

## APPLICATION OF THE $N_T$ SOLVENT NUCLEOPHILICITY SCALE TO ATTACK AT SULFUR: SOLVOLYSES OF BENZENESULFONYL CHLORIDES

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*Dedicated to Professor Otto Exner on the occasion of his 75th birthday and in recognition of his outstanding contributions to physical organic chemistry and chemometrics.*

The specific rates of solvolysis of benzenesulfonyl chloride and three 4-substituted derivatives can be very well correlated using the extended Grunwald–Winstein equation, with incorporation of  $N_T$  solvent nucleophilicity and  $Y_{Cl}$  solvent ionizing power values. In two instances, it was shown that almost identical correlations were obtained after the incorporation of methyl groups into the 2- and 6-positions of the benzene ring. No evidence was found for a dissociative ( $S_N1$ ) mechanism or for a duality of mechanism. All of the results can be rationalized in terms of a concerted bimolecular displacement ( $S_N2$ ) mechanism, involving attack by solvent at sulfur.

**Key words:** Solvolysis; Benzenesulfonyl chlorides; Extended Grunwald–Winstein equation; Solvent nucleophilicity; Reaction kinetics.

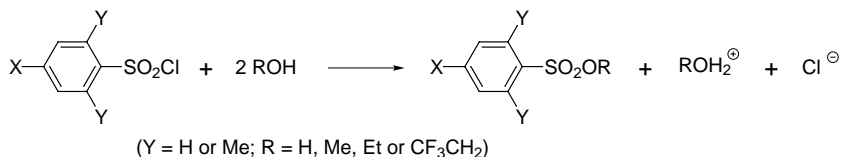
As part of an ongoing program to evaluate the application of the  $N_T$  solvent nucleophilicity scale, developed<sup>1</sup> for attack at carbon, to nucleophilic attack by solvent at a heteroatom, results from analyses using the extended (two-term) Grunwald–Winstein equation (Eq. (1)) of attack at the phosphorus atom of diaryl chlorophosphate esters have previously been presented<sup>2</sup>.

$$\log(k/k_0) = lN_T + mY_X + c \quad (1)$$

In Eq. (1),  $k$  and  $k_0$  are the specific rates of solvolysis of a substrate in a given solvent and in 80% ethanol, respectively;  $l$  is the sensitivity toward

changes in solvent nucleophilicity ( $N_T$ );  $m$  is the sensitivity toward changes in solvent ionizing power ( $Y_X$ , for a leaving group X)<sup>3</sup>; and  $c$  is a constant (residual) term.

We now present parallel analyses for attack at the sulfur atom of several 4-substituted benzenesulfonyl chlorides (Scheme 1). The kinetics of solvolysis of several benzenesulfonyl chlorides, in a variety of solvents, have previously been reported<sup>4-12</sup> and recently reviewed<sup>13</sup>. The purpose of

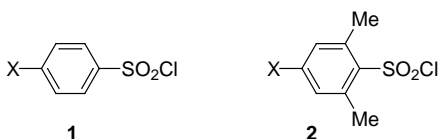


SCHEME 1

these analyses is two-fold: to see whether  $N_T$  values can be applied to attack at sulfur and, assuming reasonable correlations are obtained, to see what light can be shed upon the question<sup>13</sup> as to whether the mechanism of solvolysis is best considered as  $S_N2$ -type (one-step) or addition-elimination-type (two-steps). More recently<sup>8-10</sup>, it has been proposed that both pathways can operate side-by-side, with the addition-elimination pathway favored in less polar media and the concerted pathway favored in the more polar media (rich in water or 2,2,2-trifluoroethanol). Attempts to observe a dissociative mechanism by increases in steric hindrance and/or electron supply within the benzenesulfonyl chloride did not lead to any significant changes in the reactivity patterns<sup>11a</sup>, confirming that  $S_N1$  reactions of sulfonyl chlorides are usually less favorable than direct attack by solvent<sup>11b,12,14</sup>. There had been earlier reports<sup>4a,15</sup> favoring an interpretation for hydrolyses of moderately sterically hindered benzenesulfonyl chlorides in terms of  $S_N1$ -type mechanisms. These were rendered unlikely to be correct by the observation<sup>12</sup> that the solvolyses in the highly ionizing but weakly nucleophilic 2,2,2-trifluoroethanol (TFE)-water mixtures are relatively slow and show large negative entropies of activation. It is, however, possible that dissociative pathways can occur under extreme conditions, and formation of  $ArSO_2^+$  species has been claimed in studies of the solvolyses of benzenesulfonyl fluorides in concentrated sulfuric acid and weak oleum<sup>16</sup>.

## RESULTS AND DISCUSSION

The specific rate data have been assembled from several sources. The majority of the data are for the solvolyses at 25.0 °C of 4-methoxybenzenesulfonyl chloride (**1**, X = OMe) and 4-methylbenzenesulfonyl chloride (**1**, X = Me) and the corresponding 2,6-dimethyl substituted derivatives **2**. Most of these values are from publications by Bentley, Koo and coworkers<sup>9,10</sup>, supplemented, as indicated in footnotes to Table I, in three instances by addition of a value in 57.9% TFE (w/w), made available by Forbes and Maskill<sup>12</sup>. The 33–37 solvolyses used in the analyses involved studies in ethanol, methanol, and water, and in mixtures of water with ethanol, methanol, acetone,



dioxane, and TFE. Unfortunately, data in only one or, in one instance (for compound **2** where X = Me) two fluoroalcohol-containing solvents were available. The solvolyses included in the analyses were determined on the basis of the availability of both  $N_T$  and  $Y_{Cl}$  values, or their ready accessibility by accurate interpolation within available data. The regression analyses in terms of Eq. (1), carried out using the ABSTAT statistical package (Anderson-Bell, Arvada, Colorado, U.S.A.), are reported in Table I. Plots of  $N_T$  against  $Y_{Cl}$  for the solvents involved in the first four entries had correlation coefficients of 0.8881, 0.7333, 0.8984, and 0.7593, respectively.

Also reported in Table I are values obtained from specific rates of solvolyses at 35.0 °C for compounds of type **1**, with X = Me, H, or NO<sub>2</sub>. Only 13–16 values are available and the values are largely from Lee<sup>6</sup>, together with values interpolated from other temperatures, for water and aqueous dioxane mixtures<sup>4</sup>. For X = Me, an interpolated value, from studies at other temperatures<sup>12</sup>, for 57.9% (w/w) TFE was accessible and, for X = H or NO<sub>2</sub>, similarly interpolated values were accessible for aqueous acetone mixtures<sup>5</sup>. The three statistical analyses at 35.0 °C all led to a warning that the “results may be spurious due to multicollinearity”, and indeed, for the 13, 15, or 16 solvents involved, plots of  $N_T$  against  $Y_{Cl}$  had correlation coefficients of 0.920, 0.966, and 0.960, respectively. The major problem is a lack of solvents rich in fluoroalcohol, with 57.9% (w/w) aqueous TFE in one instance or 30 or 40% TFE in a mixture with ethanol in two instances representing the maximum TFE content. The 35.0 °C values are included in the

table despite the warning since the **1** ( $X = \text{Me}$ ) sensitivities are close to those obtained in the more rigorous analysis, with more than twice the number, and a better distribution, of solvents, at 25.0 °C. The  $m$  values are comparable in value and standard error to those obtained at 25.0 °C. The  $l$  values are also quite similar, but with much larger associated standard errors at 35.0 °C.

The good correlations obtained over the full range of solvents for the specific rates of solvolysis of each substrate suggest, but do not demand, a unity of mechanism. Certainly, if a solvent-induced change of mechanism does occur, the  $l$  and  $m$  values for the two pathways must be quite similar. The  $l$  values for compounds of type **1** in the range of  $1.10 \pm 0.17$  to  $1.39 \pm 0.50$  are consistent with a bimolecular attack of solvent and the magnitudes are consistent with the favored<sup>12,13</sup>  $\text{S}_{\text{N}}2$  mechanism, possibly with general-base catalysis<sup>9,10</sup>. The  $m$  values in the range from  $0.61 \pm 0.04$  to  $0.66 \pm 0.06$  are also consistent with an  $\text{S}_{\text{N}}2$  mechanism. It will be recalled that, for  $\text{S}_{\text{N}}2$  attack by solvent on methyl 4-methylbenzenesulfonate<sup>17</sup>, the  $l$  value is

TABLE I

Correlation of the specific rates of solvolysis of benzenesulfonyl chlorides (compounds **1** and **2**) using extended Grunwald–Winstein equation (Eq. (1))

Substrate (X)	$n^a$	$T, ^\circ\text{C}$	$l^b$	$m^b$	$c$	$s_{yx}^c$	$R^d$	$F^e$
<b>1</b> (Me)	33 <sup>f</sup>	25.0	$1.25 \pm 0.15$	$0.62 \pm 0.04$	0.21	0.20	0.967	216
<b>2</b> (Me)	37 <sup>g</sup>	25.0	$0.96 \pm 0.12$	$0.61 \pm 0.04$	0.24	0.34	0.936	119
<b>1</b> (OMe)	37 <sup>f</sup>	25.0	$1.10 \pm 0.17$	$0.61 \pm 0.04$	0.22	0.23	0.959	194
<b>2</b> (OMe)	36 <sup>h</sup>	25.0	$0.97 \pm 0.14$	$0.70 \pm 0.05$	0.13	0.35	0.940	125
<b>1</b> (Me)	13 <sup>i,j</sup>	35.0	$1.32 \pm 0.21$	$0.66 \pm 0.06$	0.20	0.20	0.975	95
<b>1</b> (H)	15 <sup>l,k</sup>	35.0	$1.24 \pm 0.32$	$0.64 \pm 0.08$	0.07	0.17	0.978	134
<b>1</b> ( $\text{NO}_2$ )	16 <sup>i,k</sup>	35.0	$1.39 \pm 0.50$	$0.65 \pm 0.13$	-0.05	0.28	0.933	44

<sup>a</sup> Number of solvents. <sup>b</sup> With associated standard errors. <sup>c</sup> Standard error of the estimate. <sup>d</sup> Correlation coefficient. <sup>e</sup> The  $F$ -test value. <sup>f</sup> Specific rate values from ref.<sup>10</sup>, except value for 57.9% TFE (w/w) from ref.<sup>12</sup>. <sup>g</sup> Specific rate values from ref.<sup>9</sup>, except value for 57.9% TFE (w/w) from ref.<sup>12</sup>. <sup>h</sup> Specific rate values from ref.<sup>10</sup>. <sup>i</sup> Specific rate values from ref.<sup>6</sup> plus values interpolated from studies at other temperatures for  $\text{H}_2\text{O}$  and aqueous dioxane mixtures reported in ref.<sup>4a</sup>. <sup>j</sup> Interpolated specific rate value from studies<sup>12</sup> at other temperatures available for 57.9% TFE. <sup>k</sup> Interpolated specific rate values for aqueous acetone mixtures from studies<sup>5</sup> at other temperatures.

$0.96 \pm 0.04$  and the  $m$  value is  $0.53 \pm 0.04$  (ref.<sup>1c</sup>), when  $N_T$  (ref.<sup>1</sup>) and  $Y_{OTs}$  (ref.<sup>3b</sup>) values are used within Eq. (1).

It is of interest that very similar  $l$  and  $m$  values are obtained after the addition of methyl groups in the two *ortho* positions of the benzene ring. This suggests very little steric hindrance to attack on the introduction of these methyl groups. Indeed, introduction of the 2,6-dimethyl groups into the substrate leads to increases in the specific rates of solvolysis<sup>8-10</sup>, and similar effects have been observed<sup>18</sup> for chloride-radiochloride exchange reactions in acetonitrile. Molecular mechanics calculations<sup>19</sup> indicate that steric screening is lowered by a reduction in the planarity of the ring which throws the sulfonyl group out of the plane, favoring a bimolecular attack by solvent of the  $S_N2$  type. However, steric factors do dominate with larger groups, and increasing reductions in the specific rates of solvolysis are observed on introduction of ethyl<sup>8a</sup> or isopropyl<sup>8a,11a</sup> groups into the *ortho* positions. In particular, our analyses give no evidence for a dissociative mechanism, even in solvents very rich in TFE. The distinction between  $S_N2$  and addition-elimination is more problematic, since no standard reactions of well determined detailed bimolecular mechanism are available for solvolyses at sulfur. We have indicated that the  $l$  and  $m$  values from our analyses are consistent with an  $S_N2$  process, but we cannot rule out the possibility, based on these sensitivity values, of the reaction being partially or totally addition-elimination in character. The appreciable second-order term observed<sup>12b</sup> on introduction of sodium trifluoroethoxide to solvolyses in 1 : 1 (v/v) water-TFE would be consistent with the operation of either mode of bimolecular attack.

In this regard, the proposal by Koo, Bentley and coworkers<sup>9,10</sup> of a duality of mechanism for the solvolyses of several benzenesulfonyl chlorides is based, in part, on a discontinuity in the plots of the logarithm of specific rates against  $Y_{Cl}$  values and, in part, on maxima observed in the selectivities for solvent attack as the composition of aqueous alcohol mixtures is varied. When there is evidence for appreciable nucleophilic participation by the solvent, attempts to interpret linear free energy plots for a given binary mixture made only against  $Y_{Cl}$  values are fraught with danger. Frequently, it is found that there is a region of solvent composition, rich in organic components, where the  $N$  values are linearly related to the  $Y$  values<sup>20</sup>. If Eq. (1) holds, the plots against  $Y_{Cl}$  will, therefore, be linear in this region. In the more aqueous region, the relationship will be very much influenced by the way in which the  $N_T$  versus  $Y_{Cl}$  relationship changes with solvent composition and deviations from the linear relationship established for the organic-rich region are to be expected. Such behavior could quite possibly, to

a reasonable approximation, be interpreted in terms of two linear regions. For aqueous methanol and aqueous ethanol, the linear region of  $N$  versus  $Y$  was found to be for solvent compositions of 100–40% alcohol (by volume)<sup>20c</sup>. With the  $Y_{Cl}$  values being 3.25 for 40% methanol and 2.75 for 40% ethanol<sup>3</sup>, these lower organic compound limit values are extremely close to the  $Y_{Cl}$  values at which the changeover of mechanism was proposed to occur<sup>9,10</sup>. Hence, it is possible that the nonlinear nature of the plots against  $Y_{Cl}$  may actually involve only one mechanism, incorporating appreciable nucleophilic participation, and the one-term (simple) Grunwald–Winstein plots can be rationalized without the need for a duality of mechanism.

To summarize, the correlation analyses using the extended Grunwald–Winstein equation can be rationalized in terms of one mechanism, probably  $S_N2$  attack at sulfur, over the full range of the solvents and substituents which have been investigated.

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