

Rate and Product Studies of 5-Dimethylamino-Naphthalene-1-Sulfonyl Chloride under Solvolytic Conditions

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The solvolysis rate constants of 5-dimethylamino-naphthalene-1-sulfonyl chloride ((CH₃)₂NC₁₀H₆SO₂Cl, **1**) in 31 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 0.96 ± 0.09 and 0.53 ± 0.03 for *l* and *m*, respectively; the correlation coefficient value was 0.955. These *l* and *m* values can be considered to support an S_N2 reaction pathway having a transition state (TS) structure similar to that of the benzenesulfonyl chloride reaction. This interpretation is further supported by the activation parameters, *i.e.*, relatively small positive Δ*H*[‡] (12.0 to 15.9 kcal·mol⁻¹) and large negative Δ*S*[‡] (-23.1 to -36.3 cal·mol⁻¹·K⁻¹) values, and the solvent kinetic isotope effects (SKIEs, 1.34 to 1.88). Also, the selectivity values (*S* = 1.2 to 2.9) obtained in binary solvents are consistent with the proposed mechanism.

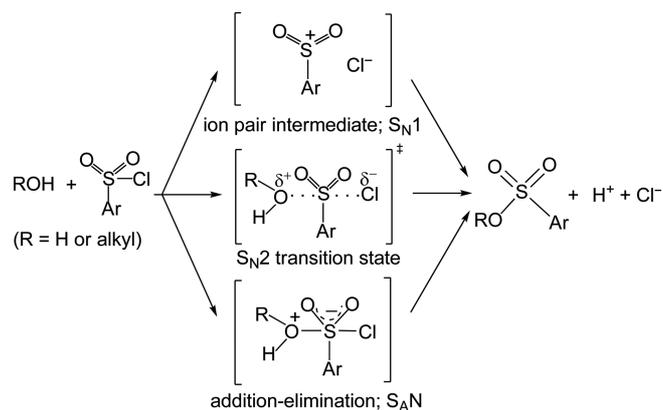
Key Words : 5-Dimethylamino-naphthalene-1-sulfonyl chloride, Extended Grunwald-Winstein equation, S_N2 mechanism, Solvent kinetic isotope effect, Product selectivity

Introduction

5-Dimethylamino-naphthalene-1-sulfonyl chloride (**1**) is used as a fluorescent label in immunofluorescence methods and in yielding fluorescent *N*-terminal amino acids and peptide derivatives. The molecular structure of **1** is similar to carbamoyl compounds involved in the biosynthesis of the pyrimidine ring and DNSC is used in studying sulfa drugs interfering with the metabolic processes in bacteria which require pyrimidine biosynthesis.¹ Substrate **1** reacts with primary amino groups in both aliphatic and aromatic amines to produce stable blue- or blue-green-fluorescent sulfonamide adducts. It can also be made to react with secondary amines. Substrate **1** is widely used to modify amino acids, specifically, protein sequencing and amino acid analysis. It can also be used to label functional groups of hydroxyl and carboxyl acids.² Substrate **1** is similar to benzenesulfonyl chloride and readily reacts with the nucleophiles like alcohols or water. If the nucleophile is an alcohol, the product is a sulfonic ester; if the nucleophile is water, the product is a sulfonic acid.

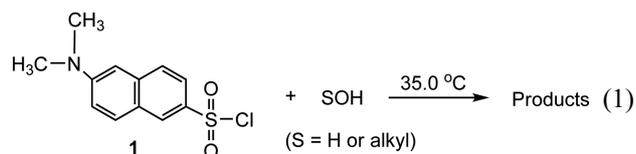
Solvolysis of benzenesulfonyl chloride derivatives has been intensively investigated because it is one of the important reagents in organic chemistry for activating alcohol groups.³ The reactions of benzenesulfonyl chloride derivatives with binary solvent mixtures have been reported to proceed through either an S_N1 (ion pair) or S_N2 pathway with addition-elimination (S_AN) processes depending on the reaction conditions. These possible pathways for a solvolysis reaction are presented in Scheme 1.⁴

We investigated the solvolysis of 5-dimethylamino-naphthalene-1-sulfonyl chloride (**1**) in a variety of pure and binary solvents at 35.0 °C to reveal the reactivity and reac-



Scheme 1

tion mechanism shown as Eq. (1). Furthermore, we discussed the *l* and *m* values, which had been determined using the extended Grunwald-Winstein equation, together with the activation parameters, the solvent kinetic isotope effects (SKIEs), and the product selectivity (*S*).



Results and Discussion

The rate constants (*k*) of solvolysis were determined by a rapid response conductivity technique for **1** in 31 solvents at 35.0 °C. The solvents used in this study consisted of ethanol, methanol, and binary mixtures of water with ethanol,

methanol, acetone, and 2,2,2-trifluoroethanol (TFE). The measured rate constants are presented in Table 1, together with the literature values for N_T ⁵ and Y_{Cl} ⁶. The rate increases in the order of acetone-H₂O < ethanol-H₂O < methanol-H₂O and the rate increases as the ratio of water increases in the binary solvent systems as shown in Table 1. These results imply that the solvolysis of **1** is dominated by a bimolecular reaction mechanism. Generally, for a bimolecular reaction, it has been reported that the rate constants are higher in the nucleophilic solvent systems and lower in the electrophilic solvent systems.⁶

The linear free energy relationship developed by Grunwald and Winstein has accepted as a useful tool in describing the correlation of the rate constants of solvolysis. The initial Grunwald-Winstein equation⁷ (eq. 2) considered the sensitivity to change in only one parameter, the solvent ionizing power (Y_{Cl}). In this equation, m is a sensitivity and it can be

Table 1. Rate constants for the solvolyses of **1** in binary solvent mixtures at 35.0 °C and the N_T and the Y_{Cl} values for the solvents^a

Solvent (%) ^b	N_T ^c	Y_{Cl} ^d	k (s ⁻¹)
100 EtOH	0.37	-2.52	3.80×10^{-5}
90 EtOH	0.16	-0.94	1.05×10^{-4}
80 EtOH	0.00	0.00	1.69×10^{-4}
70 EtOH	-0.20	0.78	2.40×10^{-4}
60 EtOH	-0.39	1.38	4.79×10^{-4}
50 EtOH	-0.58	2.02	6.17×10^{-4}
40 EtOH	-0.74	2.75	1.10×10^{-3}
30 EtOH	-0.93	3.53	1.74×10^{-3}
20 EtOH	-1.16	4.09	2.63×10^{-3}
100 MeOH	0.17	-1.17	2.14×10^{-4}
90 MeOH	-0.01	-0.18	4.79×10^{-4}
80 MeOH	-0.06	0.67	7.59×10^{-4}
70 MeOH	-0.40	1.46	1.10×10^{-3}
60 MeOH	-0.54	2.07	1.54×10^{-3}
50 MeOH	-0.57	2.70	2.00×10^{-3}
40 MeOH	-0.87	3.25	3.47×10^{-3}
30 MeOH	-1.06	3.73	4.07×10^{-3}
20 MeOH	-1.23	4.10	5.25×10^{-3}
10 MeOH	-1.36	4.39	5.89×10^{-3}
90 Acetone	-0.35	-2.39	7.76×10^{-6}
80 Acetone	-0.37	-0.83	3.09×10^{-5}
70 Acetone	-0.42	0.17	8.13×10^{-5}
60 Acetone	-0.52	1.00	1.45×10^{-4}
50 Acetone	-0.70	1.73	3.39×10^{-4}
40 Acetone	-0.83	2.46	6.17×10^{-4}
30 Acetone	-0.96	3.21	1.23×10^{-3}
20 Acetone	-1.11	3.77	2.09×10^{-3}
90 TFE ^e	-2.55	2.85	7.08×10^{-5}
80 TFE	-2.19	2.90	7.76×10^{-5}
70 TFE	-1.98	2.96	8.51×10^{-5}
50 TFE	-1.73	3.16	1.20×10^{-4}

^aUnless otherwise indicated, a 1.0 mol dm⁻³ solution of the substrate in the indicated solvent, containing 0.1% CH₃CN. ^bOn a volume-volume content at 25.0 °C, and the other component is water. ^cValues from ref. 5. ^dValues from ref. 6. ^eSolvent prepared on a weight-weight basis at 25.0 °C, and the other component is water.

determined by studying the rates of solvolysis reaction of a standard substrate ($m = 1$). The c is a constant (residual) term. The k and k_0 values are the rate constants of the solvolysis in the solvents under consideration and in the standard solvent (80% ethanol), respectively. In order to establish this equation, *tert*-butyl chloride which has a considerably hindered structure for attack at the reacting carbon was initially chosen as the standard substrate. It was expected that the solvolysis reaction of this compound would follow a rate determining ionization process.

$$\log(k/k_0) = mY_{Cl} + c \quad (2)$$

By using this Grunwald-Winstein equation (eq. 2), the solvolysis reactions of a number of compounds, for which one would expect an ionization process, were examined to yield good linear relationships against Y_{Cl} values. However, Fainberg and Winstein found that the plots for some substrates such as α -phenylethyl and 2-methyl-2-phenylpropyl (neophyl) halides showed a scattering of points in binary solvent systems like ethanol/water and dioxane/water.⁸

Therefore, a second term was suggested, which is governed by the solvent nucleophilicity. The equation, l represents the sensitivity to change in the solvent nucleophilicity (N_T) in Eq. (3). The resulting Eq. (3) is often referred to as an extended Grunwald-Winstein equation.⁹

$$\log(k/k_0) = lN_T + mY_{Cl} + c \quad (3)$$

The Grunwald-Winstein plots (eq. 2) of the rate constants in Table 1 are presented in Figure 1 using the solvent ionizing power scale (Y_{Cl}). Examination of Figure 1 shows that the plots for the three aqueous mixtures exhibit dispersions into three separate lines, even if each individual binary solvent system showed a linear relationship. In addition, the plots of the 2,2,2-trifluoro-ethanol (CF₃CH₂OH), which has low nucleophilicity and high ionizing power show a clear deviation from the others. These results strongly suggest that the solvolysis of this compound is sensitive to both solvent

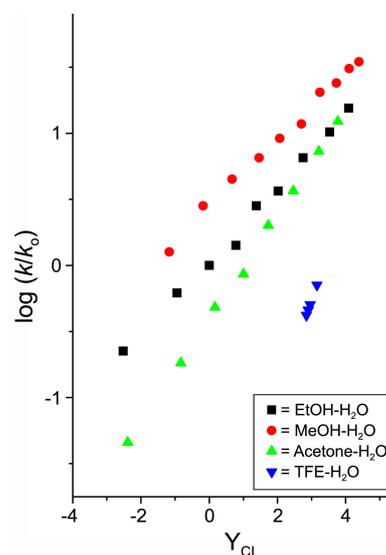


Figure 1. Plots of $\log(k/k_0)$ for the solvolysis of **1** against Y_{Cl} .

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 to determine whether a nucleophilic substitution reaction proceeds through an unimolecular reaction (S_N1 , *i.e.*, $l \approx 0$ and $m \approx 1$), a bimolecular reaction (S_N2 , *i.e.*, $l \approx 1.0$ or $m \approx 0.5$) or 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 TS.^{5,10} Application of Eq. (3) to the solvolysis of **1** led to moderately good correlations. For 31 solvents, values obtained were 0.96 ± 0.09 for l , 0.53 ± 0.03 for m , and 0.1 for c (Figure 2); the standard error of the estimate was 0.06; the correlation coefficient value was 0.955.

The l value of 0.96 is smaller than those recently reported for the reactions with an addition-elimination mechanism ($l \approx 1.5$), but is similar to those reported for the bimolecular solvolyses of diphenylthiophosphinyl chloride¹¹ ($l = 0.96$), allyl chloroformate¹² ($l = 0.53$), 9-fluorenyl chloroformate¹³ ($l = 0.95$), and N,N,N',N' -tetramethyldiamino-phosphorochloridate¹⁴ ($l = 1.14$). This result suggests an S_N2 mechanism involving a nucleophilic attack at sulfur atom of **1** by the solvent. The solvolysis of **1**, where bond formation ($l = 0.96$) is ahead of bond breaking ($m = 0.53$) and the values are still in the range of an S_N2 mechanism, reflects the degree of the nucleophilic assistance based on the measure of solvent nucleophile.^{10c,d,11-14}

Recent interpretations for the attack at sulfur have been made in terms of bimolecular attack, but with some degree of uncertainty as to whether it is concerted or stepwise. Bentley, Jones and Koo¹⁵ suggested that both mechanisms could operate, with a concerted mechanism favored in more polar solvents. A fairly recent review favored an interpretation of a concerted S_N2 mechanism, involving an attack

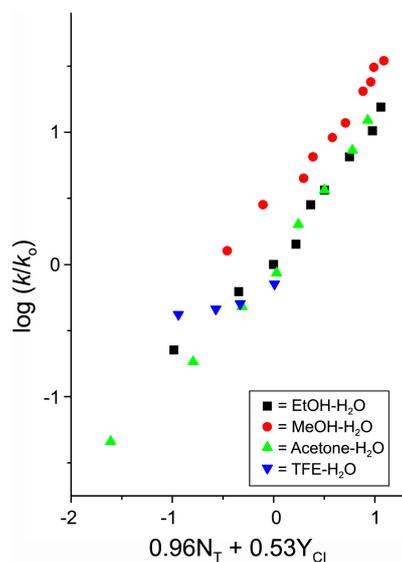


Figure 2. Plots of $\log(k/k_0)$ for the solvolysis of **1** at 35.0 °C against $(0.96N_T + 0.53Y_{Cl})$.

at sulfur by solvent.¹⁶ Our analyses are consistent with this explanation.

Rate constants for solvolysis of **1** in ethanol, methanol, 80% ethanol, 50% ethanol, and 50% acetone were measured in the range between 25.0 °C and 55.0 °C; each corresponding rate constant at 0.0 °C was calculated by the extrapolation method using the Arrhenius equation.¹⁷ The activation parameters, ΔH^\ddagger and ΔS^\ddagger , for solvolysis of **1** are summarized in Table 2. The relatively small positive ΔH^\ddagger (12.0-15.9 kcal·mol⁻¹) and large negative ΔS^\ddagger (-23.1 ~ -36.3 cal·mol⁻¹K⁻¹) values in Table 2 are the characteristics of a reaction involving a partial development of charge with a low degree of bond cleavage in the TS. These values exist in the range normally observed for bimolecular reactions with polar TS.¹⁸

The replacement of one or more atoms in a reacting system with respective isotopes is one of the most stable structural perturbations. Changes in the reaction rate induced by an isotopic substitution are known as kinetic isotope effects and provide mechanistic information. The solvent kinetic isotopic effects (SKIEs, 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.¹⁹ We have determined the SKIEs, k_{SOH}/k_{SOD} , for the substrate using deuterated methanol (CH₃OD), 80% CH₃OD-20% D₂O, and 50% CH₃OD-50% D₂O, and the results are presented in Table 3. For 5-dimethylamino-naphthalene-1-

Table 2. Rate constants and activation parameters for the solvolyses of **1**^a at various temperatures

Solvent (%) ^b	T (°C)	k (s ⁻¹) ^c	ΔH^\ddagger (kcal/mol)	$-\Delta S^\ddagger$ (cal/mol·K)
100 EtOH	25	1.92×10^{-5}	15.9 ± 0.4^d	23.1 ± 1.2
	35	3.80×10^{-5}		
	45	7.70×10^{-5}		
	55	13.5×10^{-5}		
80 EtOH	25	7.35×10^{-5}	12.0 ± 0.4	36.3 ± 1.4
	35	1.69×10^{-4}		
	45	4.03×10^{-4}		
	55	9.53×10^{-4}		
50 EtOH	25	2.94×10^{-4}	12.1 ± 0.5	35.8 ± 1.7
	35	6.17×10^{-4}		
	45	13.5×10^{-4}		
	55	20.0×10^{-4}		
100 MeOH	25	1.02×10^{-4}	14.5 ± 0.3	27.8 ± 1.0
	35	2.14×10^{-4}		
	45	4.60×10^{-4}		
	55	10.6×10^{-4}		
50 Acetone	25	1.19×10^{-4}	15.5 ± 0.4	24.5 ± 1.3
	35	3.39×10^{-4}		
	45	6.77×10^{-4}		
	55	14.9×10^{-4}		

^aA 1.0 mol dm⁻³ solution of the substrate in the indicated solvent, also containing 0.1% CH₃CN. ^bOn a volume-volume content at 25.0 °C, and the other component is water. ^cAverages of three or more runs. ^dThe activation parameters are accompanied by the standard error.

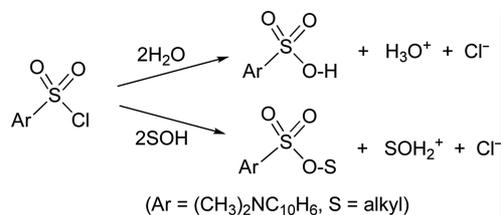
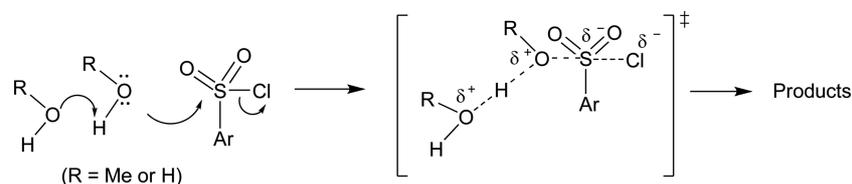
Table 3. Solvent kinetic isotope effects (SKIEs) for solvolyses of **1** at 35.0 °C

Solvent (%)	k_{SOH} (s)	k_{SOD} (s)	SKIE
100 MeOH	2.14×10^{-4}	1.14×10^{-4}	1.88
80 MeOH-20 H ₂ O	7.59×10^{-4}	4.45×10^{-4}	1.71
50 MeOH-50 H ₂ O	2.00×10^{-3}	1.49×10^{-3}	1.34

sulfonyl chloride, the SKIEs are 1.88 for CH₃OD, 1.71 for 80% CH₃OD-20% D₂O and 1.34 for 50% CH₃OD-50% D₂O. These are similar to those values previously reported for the corresponding solvolyses of benzyl chloride²⁰ ($k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 1.43$), benzoyl chloride²⁰ ($k_{\text{MeOH}}/k_{\text{MeOD}} = 1.55$), diphenylthiophosphinyl chloride²¹ ($k_{\text{MeOH}}/k_{\text{MeOD}} = 1.83$), and a series of benzenesulfonyl chlorides²² ($k_{\text{SOH}}/k_{\text{SOD}} = 1.58\text{--}2.39$) at 25.0 °C in which the reactions were believed to be S_N2 mechanism in character.

The ratio of l and m values (l/m) has also been suggested as a useful mechanistic criterion. 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).¹⁸ The l/m value is 1.8 for the solvolysis of **1**, which suggests that the solvolysis reactions of this compound in the more nucleophilic solvent systems are very sensitive toward changes in solvent nucleophilicity and a bimolecular mechanism (S_N2) or an addition-elimination pathway (A-E) is dominated by the bond formation between the reaction center of sulfonyl sulfur and solvent in the rate-determining step.²³

The reaction with water of **1** produces two equivalents of strong acid, whereas the reaction with alcohol produces only one equivalent of strong acid. If a water-alcohol solvent is used, the reaction, as presented in Scheme 2, is simplified by the second solvent molecule is used to extract the proton from the molecule serving as the nucleophile could be either water or alcohol. Furthermore, the amounts of two protonat-

**Scheme 2****Scheme 3****Table 4.** Product selectivity values (S)^a for the solvolyses of **1** in the binary mixtures after one half-life at 35.0 °C

Solvent ^b	% Ester	S
90% EtOH-H ₂ O	77	1.2
70% EtOH-H ₂ O	61	2.1
50% EtOH-H ₂ O	54	2.8
90% MeOH-H ₂ O	86	1.5
70% MeOH-H ₂ O	64	1.7
40% MeOH-H ₂ O	45	2.7
20% MeOH-H ₂ O	24	2.9

^aAs defined in equation 4. ^bMolar percentage of ester formed in competition with the acid; average deviation $< \pm 3\%$.

ed solvent species are determined by a rapid equilibration within the mixed solvent.²³

Product selectivities (S), defined by Eq. (4) using molar concentration, for the solvolyses of **1** at 35.0 °C in the mixtures of water with ethanol and methanol are presented in Table 4. The values for the percentages of ester formation in the reaction of **1**, at 35.0 °C, in the mixtures of water with ethanol or methanol are also presented in Table 4.

$$S = \frac{([\text{Ester in product}]/[\text{Acid in product}]) \times ([\text{Water in solvent}]/[\text{Alcohol in solvent}])}{1} \quad (4)$$

The product selectivity (S) for aqueous ethanol and methanol mixtures increases with increasing water ratio; thus the reactivity-selectivity principle (RSP)²⁴ is not applicable to ethanol and methanol mixtures. The greater value of S in the more aqueous media for **1** indicates that the role of alcohol as a nucleophile is important and the effect of the ionizing power is not significant in the product-determining step of the reaction of **1**. Similar selectivity changes have been shown to be typical for a general based-catalyzed bimolecular reaction mechanism channel in aqueous alcohol media.²⁵

Conclusions

Multiple correlation analysis of the rate constants of solvolysis of 5-dimethylamino-naphthalene-1-sulfonyl chloride (**1**) against the combination of solvent nucleophilicity (N_T) values and solvent ionizing power (Y_{Cl}) values leads to a sensitivity toward changes in solvent nucleophile (l value) of 0.96 and a sensitivity toward changes in solvent ionizing power (m value) of 0.53. Therefore, we could conclude that the solvolysis of **1** proceeds through an S_N2 mechanism (Scheme 3) with a transition state (TS) structure similar to

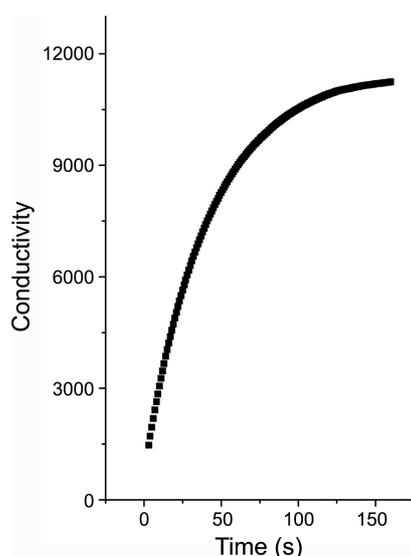


Figure 3. Kinetic experimental curve of conductivity vs. time for pseudo first order system (k_{obsd}). Solvolysis of **1** in 60% EtOH at 35 °C.

that of the benzenesulfonyl chloride reaction, in which the bond formation is ahead of the bond breaking on the bases of the magnitudes of l ($= 0.96$) and m ($= 0.53$). This interpretation is further supported by the activation parameters (*i.e.*, relatively small positive ΔH^\ddagger and large negative ΔS^\ddagger) and by the solvent kinetic isotope effects ($k_{\text{SOH}}/k_{\text{SOD}} = 1.34$ – 1.88). The selectivity values ($S = 1.2$ – 2.9) obtained in binary solvents are also consistent with the proposed mechanism.

Experimental

The solvents were purified as previously described.^{14,18} 5-Dimethylamino-naphthalene-1-sulfonyl chloride (**1**, 98%) was used as received. The kinetic experiments were performed by allowing a conductivity cell containing 12.5 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. Then, a 12 μL portion of a 1.0 mol dm^{-3} stock solution of **1** in acetonitrile was added. The monitoring of the conductivity increases with time (Figure 3) and the rate constant calculations were conducted as previously reported.^{4,20} Multiple regression analyses were performed using commercially available packages.²⁰ The uncertainty in the k_{obsd} values was estimated to be less than $\pm 3\%$ from replicate runs. 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.^{23d} A 0.43 M solution of the substrate in acetonitrile was prepared and 0.30 mL were added to 20 mL of the binary solvent mixture under investigation. To standardize the measurements, each compositions of an aqueous alcohol mixture was accompanied by solvolysis in 60% acetone (2 equivalents of acid produced). All determinations were in duplicate and 5.0 mL portions were titrated in the usual manner^{22,23d} at 10, 15, and 20 half-lives. The product selectivities (S) were also calculated using Eq. (4).

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