

Correlation of the Rates of Solvolysis of Diphenylthiophosphinyl Chloride Using an Extended form of the Grunwald-Winstein Equation

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Rate of solvolysis of diphenylthiophosphinyl chloride in ethanol, methanol, and aqueous binary mixtures incorporating ethanol, methanol, acetone, 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) are reported. Solvolyses were also carried out in TFE-ethanol mixtures. For five representative solvents, studies were made at several temperatures and activation parameters determined. The 29 solvents gave a reasonably precise extended Grunwald-Winstein equation plot, correlation coefficient (*R*) of 0.933, which improved to 0.983 when the four TFE-ethanol points were excluded. The sensitivities (*l* = 1.00 and *m* = 0.64) were similar to those obtained for dimethyl phosphorochloridate and phosphorochloridothionate and diphenylphosphinyl chloride (**1**). As with the four previously studied solvolyses, an S_N2 pathway is proposed for the solvolyses of diphenylthiophosphinyl chloride. The activation parameters, Δ*H*[‡] and Δ*S*[‡], were determined and they are also in line with values expected for an S_N2 reaction.

Key Words : Diphenylthiophosphinyl chloride, Extended Grunwald-Winstein equation, S_N2 pathway

Introduction

Phosphoryl transfer is an important aspect of biological chemistry and organic syntheses.¹ The mechanism of phosphoryl transfer from phosphate monoesters and diesters has been the subject of many recent investigations.² In particular a considerable amount of work has been devoted to elucidating the problem of whether the reaction proceeds through a pentacoordinate phosphorane intermediate or concertedly with a single transition state (TS).³ The mechanism of reaction of phosphinothioyl compounds, such as of the diphenylthiophosphinyl chloride (Ph₂PSCl, **1**), has been less studied, in spite of their importance as highly reactive chemical intermediates. There has been a recent mechanistic study of the reaction with pyridine in acetonitrile as solvent.³ⁱ

Previous studies by Kevill and co-workers have been of diaryl⁴ and dimethyl⁵ phosphorochloridates, (RO)₂POCl, the sulfur-for-oxygen substituted dimethyl phosphorochloridothionate, (MeO)₂PSCl,⁵ *N,N,N',N'*-tetramethyldiamidophosphorochloridate, (Me₂N)₂POCl,⁶ and diphenylphosphinyl chloride, Ph₂POCl.⁷ The extended Grunwald-Winstein equation plot for solvolyses of stated most substrates containing the P-atom as the reaction center, eq. (1), led, except for the poorly correlated solvolyses of diaryl phosphorochloridates, with phenyl or *p*-chlorophenyl as the aryl group,⁴ to acceptable correlations, with very similar *l* and *m* values.

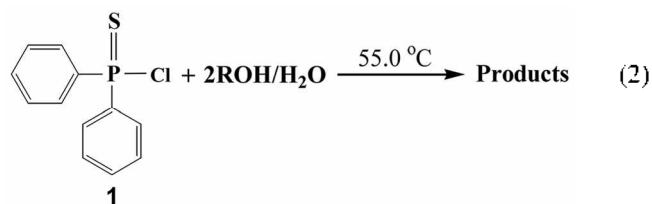
The Grunwald-Winstein equation in its original form⁸ correlates the rates of solvolysis of ionization reactions against the solvent ionizing power values.⁹ Whereas the Hammett equation involves changes in a remote substituent under otherwise constant conditions, this equation involves changes in the solvent composition under otherwise constant conditions. The Grunwald-Winstein equation can be extended to cover reactions in which the solvent also acts as a

nucleophile by the addition of a second term, involving a scale of solvent nucleophilicity.¹⁰ This is the same basic philosophy as in the Taft equation, which extends the Hammett equation by adding a second term involving a scale of steric parameters.

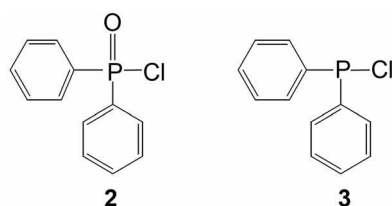
The extended Grunwald-Winstein equation can be expressed as in eq. (1). In eq. (1), *k* and *k*₀ represent the specific rates of solvolysis of a substrate RX in a given solvent and in the standard solvent (80% ethanol), respectively, *l* is the sensitivity of the solvolysis to changes in solvent nucleophilicity (N_T)¹⁰; *m* is the sensitivity of the solvolysis to changes in solvent ionizing power (Y_X, for a leaving group X)⁹; and *c* is a constant (residual) term.

$$\log(k/k_0) = l N_T + m Y_X + c \quad (1)$$

In this work, we have attempted to investigate the reaction mechanism involved in the solvolysis of diphenylthiophosphinyl chloride (Ph₂PSCl, **1**), with a variety of pure and mixed solvents at 55.0 °C, eq. (2), by determining on the magnitudes of the *l* and *m* of the extended Grunwald-Winstein equation, eq. 1. Further evidence is obtained from the activation parameters and the kinetic solvent deuterium isotope effect.



The study can be used to help to clarify the phosphoryl transfer mechanism, and to compare the reactivity with that of diphenylphosphinyl chloride (Ph₂POCl, **2**),⁷ and chloro diphenylphosphine (Ph₂PCl, **3**).¹¹



Results and Discussion

The specific rates of solvolysis of diphenylthiophosphinyl chloride (Ph_2PSCl , **1**) have been determined in 29 solvents at 55.0 °C. The solvents consisted of ethanol, methanol, and binary mixtures of water with ethanol, methanol, acetone, 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and four binary mixtures of TFE and ethanol.

Table 1. Specific rates of solvolysis (k) of diphenylthiophosphinyl chloride (Ph_2PSCl , **1**)^a at 55.0 °C and N_T and Y_{Cl} values of the solvents

Solvent ^a	$10^3 k$ (s ⁻¹)	N_T ^b	Y_{Cl} ^c
100%EtOH	0.701 ± 0.011	0.37	-2.52
90%EtOH	4.47 ± 0.02	0.16	-0.94
80%EtOH	8.58 ± 0.04	0.0	0.0
70%EtOH	14.8 ± 0.6	-0.20	0.78
60%EtOH	23.8 ± 0.6	-0.38	1.38
50%EtOH	34.7 ± 0.4	-0.58	2.02
100%MeOH	4.31 ± 0.04 ^d	0.17	-1.17
90%MeOH	9.33 ± 0.07	-0.01	-0.18
80%MeOH	21.4 ± 0.6	-0.06	0.67
70%MeOH	34.1 ± 0.4	-0.40	1.46
60%MeOH	56.9 ± 1.0	-0.54	2.07
95%Acetone	0.0162 ± 0.0005	-0.49	-3.19
90%Acetone	0.0955 ± 0.0006	-0.35	-2.39
80%Acetone	1.19 ± 0.02	-0.37	-0.83
70%Acetone	5.01 ± 0.03	-0.42	0.17
60%Acetone	9.12 ± 0.05	-0.52	0.95
50%Acetone	20.9 ± 0.4	-0.70	1.73
90%TFE	1.07 ± 0.03	-2.55	2.85
80%TFE	3.37 ± 0.04	-2.19	2.90
70%TFE	8.78 ± 0.05	-1.98	2.96
50%TFE	31.6 ± 0.5	-1.73	3.16
90%HFIP	0.167 ± 0.002	-5.26	5.17
80%HFIP	1.06 ± 0.03	-3.84	4.31
70%HFIP	2.88 ± 0.04	-2.94	3.83
50%HFIP	3.16 ± 0.05	-2.49	3.80
80T-20E ^e	0.178 ± 0.002	-1.76	1.89
60T-40E ^e	0.331 ± 0.003	-0.94	0.63
40T-60E ^e	0.537 ± 0.005	-0.34	-0.48
20T-80E ^e	0.714 ± 0.006	0.08	-1.42

^aUnless otherwise indicated, a 10^{-3} M solution of the substrate in the indicated solvent, also containing 0.1% CH_3CN within the solvent. ^bOn a volume-volume basis at 25.0 °C, except for TFE-H₂O and HFIP-H₂O mixtures, which are on a weight-weight basis. ^cWith associated standard deviations. ^dValues from ref. 10. ^eValues from ref. 9. ^fValues of 2.36 (± 0.03) in methanol-*d* (MeOD), corresponding to $k_{\text{MeOD}}/k_{\text{MeOH}}$ value of 1.85 ± 0.05 [with associated standard error (Crumpler, T. B.; Yoh, J. H. Chemical Computations and Error, Wiley: New York, 1940, p. 178)]. ^gT-E indicates TFE-EtOH mixtures.

The specific rates of solvolysis are presented in Table 1, together with N_T ¹⁰ and Y_{Cl} ⁹ values. Also, the specific rates of solvolysis of **1** were not found to depend on the initial concentration of the substrate, as shown in Table 2.

For five of the solvents, specific rates of solvolysis were measured at three additional temperatures. These values are reported in Table 3 and, together with the values at 55.0 °C from Table 1, they are used to calculate the enthalpies and entropies of activation, also reported in Table 3.

In the present paper, we are concerned with the specific rates of the solvolyses represented in eq. 2. In most solvents,

Table 2. Constancy of the specific rates of solvolysis (k) of diphenylthiophosphinyl chloride (Ph_2PSCl , **1**) with variation of the concentration of the substrate at 55.0 °C

Solvent	$[\text{Ph}_2\text{PSCl}]$, M ^a	$10^3 k$, s ⁻¹
100%EtOH	0.543	0.697 ± 0.012
	1.013	0.704 ± 0.011
	2.179	0.702 ± 0.013
80%EtOH	0.543	8.61 ± 0.05
	1.013	8.50 ± 0.04
	2.179	8.63 ± 0.06
50%EtOH	0.543	34.2 ± 0.5
	1.013	34.6 ± 0.4
	2.179	35.3 ± 0.4

^aConcentration of stock solution in MeCN. ^bThe k values are the averages of more than two runs and errors are standard deviations.

Table 3. Specific rates and activation parameters for the solvolysis of diphenylthiophosphinyl chloride^a (Ph_2PSCl , **1**) in pure and aqueous solvents at various temperatures

Solvent	Temperature (°C)	$10^3 k$ (s ⁻¹)	ΔH^\ddagger (kcal·mol ⁻¹) ^c	$-\Delta S^\ddagger$ (cal·mol ⁻¹ ·K ⁻¹) ^c
100%EtOH	25	0.120 ± 0.002	10.7 ± 0.1	40.7 ± 0.3
	35	0.216 ± 0.003		
	45	0.369 ± 0.005		
	55	0.701 ± 0.011 ^d		
80%EtOH ^e	25	1.75 ± 0.03	10.0 ± 0.1	37.8 ± 0.3
	35	2.80 ± 0.03		
	45	5.05 ± 0.04		
	55	8.58 ± 0.04 ^d		
100%MeOH	25	0.701 ± 0.003	11.1 ± 0.1	35.8 ± 0.3
	35	1.26 ± 0.02		
	45	2.27 ± 0.03		
	55	4.31 ± 0.04 ^d		
90%TFE ^f	25	0.219 ± 0.002	9.6 ± 0.1	43.1 ± 0.4
	35	0.350 ± 0.003		
	45	0.594 ± 0.004		
	55	1.07 ± 0.03 ^d		
90%HFIP ^f	25	0.0209 ± 0.0004	12.9 ± 0.1	36.7 ± 0.3
	35	0.0398 ± 0.0005		
	45	0.0835 ± 0.0003		
	55	0.167 ± 0.002 ^d		

^aA 10^{-3} M solution of the substrate in the indicated solvent, also containing 0.1% CH_3CN . ^bWith associated standard deviation. ^cThe activation parameters are accompanied by the standard error. ^dFrom Table 1. ^eOn a volume-volume basis at 25.0 °C. ^fOn a weight-weight basis.

the reactions were fast, and the use of an apparatus allowing a rapid response to changes in conductivity^{12,13} was a convenient way of following the extent of reaction as a function of time. To promote a rapid dissolution in the solvent, the substrate was usually added as a small volume of a concentrated stock solution in acetonitrile, such that the reaction solution contained about 0.1% acetonitrile.

The specific rates were observed to increase with increasing water content for binary aqueous mixtures. The specific rates of ethanolysis of **1** were lower ($k = 1.20(\pm 0.02) \times 10^{-4} \text{ s}^{-1}$ at 25.0 °C) than the specific rates of ethanolysis of diphenylphosphinyl chloride⁷ ($k = 7.02(\pm 0.10) \times 10^{-3} \text{ s}^{-1}$ at 25.0 °C). This means that in the reaction of **1**, eq. (2), the solvents are somewhat loosely bound in transition state (TS) and the extent of bond cleavage of the leaving group (Cl) at the TS is rather low. The difference in the magnitude, *i.e.*, a lower rates of solvolysis of **1** than of solvolysis of diphenylphosphinyl chloride reflects that, under similar conditions, the P=S group favours the Cl-bonded nucleofuge (Cl⁻) expulsion less than the P=O group.

Phosphate systems are more reactive than their thiophosphate counterparts by one or more orders of magnitude,¹⁴ while phosphinate systems are less sensitive to S substitution in the P=O bond,¹⁵ in accordance with our results. The P=O systems are generally more reactive than their P=S counterparts for several reasons, including the so-called thio effect, which is mainly the electronegativity difference between O and S which favors O over S.¹⁶

Activation parameters for solvolysis of **1** are shown in Table 3. The values of ΔH^\ddagger , and ΔS^\ddagger were obtained from the slope and intercept, respectively, of Eyring plots, by least-squares analysis. The ΔH^\ddagger values are relatively low whereas the ΔS^\ddagger values are large and negative, observations which are consistent with an S_N2 mechanism.¹⁷

Halmann¹⁸ found, for the ethanolysis of the related diethylphosphinyl chloride, Et₂POCl, that the specific rate of solvolysis was dependent upon the concentration of the substrate for the range from 2.5×10^{-3} to 17×10^{-3} M. We found no perturbation of this nature over a threefold variation at our lower concentrations ($0.5 \sim 2 \times 10^{-3}$ M) of diphenylthiophosphinyl chloride undergoing solvolysis in ethanol and 80% or 50% ethanol, Table 2. Similarly, in previous work, we found no concentration dependent perturbation for solvolyses of diphenylphosphinyl chloride (Ph₂POCl, **2**),⁷ or chlorodiphenylphosphine (Ph₂PCL, **3**).¹¹

The solvolysis of organophosphorus halides has been the subject of several studies. At tetracoordinated phosphorus, reactions with nucleophilic reagents were found to usually proceed by bimolecular mechanisms.¹⁹ Pentacovalent intermediates were most frequently proposed.²⁰ Occasionally, unimolecular mechanisms, with a rate determining dissociation of the phosphorus-halogen bond have been postulated.^{21,22}

A useful tool for quantitatively estimating the rate-controlling influence of nucleophilic participation by solvent during a solvolysis reaction involves the application of the extended Grunwald-Winstein equation, eq. (1).⁵⁻⁷ Appli-

cation of eq. (1) to the solvolyses of **1** led to only moderately good correlations, with dispersal for different binary mixtures. For 29 solvents, values were obtained of 1.03 ± 0.08 for *l*, 0.66 ± 0.05 for *m*, and -0.06 for *c*; the standard error of the estimate was 0.08, and the R value was 0.933. Inspection of the plot corresponding to this correlation (Figure 1) showed that the four data points for solvolysis in TFE-ethanol mixtures lay below the plot. Recalculation with omission of these points led to values for *l* of 1.00 ± 0.04 , for *m* of 0.64 ± 0.03 , and for *c* of 0.03 (Fig. 1); the standard error of the estimate was 0.04, and the R value was 0.983. Inspection of Figure 1 shows the considerable deviation for the four solvolyses in TFE-ethanol mixtures. Also, in earlier correlations of other solvolyses, data points for these TFE-ethanol solvent systems usually lay below the correlation line.²³⁻²⁶ The sensitivity values, *l* and *m*, and the goodness-of-fit parameters are reported in Table 4, where they can be compared with literature values for related substrates.

The *l* and *m* values obtained are very similar to those recently reported, after an analysis in terms of eq. (1), for the specific rates of solvolysis of *N,N,N',N'*-tetramethyldiamidophosphorochloridate ($l = 1.20 \pm 0.07$, $m = 0.69 \pm 0.04$),⁶ *p*-methylbenzenesulfonyl chloride ($l = 1.25 \pm 0.15$, $m = 0.62 \pm 0.04$),²⁷ and *p*-methoxybenzenesulfonyl chloride ($l = 1.10 \pm 0.17$, $m = 0.61 \pm 0.04$).²⁷ The conclusions from studies of nucleophilic attack at the sulfur of arenesulfonyl chlorides are closely related to those for attack at the phosphorus of *N,N,N',N'*-tetramethyldiamidophosphorochloridate, with the initial suggestions of the operation of S_N1-type mechanisms⁶ now considered highly unlikely to be correct. Recent inter-

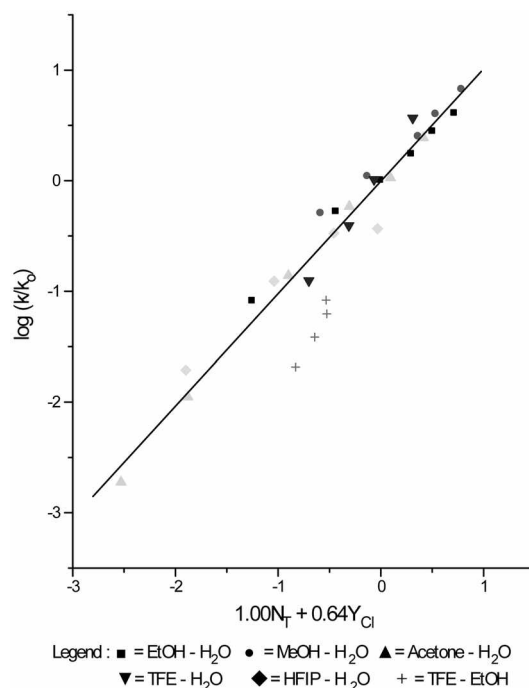
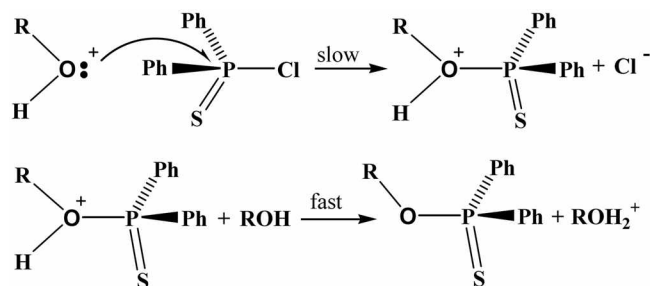


Figure 1. Plot of $\log(k/k_0)$ for solvolyses of diphenylthiophosphinyl chloride at 55.0 °C against $(1.00N_T + 0.64Y_{Cl})$. The TFE-EtOH points are not included in the calculation of the regression line. They are included in the plot to show the extent of their deviation from the line.

Table 4. Coefficients from the extended Grunwald-Winstein equation (1) correlations of the specific rates of solvolysis of diphenylthio-phosphinyl chloride (Ph_2PSCl , **1**) at 55.0 °C and a comparison with the corresponding values for other solvolytic displacements of chloride ion from phosphorus (V)

Substrate	n^a	l^b	m^b	c^b	R^c
Ph_2PSCl	29	1.03 ± 0.08	$0.66 = 0.05$	-0.06 ± 0.08	0.933
Ph_2PSCl^d	25	1.00 ± 0.04	$0.64 = 0.03$	0.03 ± 0.04	0.983
Ph_2POCl^e	31	1.44 ± 0.13	$0.58 = 0.09$	0.15 ± 0.14	0.920
Ph_2POCl^d	27	1.42 ± 0.10	$0.54 = 0.07$	$0.32 = 0.11$	0.956
Ph_2PCl^f	29	1.31 ± 0.14	$0.51 = 0.09$	0.12 ± 0.14	0.899
Ph_2PCl^d	25	1.25 ± 0.09	$0.46 = 0.06$	0.24 ± 0.09	0.954
$(\text{MeO})_2\text{POCl}^g$	22	1.36 ± 0.23	$0.54 = 0.13$	-0.02 ± 0.17	0.844
$(\text{MeO})_2\text{POCl}^{d,g}$	18	1.24 ± 0.14	$0.45 = 0.08$	$0.18 = 0.11$	0.941
$(\text{MeO})_2\text{PSCl}^g$	31	1.21 ± 0.10	$0.60 = 0.04$	0.22 ± 0.07	0.943
$(\text{MeO})_2\text{PSCl}^{d,g}$	28	1.16 ± 0.08	$0.55 = 0.03$	0.30 ± 0.06	0.966
$(\text{Me}_2\text{N})_2\text{POCl}^h$	31	1.20 ± 0.07	$0.69 = 0.04$	0.03 ± 0.32	0.958
$(\text{Me}_2\text{N})_2\text{POCl}^{d,h}$	27	1.14 ± 0.05	$0.63 = 0.03$	0.17 ± 0.21	0.982
$(\text{PhO})_2\text{POCl}^i$	38	1.72 ± 0.18	$0.68 = 0.06$	0.42 ± 0.15	0.885
$(p\text{-ClC}_6\text{H}_4\text{O})_2\text{POCl}^i$	31	1.79 ± 0.20	$0.58 = 0.08$	0.11 ± 0.18	0.863

^aNumber of data points. ^bFrom eq. 1. ^cCorrelation coefficient. ^dData points for TFE-ethanol (T-E) mixtures excluded. ^eFrom ref. 7. ^fFrom ref. 11. ^gFrom ref. 5. ^hFrom ref. 5. ⁱFrom ref. 4.



Scheme 1

pretations 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 Koo²⁸ suggested that both mechanisms can operate, with the concerted mechanism favored in the more polar solvents. A fairly recent review²⁹ favored an interpretation in terms of a concerted bimolecular displacement ($\text{S}_{\text{N}}2$) mechanism, involving an attack by solvent at sulfur. Our analyses are considered to be consistent with such an explanation. The close similarity of both the l and the m values for attack at sulfur to those for the attack at the phosphorus of **1** gives an indication that the solvolyses of **1** could also be concerted, Scheme 1.

We found that the use of N_{T} values in conjunction with Y_{Cl} values leads to acceptable correlations, with l and m values similar to those obtained in analyses of the specific rates of solvolysis for other entries within Table 4. The major difference is a somewhat smaller l value for the solvolyses of **1**, possibly reflecting a decreased nucleophilic participation at the transition state due to reduced interaction involving the phosphinyl sulfur ($\text{P}=\text{S}$) relative to the $\text{P}=\text{O}$ bond, containing a more electronegative oxygen.

In methanol (MeOH) and methanol- d (MeOD) a kinetic solvent deuterium isotope effect ($k_{\text{MeOH}}/k_{\text{MeOD}}$) of 1.83 ± 0.05 at 55.0 °C is observed (Table 1). This is in the range of values from 1.58 ± 0.05 to 2.31 ± 0.07 that was observed³⁰

for the corresponding methanolyse of a series of benzene-sulfonyl chlorides at 25.0 °C, reactions believed to be $\text{S}_{\text{N}}2$ in character. Similarly, the methanolyse of meta- and para-chlorobenzyl chloride and of para-nitrobenzyl chloride, believed to be $\text{S}_{\text{N}}2$ in character, show values in the 1.49 ± 0.05 to 1.89 ± 0.07 range.³¹ Indications are that a value in these ranges can be considered as good supporting evidence for the postulation of an $\text{S}_{\text{N}}2$ mechanism for a methanolysis.

Conclusions

The solvolyses of **1** proceed rather rapidly at 55.0 °C and the progress of reaction as a function of time can be conveniently monitored using a rapid-response conductivity technique. For five typical solvents, activation parameters were determined and the large negative entropies of activation are consistent with a bimolecular process. Kinetic solvent deuterium isotope effects for the solvolyses ($k_{\text{MeOH}}/k_{\text{MeOD}}$) are also consistent with a bimolecular process.

Application of the extended Grunwald-Winstein equation (eq. 1) in 25 solvents led to an l value of 1.00 and an m value of 0.64 (correlation coefficient of 0.983). These values are shown (Table 4) to be similar to previously determined values for nucleophilic attack by solvent at phosphorus(V). They are, also, very close to literature values for the solvolyses of sulfonyl chlorides. Previously-studied solvolytic displacements at phosphorus or sulfur have usually been proposed to follow an $\text{S}_{\text{N}}2$ pathway, and such a pathway is also proposed for the solvolyses of **1** (Scheme 1).

Experimental

The purification of acetone, methanol and ethanol were carried out as previously described.³² The purification of 1,1,1,3,3,3-hexafluoro-2-propanol,³³ and 2,2,2-trifluoroethanol³⁴ were also carried out by use of previously reported procedures. Water was used after distillation. Diphenylthio-

phosphinyl chloride was commercially available from Wako Pure Chemicals Industries, Ltd. The substrate did not react with the pure acetonitrile within the stock solution.

Kinetic runs were performed with 10 μL of the stock solution of the substrate (1 M) and 5 mL of the reaction solvent. All kinetic runs were performed, at least, in duplicate. The reaction cell was washed with water and acetone several times and dried prior to each run. A 5 mL portion of solvent was added to the reaction cell and allowed to sit for a few minutes until it reached a temperature equilibrium with the constant temperature bath. A 10 μL portion of the stock solution was then added and the reaction cell was shaken vigorously. The change of the conductance in the reaction with time was saved in the computer as a data file.

Rates were measured conductometrically at 55.0 $^{\circ}\text{C}$. All kinetic measurements were carried out in a constant temperature bath maintained within ± 0.05 $^{\circ}\text{C}$. The conductivity bridge used in this work was a self-made computer automatic A/D converter conductivity bridge. First-order solvolysis rate coefficients (k_{obs}), with the solvent in large excess, were determined by a curve fitting analysis of the computer data with a modified version of the Origin Program, which fits conductance vs. time data to the equation, $A = A_{\infty} + (A_0 - A_{\infty})\exp(-k_{\text{obs}} \times t)$, where A is the observed conductivity and A_{∞} , $A_0 - A_{\infty}$, and k_{obs} are iteratively optimized to achieve the best possible least-squares fit.

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