

## Product-Rate Correlations for Solvolyses of 2,4-Dimethoxybenzenesulfonyl Chloride

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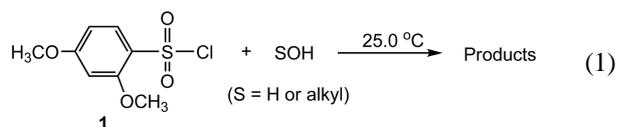
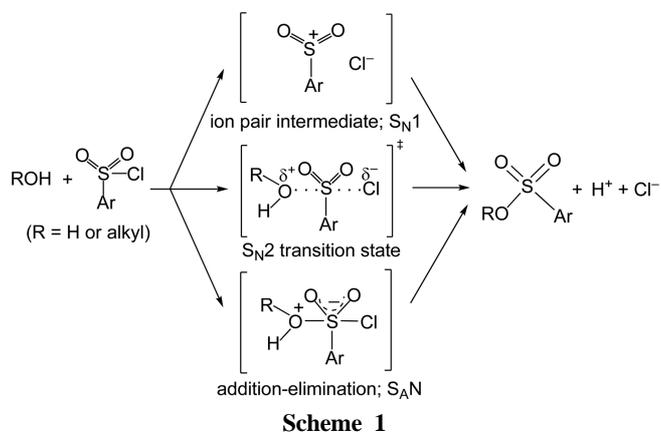
The solvolysis rate constants of 2,4-dimethoxybenzenesulfonyl chloride (**1**) in 30 different solvents are well correlated with the extended Grunwald-Winstein equation, using the  $N_T$  solvent nucleophilicity scale and  $Y_{Cl}$  solvent ionizing scale, with sensitivity values of  $0.93 \pm 0.14$  and  $0.65 \pm 0.06$  for  $l$  and  $m$ , respectively. These  $l$  and  $m$  values can be considered to support a  $S_N2$  reaction pathway. The activation enthalpies ( $\Delta H^\ddagger$ ) were 12.4 to 14.6 kcal·mol<sup>-1</sup> and the activation entropies ( $\Delta S^\ddagger$ ) were  $-15.5$  to  $-32.3$  cal·mol<sup>-1</sup>·K<sup>-1</sup>, which is consistent with the proposed bimolecular reaction mechanism. The solvent kinetic isotope effects (SKIE) were 1.74 to 1.86, which is also in accord with the  $S_N2$  mechanism and was possibly assisted using a general-base catalysis. The values of product selectivity ( $S$ ) for solvolyses of **1** in alcohol/water mixtures was 0.57 to 6.5, which is also consistent with the proposed bimolecular reaction mechanism. Third-order rate constants,  $k_{ww}$  and  $k_{aa}$ , were calculated from the rate constants ( $k_{obs}$ ), together with  $k_{aw}$  and  $k_{wa}$  calculated from the intercept and slope of the plot of  $1/S$  vs. [water]/[alcohol]. The calculated rate constants,  $k_{calc}$  ( $k_{ww}$ ,  $k_{aw}$ ,  $k_{wa}$  and  $k_{aa}$ ), are in satisfactory agreement with the experimental values, supporting the stoichiometric solvation effect analysis.

**Key Words** : Extended Grunwald-Winstein equation,  $S_N2$  mechanism, Solvent kinetic isotope effect, Product selectivity, Third-order rate constant

## Introduction

The substituted benzenesulfonyl chlorides are important reagents in organic chemistry for activating alcohol groups,<sup>1</sup> and their solvolyses and nucleophilic substitution reactions bridge inorganic and organic chemistry.<sup>2</sup> Studies of solvolyses of benzenesulfonyl chloride derivatives hardly distinguish the mechanism of simple nucleophilic substitutions. However, there has been much dispute over whether the mechanism is an ion pair (I.P or  $S_N1$ ),  $S_N2$  or addition-elimination (A-E) processes. Three possible pathways for a solvolysis reaction are presented in Scheme 1. The  $S_N2$  reaction coordinate is the one expected for a symmetrical process in which S-Cl bond cleavage and O-S bond formation proceed at the same rate. The transition state for this process will have trigonal bipyramidal transition state and no charge development on the center of S. The  $S_{AN}$  reaction coordinate goes through an intermediate of addition compound, whereas  $S_{N1}$  goes through an intermediate of fully broken bond.<sup>3</sup> Earlier researchers reported the results of *di*- and *tri*-substituted substrates<sup>4</sup> including the effects of steric hindrance on the *ortho*-position and resonance on the *ortho* and *para*-position of a benzene ring.

Because the steric hindrance of the *ortho*-substituent prevents the bimolecular character at the sulfur from being a reaction center, and also the resonance effect of the *ortho* and *para*-substituent helps the unimolecular characters in solvolysis. In order to gain further understanding about the mechanism of a sulfonyl compound, a kinetic study was undertaken of the solvolysis of **2** (*ortho*), **4** (*para*)-dimethoxybenzenesulfonyl chloride (**1**) in a variety of pure and binary solvents at 25.0 °C, shown as Eq. (1). Furthermore, the  $l$  and  $m$  values were determined using the extended Grunwald-Winstein equation, together with the enthalpies and entropies of activation, the solvent kinetic isotope effect (SKIE), product selectivity ( $S$ ) and third-order rate constants ( $k_{ww}$ ,  $k_{aw}$ ,  $k_{wa}$  and  $k_{aa}$ ).



## Experimental

The solvents for the kinetic studies and for HPLC were

described previously.<sup>9a,25</sup> The substrate, **1**, was Alpha GR purchased. D<sub>2</sub>O and CH<sub>3</sub>OD were Aldrich (99.9%D). Distilled water was redistilled in a Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain a specific conductivity of less than  $1 \times 10^{-6}$  scm<sup>-1</sup>. The kinetic experiments were performed by allowing a conductivity cell containing 5 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. Then, a 5  $\mu$ L portion of a 1.0 mol dm<sup>-3</sup> stock solution of **1** in acetonitrile was added. The monitoring of the conductivity increases with time and the rate constant calculations were conducted as previously reported.<sup>9a,25</sup> Multiple regression analyses were performed using commercially available packages.

The solvolysis products (ester and acid) were determined by HPLC analysis as reported previously,<sup>21,27</sup> and the product selectivities (*S*) were calculated from Eq. (4). The *S* values were calculated from the observed peak area ratios of ester and acid divided by the appropriate response factor. For response calibrations, area ratios from the solvolyses of **1** in pure alcohol and in 40% acetonitrile-water mixtures were used. The eluant was a 60% methanol-water mixture and the flow rate was adjusted to 1 mL min<sup>-1</sup>. The HPLC system was a Hewlett-Packard 1050 Series instrument, with 250  $\times$  4 mm Spherisorb ODS reversed phase column.

## Results and Discussion

The rate constants (*k*) for the solvolysis of **1** were determined at 25.0 °C in 30 solvents. The solvents consisted of ethanol, methanol, and binary mixtures of water with ethanol, methanol, acetone, and 2,2,2-trifluoroethanol (TFE). These values are reported in Table 1, together with the solvent nucleophilicity (*N<sub>T</sub>*)<sup>5</sup> and solvent ionizing power (*Y<sub>Cl</sub>*)<sup>6</sup> values. The rate constants increased as the amount of water in the binary solvent systems was increased as shown in Table 1. This phenomenon supports an interpretation that the solvolysis of **1** is dominated by a bimolecular reaction mechanism. Generally, for a bimolecular reaction, it is to be expected that the rate constants are highest in the nucleophilic solvent systems and lowest in the electrophilic solvent systems, as was observed.

*tert*-Butyl chloride is the model substrate for the Winstein-Grunwald equation, Eq. (2), where *k* is the rate of solvolysis in any solvent relative to *k<sub>o</sub>* for 80% v/v ethanol/water; *m* is the response to solvent ionizing power *Y*, defined by *m* = 1 for solvolyses of *tert*-butyl chloride at 25.0 °C for S<sub>N</sub>1 processes. It is assumed that solvolyses of *tert*-butyl chloride are insensitive to solvent nucleophilicity.<sup>7</sup> A second term was suggested, which is governed by the sensitivity *l* to solvent nucleophilicity, for solvolyses for participating S<sub>N</sub>2 reactions. The resulting Eq. (3) is often referred to as an extended Winstein-Grunwald equation.<sup>8</sup> Again, application of Eq. (3) to the solvolyses of *tert*-butyl chloride plays a key role: *l* = 0 and *m* = 1 where *l* = 0 implies model S<sub>N</sub>1 behavior.<sup>8b</sup>

$$\log(k/k_o) = mY \quad (2)$$

$$\log(k/k_o) = lN + mY \quad (3)$$

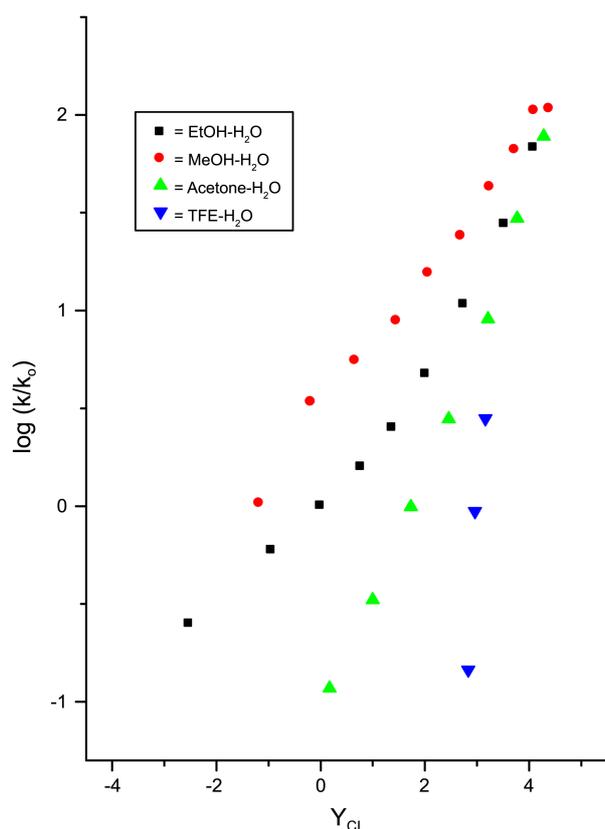
**Table 1.** Rate constants for the solvolyses of **1** in binary solvent mixtures at 25.0 °C and the *N<sub>T</sub>* and the *Y<sub>Cl</sub>* values for the solvent<sup>d</sup>

Solvent (%) <sup>b</sup>	<i>N<sub>T</sub></i> <sup>c</sup>	<i>Y<sub>Cl</sub></i> <sup>d</sup>	<i>k</i> (s <sup>-1</sup> )
100EtOH	0.37	-2.52	1.97 $\times 10^{-5}$
90EtOH	0.16	-0.94	4.68 $\times 10^{-5}$
80EtOH	0.00	0.00	7.90 $\times 10^{-5}$
70EtOH	-0.20	0.78	1.25 $\times 10^{-4}$
60EtOH	-0.39	1.38	1.98 $\times 10^{-4}$
50EtOH	-0.58	2.02	3.73 $\times 10^{-4}$
40EtOH	-0.74	2.75	8.46 $\times 10^{-4}$
30EtOH	-0.93	3.53	2.20 $\times 10^{-3}$
20EtOH	-1.16	4.09	5.37 $\times 10^{-3}$
H <sub>2</sub> O	-1.38	4.57	1.39 $\times 10^{-2}$
100MeOH	0.17	-1.17	8.13 $\times 10^{-5}$
90MeOH	-0.01	-0.18	2.68 $\times 10^{-4}$
80MeOH	-0.06	0.67	4.36 $\times 10^{-4}$
70MeOH	-0.40	1.46	6.98 $\times 10^{-4}$
60MeOH	-0.54	2.07	1.21 $\times 10^{-3}$
50MeOH	-0.57	2.70	1.91 $\times 10^{-3}$
40MeOH	-0.87	3.25	3.35 $\times 10^{-3}$
30MeOH	-1.06	3.73	5.25 $\times 10^{-3}$
20MeOH	-1.23	4.10	8.24 $\times 10^{-3}$
10MeOH	-1.36	4.39	8.51 $\times 10^{-3}$
70Acetone	-0.42	0.17	9.27 $\times 10^{-6}$
60Acetone	-0.52	1.00	2.62 $\times 10^{-5}$
50Acetone	-0.70	1.73	7.82 $\times 10^{-5}$
40Acetone	-0.83	2.46	2.20 $\times 10^{-4}$
30Acetone	-0.96	3.21	7.13 $\times 10^{-4}$
20Acetone	-1.11	3.77	2.34 $\times 10^{-3}$
10Acetone	-1.23	4.28	6.07 $\times 10^{-3}$
97TFE <sup>e</sup>	-3.30	2.83	1.15 $\times 10^{-5}$
70TFE	-1.98	2.96	8.41 $\times 10^{-5}$
50TFE	-1.73	3.16	2.21 $\times 10^{-4}$

<sup>a</sup>Unless otherwise indicated, a 1.0 mol dm<sup>-3</sup> solution of the substrate in the indicated solvent, containing 0.1% CH<sub>3</sub>CN. <sup>b</sup>On a volume-volume content at 25.0 °C, and the other component is water. <sup>c</sup>Values from ref. 5. <sup>d</sup>Values from ref. 6. <sup>e</sup>Solvent prepared on a weight-weight basis at 25.0 °C, and the other component is water.

The overall analysis by the simple Grunwald-Winstein equation showed considerable deviation (Figure 1), even if each individual binary solvent system showed a good linear relationship. This strongly suggests that the solvolysis of this compound is sensitive to both solvent nucleophilicity and solvent ionizing power.

The extended Grunwald-Winstein equation, Eq. (3), is useful for determining the extent of nucleophilic participation using the solvent because the magnitudes of *l* and *m* in Eq. (3) are the indicators used to determine whether a nucleophilic substitution reaction proceeds through an unimolecular, (S<sub>N</sub>1, *i.e.*, *l*  $\approx$  0 and *m*  $\approx$  1) or a bimolecular reaction, (S<sub>N</sub>2, *i.e.*, *l*  $\approx$  1.0 and *m*  $\approx$  0.5) and an addition-elimination mechanism (*i.e.*, *l*  $\approx$  1.5 and *m*  $\approx$  0.6). Therefore, the determination of the *l* and *m* values would provide valuable information concerning the structure of the transition state for the solvolyses.<sup>5,9</sup>



**Figure 1.** Plot of  $\log(k/k_0)$  for the solvolysis of **1** against  $Y_{Cl}$ .

Application of Eq. (3) to the solvolyses of **1** led to only moderately good correlations. For 30 solvents, with use of the Eq. (3),  $l$ , and  $m$  values of  $0.93 \pm 0.14$ , and  $0.65 \pm 0.06$  the standard error of the estimate was 0.3 and the correlation coefficient ( $R$ ) value was 0.918. This relationship is presented graphically in Figure 2.

The  $l$  value of 0.93 was smaller than those recently reported for reactions proceeding through an addition-elimination mechanism ( $l \approx 1.5$ ), whereas these values were similar to those previously reported for the bimolecular solvolyses of diphenylthiophosphinyl chloride<sup>10</sup> ( $l = 1.0$ ), allyl chloroformate<sup>11</sup> ( $l = 0.93$ ), 9-fluorenyl chloroformate<sup>12</sup> ( $l = 0.95$ ), and  $N,N,N',N'$ -tetramethyldiamidophosphoro-chloridate<sup>13</sup> ( $l = 1.14$ ). This suggests an  $S_N2$  mechanism involving nucleophilic attack by the solvent at sulfur atom of **1**. The solvolysis of **1**, where bond making ( $l = 0.93$ ) is more progressed than bond breaking ( $m = 0.65$ ), and the values are still in the range of the  $S_N2$  mechanism, reflects the degree of the nucleophilic assistance based on the measure of solvent nucleophile.<sup>9c,d,10-13</sup>

Recent interpretations for attack at sulfur have been in terms of bimolecular attack, but with some degree of uncertainty as to whether this is concerted or stepwise. Bentley, Jones and Koo<sup>14</sup> suggested that both mechanisms can operate, with the concerted mechanism favored in the more polar solvents. A fairly recent review<sup>15</sup> favored an interpretation of a concerted bimolecular displacement ( $S_N2$ ) mechanism, involving an attack by solvent at sulfur. Our analyses are considered to be consistent with such an explanation.

Accordingly, rate constants for solvolysis in the mixtures of ethanol-water, methanol-water and acetone-water were measured in the range between 25.0 °C and 45.0 °C; the corresponding rate constant at 0.0 °C was calculated by the extrapolation method using the Arrhenius equation.<sup>16</sup> The activation parameters,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , for solvolysis of **1** are summarized in Table 2. Relatively small  $\Delta H^\ddagger$  (12.4–14.6 kcal·mol<sup>-1</sup>) and large negative  $\Delta S^\ddagger$  (–15.5–32.3 cal·mol<sup>-1</sup>·K<sup>-1</sup>) values are as expected for bimolecular reactions with polar transition states.<sup>17</sup>

The kinetic isotope effect, a change of rate that occurs upon isotopic substitution, is a widely used tool for elucidating reaction mechanism. The most common isotopic substitution is D for H. The solvent kinetic isotope effects (SKIE,  $k_{MeOH}/k_{MeOD}$  and  $k_{H_2O}/k_{D_2O}$ ) are frequently observed when reactions are carried out in solvents with O-H (O-D) groups, ordinarily water or alcohols.

Their measurement can give information about mechanisms involving processes like acid catalysis.<sup>18</sup> The solvent kinetic isotope effects of 1.74–1.86 were observed at 25.0 °C (Table 3). These are within the SKIE values of 1.43–2.35, which were reported for the corresponding solvolyses of benzyl chloride<sup>19</sup> ( $k_{H_2O}/k_{D_2O} = 1.43$ ), benzoyl chloride<sup>19</sup> ( $k_{MeOH}/k_{MeOD} = 1.55$ ), diphenylthiophosphinyl-chloride<sup>20</sup> ( $k_{MeOH}/k_{MeOD} = 1.83$ ) and a series of benzene-sulfonyl chlorides<sup>21</sup> ( $k_{MeOH}/k_{MeOD} = 1.58$ –2.39) at 25.0 °C in which the reactions were believed to be  $S_N2$  in character.

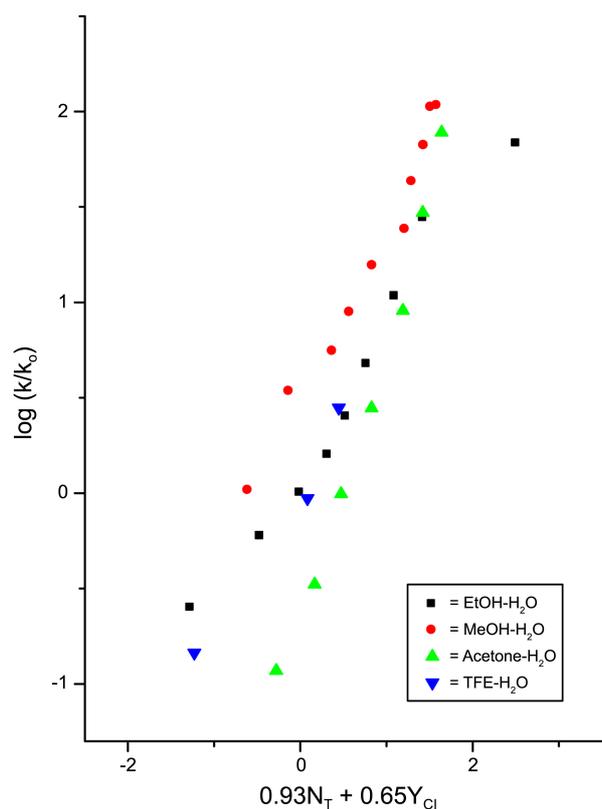
**Table 2.** Rate constants and activation parameters for the solvolyses of **1**<sup>a</sup> at various temperatures

Solvent (%) <sup>b</sup>	T (°C)	$k$ (s <sup>-1</sup> ) <sup>c</sup>	$\Delta H^\ddagger$ (kcal/mol)	$-\Delta S^\ddagger$ (cal/mol·K)
80EtOH	25	$7.90 \times 10^{-5}$	12.6	32.3
	35	$1.50 \times 10^{-4}$		
	45	$3.22 \times 10^{-4}$		
50EtOH	25	$3.73 \times 10^{-4}$	14.6	21.1
	35	$7.14 \times 10^{-4}$		
	45	$1.87 \times 10^{-3}$		
80MeOH	25	$4.36 \times 10^{-4}$	12.8	27.6
	35	$7.65 \times 10^{-4}$		
	45	$1.81 \times 10^{-3}$		
50Acetone	25	$7.82 \times 10^{-5}$	14.6	15.5
	35	$1.65 \times 10^{-4}$		
	45	$3.94 \times 10^{-4}$		

<sup>a</sup>A 1.0 mol dm<sup>-3</sup> solution of the substrate in the indicated solvent, also containing 0.1% CH<sub>3</sub>CN. <sup>b</sup>On a volume-volume content at 25.0 °C, and the other component is water. <sup>c</sup>Averages of three or more runs. <sup>d</sup>The activation parameters are accompanied by the standard error.

**Table 3.** Kinetic solvent isotope effects (KSIE) for solvolyses of **1** at 25.0 °C

Solvent	$k_{SOH}$ (s)	$k_{SOD}$ (s)	KSIE
100% MeOH	$8.13 \times 10^{-5}$	$4.68 \times 10^{-5}$	1.74
50% MeOH	$1.91 \times 10^{-3}$	$1.09 \times 10^{-3}$	1.76
Water	$1.39 \times 10^{-2}$	$7.48 \times 10^{-3}$	1.86

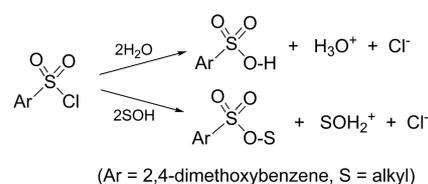


**Figure 2.** Plot of  $\log(k/k_0)$  for the solvolysis of **1** at 25 °C against  $(0.93N_T + 0.65Y_{Cl})$ .

The  $l$  to  $m$  ratios have also been suggested as a useful mechanistic criteria. The  $l/m$  values from the extended Grunwald-Winstein equation could be classified into two classes of mechanism;  $l/m$  values of 1.2 to 3.5 for bimolecular mechanism ( $S_N2$ ) or an addition-elimination pathway (A-E), and  $l/m$  values below 0.7 for an ionization pathway (I.P).<sup>17</sup>

For the solvolysis of **1**, the  $l/m$  value was 1.4 which is similar to those of previous studies investigating the solvolyses of diphenylphosphinyl chloride<sup>22</sup> ( $l/m = 1.6$ ),  $N,N$ -dimethylsulfamoyl chloride<sup>23</sup> ( $l/m = 1.7$ ),  $N,N,N',N'$ -tetramethyldiamidophosphorochloridate<sup>24</sup> ( $l/m = 1.8$ ), and these similarities suggest the existence of a bimolecular mechanism ( $S_N2$ ) or an addition-elimination pathway (A-E).

In addition, the  $k_{80\%EtOH}/k_{100\%EtOH}$  ratio has also been suggested as a useful mechanistic criterion.<sup>21,25</sup> The  $k_{80\%EtOH}/k_{100\%EtOH}$  values of 95 to 320 are considered to represent the  $S_N1$  reaction or ionization pathway.<sup>4a,7a</sup> In contrast, several  $k_{80\%EtOH}/k_{100\%EtOH}$  values were reported for the proposed  $S_N2$  reactions: the solvolyses of methyl chloroformate<sup>24</sup> ( $k_{80\%EtOH}/k_{100\%EtOH} = 4.0$ ), isopropenyl chloroformate<sup>25</sup> ( $k_{80\%EtOH}/k_{100\%EtOH} = 2.0$ ), benzyl chloroformate<sup>9c</sup> ( $k_{80\%EtOH}/k_{100\%EtOH} = 3.4$ ), and  $p$ -methylbenzoyl chloride<sup>21</sup> ( $k_{80\%EtOH}/k_{100\%EtOH} = 5.3$ ). These values ( $k_{80\%EtOH}/k_{100\%EtOH} = 2.0$ -5.3) have less sensitivity due to the solvent ionizing power. The  $k_{80\%EtOH}/k_{100\%EtOH}$  value of 4.0 obtained for the solvolysis of **1** is similar to those obtained from the four substrates that are believed to proceed through the  $S_N2$  mechanism.



**Scheme 2**

The product formation through reactions with water produces of aromatic sulfonic acid HCl ( $\text{H}_3\text{O}^+ + \text{Cl}^-$ ) and the reaction with an alcohol produces sulfonic ester and HCl ( $\text{SOH}_2^+ + \text{Cl}^-$ ). The situation is summarized in Scheme 2. If a water-alcohol solvent is used, the reaction, as presented in Scheme 2, is simplified in that the second solvent molecule, which is used to extract the proton from the molecule serving as the nucleophile, could be either water or alcohol. Furthermore, the amounts of each of the two protonated solvent species shown are determined *via* a rapid equilibrium within the mixed solvent.

The partitioning ratio ( $[\text{ester}]/[\text{acid}]$ ) is used in conjunction with the molar composition ratio for the solvent involved ( $[\text{H}_2\text{O}]/[\text{SOH}]$ ) in order to calculate the selectivity value ( $S$ ), as defined in Eq. (4). The values for the percentages of reactions proceeding with ether formation

$$S = \frac{[\text{Ester in product}]}{[\text{Acid in product}]} \times \frac{[\text{Water in solvent}]}{[\text{Alcohol in solvent}]} \quad (4)$$

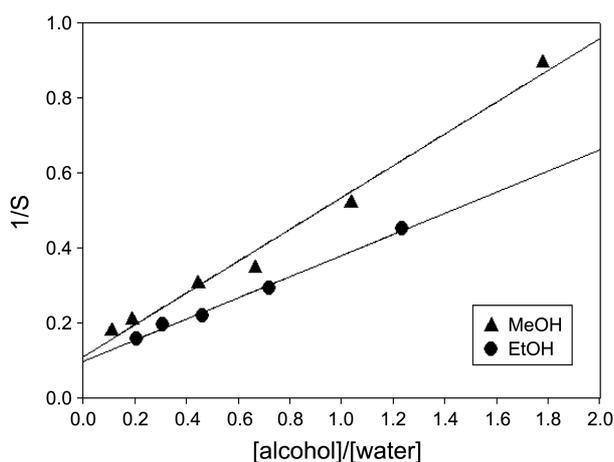
(x%) for solvolyses of **1**, at 25.0 °C, in mixtures of water with ethanol and methanol are reported in Table 4. Selectivity data were obtained from product analyses as soon possible after completion of 10 half-lives of reaction. The  $S$  values were obtained using in Eq. (4), which are also presented in Table 4.

The product selectivities ( $S$ ) reveal that for aqueous ethanol and methanol mixtures the selectivity increases with increases in the water content; thus, the reactivity-selectivity principle (RSP)<sup>26</sup> is not followed in ethanol and methanol mixtures. The greater value of  $S$  in the more aqueous media for **1** is a

**Table 4.** Selectivities ( $S$ ) for the solvolyses of **1** in alcohol-water mixtures after one half-life at 25.0 °C.<sup>a,b</sup>

Alcohol <sup>b</sup> (% v/v)	Methanol		Ethanol	
	[ester]/[acid]	$S$	[ester]/[acid]	$S$
90	2.3	0.57	2.6	0.94
80	2.0	1.1	2.7	2.2
70	2.0	1.9	2.4	3.4
60	1.9	2.9	2.1	4.6
50	1.5	3.3	1.6	5.7
40	1.5	5.0	1.3	6.5
30	0.91	4.8	0.79	5.9
20	0.62	5.6	0.38	4.8
10	0.19	3.8	0.15	4.4

<sup>a</sup>Determined by duplicate HPLC analyses of two solutions of each solvent composition; average deviation < 1.0%. <sup>b</sup>Injected 5  $\mu\text{L}$  of a 5% solution of **1** in acetonitrile into 5 mL of solvent. <sup>c</sup>Volume/volume basis at 25.0 °C.



**Figure 3.** Correlation of  $1/S$  and alcohol-water molar ratio for solvolyses of **1**. For methanol-water: slope = 0.424, intercept = 0.112,  $r = 0.993$ . For ethanol-water: slope = 0.281, intercept = 0.101,  $r = 0.997$ .

**Table 5.** Third-order rate constants,  $k_{ww}$ ,  $k_{aw}$ ,  $k_{wa}$ , and  $k_{aa}$ , for solvolyses of **1** in alcohol-water mixtures

Solvent	$k_{\text{calc}} (10^{-5} \text{ M}^{-2}\text{s}^{-1})$			
	$k_{ww}$	$k_{aw}$	$k_{wa}$	$k_{aa}$
Methanol	0.456	4.45	1.91	0.0133
Ethanol	0.456	3.86	1.09	0.00670

strong indication that the role of alcohol as a nucleophile is important while the effect of the ionizing power is insignificant in the product-determining step of the reaction of **1**. Similar selectivity changes have been shown to be typical for a general bimolecular reaction mechanism channel in aqueous alcohol media.<sup>27</sup>

Third-order rate constants,  $k_{ww}$  and  $k_{aa}$ , were calculated from the rate constants ( $k_{\text{obs}}$ ), together with  $k_{aw}$  and  $k_{wa}$  calculated from the intercept and slope of the plot of  $1/S$  vs.  $[\text{water}]/[\text{alcohol}]$  (eqs. 5, 6). According to the third-order treatment, the individual contributions

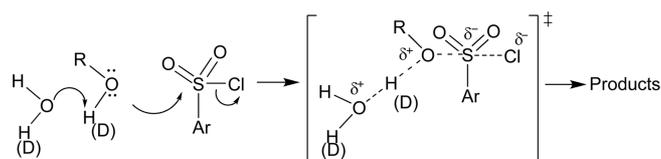
$$k_{\text{obs}} = k_{\text{aa}}[\text{ROH}]^2 + (k_{\text{aw}} + k_{\text{wa}})[\text{ROH}][\text{H}_2\text{O}] + k_{\text{ww}}[\text{H}_2\text{O}]^2 \quad (5)$$

$$1/S = (k_{\text{wa}}/k_{\text{aw}}) \times ([\text{ROH}]/[\text{H}_2\text{O}]) + k_{\text{ww}}/k_{\text{aw}} \quad (6)$$

of the four third-order terms to the observed first order rate constants (Table 5) show that  $k_{\text{aw}}$  makes the largest contribution *i.e.*, alcohol is acting as a nucleophile and water is acting as a general base catalyst.

### Conclusion

The application of the extended Grunwald-Winstein equation to the solvolysis of **1** led to an  $l$  value of 0.93 and an  $m$  value of 0.65. It can be concluded that the solvolysis of **1** proceeds through an  $S_N2$  mechanism (Scheme 3), in which the bond making ( $l = 0.93$ ) is more progressed than the bond breaking ( $m = 0.65$ ) based on the magnitudes of  $l$  and  $m$ . This conclusion can be further supported by reasonable



**Scheme 3**

activation parameters (*i.e.*, relatively small  $\Delta H^\ddagger$  and large negative  $\Delta S^\ddagger$ ) and the solvent kinetic isotope effects (1.74–1.86). The selectivity values ( $S$ ) obtained in the binary solvents were consistent with the proposed mechanism. Third-order rate constants,  $k_{ww}$  and  $k_{aa}$ , were calculated from the rate constants, together with  $k_{aw}$  and  $k_{wa}$  calculated from the intercept and slope of the plot of  $1/S$  vs.  $[\text{water}]/[\text{alcohol}]$ . The calculated third-order rate constants,  $k_{\text{calc}}$  ( $k_{ww}$ ,  $k_{aw}$ ,  $k_{wa}$  and  $k_{aa}$ ), are in satisfactory agreement with the experimental values, supporting the stoichiometric solvation effect analysis.

### References

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