have been found to give a good linear correlation with the previously determined specific rates of solvolysis of the triethyloxonium ion, and hence with the solvent nucleophilicity scale established from the triethyloxonium ion study. A value for the sensitivity to changes in solvent nucleophilicity (1) of greater than unity (1.15) is in accord with reactivity-selectivity considerations.

Scales of solvent ionizing power based on the variation of specific rate of solvolysis of a standard substrate, initially t-butyl chloride [2], with variation in solvent composition are well established (equation 1). In equation 1, k is

$$\log (k/k_o) = m\ Y \qquad (1)$$

the specific rate of solvolysis of a substrate in a given solvent, k_o is the corresponding specific rate in 80% aqueous ethanol, Y is the solvent ionizing power, and m is a measure of the sensitivity of the specific rate of solvolysis of the substrate to changes in solvent ionizing power.

Grunwald and Winstein also attempted [3] to analyze solvolyses which exhibit a dependence on solvent nucleophilicity by addition of a second term (equation 2). In equation 2, the added term involves N, a measure of solvent nucleophilicity, and 1, the sensitivity of the specific

$$\log (k/k_o) = 1\ N + m\ Y \qquad (2)$$

rate of solvolysis of the substrate to changes in solvent nucleophilicity. The earliest extensive compilation of N values was using methyl p-toluenesulfonate as the standard subtrate [4]. A major difficulty in establishing a N scale is the estimation of the m value to be used for the standard substrate within equation 2; the use of a m value of 0.3 for methyl p-toluenesulfonate solvolysis [4] has been questioned [5,6].

The S_N1 solvolyses of R-X$^+$ substrates vary far less in their specific rates, with solvent changes, than the S_N1 solvolyses of R-X substrates [7] and it was argued [5] that influences operating at the leaving group must cause considerably smaller variations in rate for R-X$^+$ substrates. It follows that the $1\ N$ term can dominate, and a better estimate can be made of the solvent nucleophilicity values, when a R-X$^+$ substrate is taken as the standard ($1 = 1$).

A scale of solvent nucleophilicities based upon the solvolysis of the triethyloxonium ion (TEO) was developed [5] several years ago. Initially, small corrections for variations
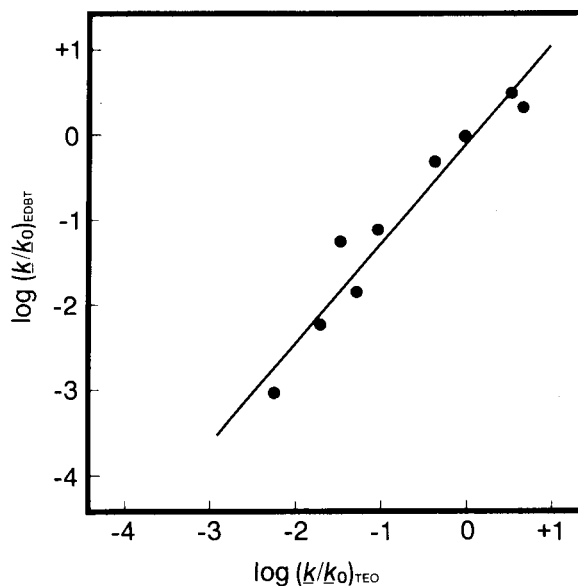
Logarithmic plot of the specific rate of solvolysis in a given solvent relative to the specific rate of solvolysis in 80% ethanol for the S-ethyldibenzothiophenium ion at 25.0° against the triethyloxonium ion at 0°.

in influences at the leaving-group were made based upon variations with solvent composition of the specific rates of solvolysis of the t-butyldimethylsulfonium ion [8]. It was subsequently demonstrated [9] that the t-butyldimethylsulfonium ion specific rate variations were dominated by solvent nucleophilicity considerations and the corrections that had been made, fortunately small, were in the wrong direction. A study of a tertiary bridgehead substrate (the 1 - adamantyldimethylsulfonium ion), where rearside nucleophilic attack is prohibited, showed little variation of specific solvolysis rate with changes in solvent composition [10] and it was concluded that the solvent nucleophilicity scale (N_{TEO}) could be based in a simple manner upon the specific rates of solvolysis of the triethyloxonium ion

$$\log (k/k_o)_{TEO} = N_{TEO} \qquad (3)$$

(equation 3), without the need for leaving-group effect corrections.

For other R-X$^+$ substrates, it should be possible to correlate the specific rates of solvolysis by equation 4, where l is a measure (relative to triethyloxonium ion solvolysis)

$$\log (k/k_o)_{R-X^+} = l \, N_{TEO} \qquad (4)$$

of the sensitivity of the solvolysis rates of R-X$^+$ towards changes in solvent nucleophilicity. The methyldiphenylsulfonium ion was found, at 50.0°, to have specific rates of solvolysis which correlated quite well (correlation coefficient of 0.957; 21 solvents) with N_{TEO} values; the slope (l value) was 0.99 [11]. However, even at 50°, the rates were too slow for convenient study in solvents with N_{TEO} values below −1.5.

It has been demonstrated that substrates with heterocyclic leaving groups can be very useful for study of nucleophilic substitution reactions, including solvolyses, of R-X$^+$ substrates [12]. If we imagine two *ortho* hydrogens being removed from diphenyl sulfide and the rings being linked together, we arrive at the heterocyclic dibenzothiophene molecule. Acheson and Harrison have reported [13] a specific rate of methanolysis of the S-methyldibenzothiophenium ion at room temperature (24°) of 2.1 x 10^{-4}s^{-1}, a value 198 times larger than that for methanolysis of the methyldiphenylsulfonium ion at 50° [11]. The higher reactivity of thiophenium salts, relative to simple sulfonium salts, arises from a disruption of the aromaticity upon alkylation at the sulfur [14]. The lost aromaticity is regained upon solvolysis, giving a driving force not present for expulsion of sulfide molecules from simple sulfonium salts.

The S-ethyldibenzothiophenium ion has been prepared associated with a counter ion of low nucleophilicity (trifluoromethanesulfonate). It is of interest to see how well the rates of solvolysis at the ethyl group of this cation, with expulsion of the dibenzothiophene molecule, correlate with the rates of solvolytic attack at the ethyl group of the

Scheme

+EtOR+ROH$_2^+$+SO$_3$CF$_3^-$
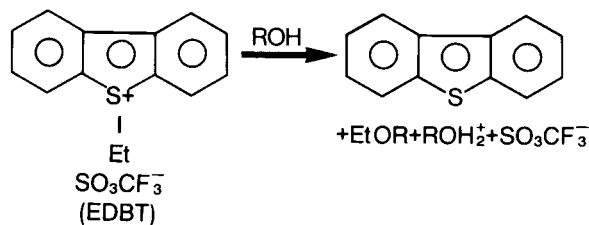
triethyloxonium ion, with expulsion of diethyl ether. Not only are the leaving groups very different in character but, also, the solvolyses of the dibenzothiophenium salt are slower than those of the oxonium salt. For example, at 25°, the rate coefficient for formolysis of the triethyloxonium

ion [5] is 260 times larger than the value for the S-ethyldibenzothiophenium ion obtained in this study (Table I).

The specific rates of solvolysis have been measured directly at 25° for eight solvents with N_{TEO} values ranging from +0.5 to −1.7 (Table I). Specific rates at 24.9° were obtained for three additional solvents of lower nucleophilicity (Table I) by extrapolation, using the Arrhenius equation, of data obtained at higher temperature (Table II). The N_{TEO} values are available for the first nine of the solvents listed in Table I and a linear free energy relationship plot of the specific rates of solvolysis of the S-ethyldibenzothiophenium ion (EDBT) against the specific rates of solvolysis of the triethyloxonium ion (TEO) is presented in the figure. A good linear correlation is obtained (correlation coefficient of 0.976; 9 solvents), with only the point for acetolysis showing appreciable deviation. This supports the suggested [10] utility of the N_{TEO} scale in a simple (one-term) correlation of the rates of solvolysis of R-X$^+$ substrates. The slope of 1.15 ± 0.10 (standard error) indicates a larger sensitivity to variations in solvent nucleophilicity than for the standard substrate, the triethyloxonium ion. This is the trend that would be expected from the reactivity-selectivity principle [15], with a lower reactivity leading to a greater selectivity.

Table I

First-order Rate Coefficients for the Solvolysis of S-Ethyldibenzothiophenium Trifluoromethanesulfonate at 24.9°

Solvent [a]	$10^6 k$, s^{-1} [b]			$\log(k/k_o)_{EDBT}$
100% EtOH	359	±	22 [c]	+0.47
80% EtOH	121	±	6	0.00
60% EtOH	63.2	±	2.7 [c]	−0.28
MeOH	267	±	17	+0.34
H$_2$O	9.97	±	0.37	−1.08
CH$_3$CO$_2$H	7.04	±	0.38	−1.24
HCO$_2$H	0.730	±	0.021 [c]	−2.22
70% TFE	1.85	±	0.09	−1.82
97% TFE	0.117 [d]			−3.01
97% HFIP	0.000669	±	0.000052 [d,e]	−5.26
90% HFIP	0.0235	±	0.0032 [d,e]	−3.71

[a] Aqueous-ethanol on volume-volume and aqueous 2,2,2-trifluoroethanol (TFE) and aqueous 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) on weight-weight basis. [b] With associated standard deviations, k_o is the value for 80% ethanol. [c] At 25.4°. [d] Extrapolated from data at higher temperatures (see Table II). [e] With associated standard error.

The specific rate of methanolysis of 0.013 M S-ethyldibenzothiophenium trifluoromethanesulfonate, at 24.9°, is only about one-half of the approximate value of 4.5 x 10^{-4}s^{-1} reported [13] at room temperature (24°) for 2.5 x 10^{-4} M S-ethyldibenzothiophenium tetrafluoroborate. While it is possible that the counter-ion and concentration variation could contribute towards this difference, only a

Table II

First-Order Rate Coefficients for the Solvolysis of S-Ethyldibenzothiophenium Trifluoromethanesulfonate at Various Temperatures

Solvent [a]	T°C	$10^6 k$,s^{-1} [b]		
97% TFE	80.0	75.8	±	2.6
97% TFE	49.7	2.83	±	0.17
97% HFIP	90.2	12.6	±	0.6
97% HFIP	80.1	3.22	±	0.18
97% HFIP	68.9	0.770	±	0.031
90% HFIP	90.2	103	±	8
90% HFIP	80.1	40.5	±	1.6
90% HFIP	68.9	9.43	±	0.56

[a] See footnote [a] to Table I. [b] With associated standard deviations.

very low counter-ion and concentration dependence was observed for solvolyses of <0.01 M triethyloxonium ion [5].

The low log $(k/k_o)_{EDBT}$ value of -5.26 for 97% 1,1,1,3,-3,3-hexafluoroisopropanol (HFIP) is consistent with a low value for 97% HFIP solvent nucleophilicity (N_{OTs}) of -4.27 calculated [4] from studies of methyl p-toluenesulfonate and 2-adamantyl p-toluenesulfonate solvolyses. For comparison of N_{OTs} values with N_{TEO} values, it has been suggested [6] that a sensitivity towards solvent ionizing power value of 0.55 for methyl p-toluenesulfonate solvolysis, within the two-term equation 2, is to be preferred to the value of 0.3 [4] and that a proportionality factor of 0.83 interrelates the scale based on attack at methyl with that based on attack at ethyl [5]. The revised N_{OTs} value is -5.17 [16] and, multiplying by 0.83, we arrive at a value comparable to N_{TEO} of -4.29. Using the l value of 1.15 obtained in this study, we can estimate $\log(k/k_o)_{EDBT}$ for 97% HFIP as 1.15 x -4.29 = -4.93, in good agreement with the observed value of -5.26.

In conclusion, it has been demonstrated that the specific rates of solvolysis of an Et-X$^+$ substrate with a heteroaromatic leaving group, dibenzothiophene, can be considered together with, and corelated against, the specific rates of solvolysis of an Et-X$^+$ substrate with a simple aliphatic leaving group, diethyl ether. The difference, between the two substrates, in sensitivity towards changes in solvent nucleophilicity is consistent with the reactivity-selectivity principle.

EXPERIMENTAL

Materials.

The purifications of ethanol [17], methanol [17], 1,1,1,3,3,3-hexafluoro-2-propanol [18], 2,2,2-trifluoroethanol [19], acetic acid [8], formic acid

[20], and benzene [21] were as previously described. Iodoethane was purified by fractional distillation. Silver trifluoromethanesulfonate (Aldrich) and dibenzothiophene (Aldrich) were used without further purification.

Synthesis of S-Ethyldibenzothiophenium Trifluoromethanesulfonate.

To a stirred slurry of 30 ml of dry benzene, 4.63 g (0.018 mole) of silver trifluoromethanesulfonate, and 2.50 g (0.014 mole) of dibenzothiophene was added, over a 6 minute period, 7.8 ml (0.098 mole) of iodoethane. After stirring for 2½ hours, the resultant slurry was suction filtered and the filter cake washed with benzene (2 x 10 ml) and acetonitrile (5 x 20 ml). Concentration of the filtrate gave an off-white solid, which was transferred to a Büchner funnel and washed with ether; drying under vacuum gave 1.20 g (24%) of a fine white powder, mp 101.5-104°. The uv, ir, and pmr spectral data were in good agreement with those previously reported [13] for the corresponding tetrafluoroborate salt.

Anal. Calcd. for $C_{15}H_{13}S_2F_3O_3$: C, 49.70; H, 3.61; S, 17.70. Found: C, 49.56; H, 3.85; S, 17.73.

Kinetic Procedures.

Each run was carried out by withdrawing, at suitable time intervals, 1 ml portions from 10 ml of (0.007-0.013 M) reactant solution. For runs below 50°, the solution was within a flask held in a constant-temperature bath. Above 50°, the runs were carried out by sealing 1 ml portions within Kimble Neutraglass ampules prior to immersion within the constant-temperature bath. For runs in water, alcohols, and aqueous-organic mixtures, the 1 ml portions were removed from the constant-temperature bath at appropriate time intervals and added to 25 ml of acetone, containing Lacmoid (resorcinol blue) indicator, cooled within a solid carbon dioxide-acetone slush bath. The acid produced was titrated against a standardized solution of sodium methoxide in methanol. During the runs in water, early precipitation (<5% reaction) of dibenzothiophene was observed; this did not cause any trend in the calculated first-order rate coefficients.

The titration procedures for runs in acetic acid and formic acid and the calculation of the first-order solvolytic rate coefficients were as previously described [5]. All of the integrated values from duplicate runs were averaged to arrive at the values reported within Tables I and II.

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