

Solvolysis Reaction Kinetics, Rates and Mechanism for Phenyl *N*-Phenyl Phosphoramidochloridate

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The rate constants of solvolysis of phenyl *N*-phenyl phosphoramidochloridate (PhNHPO(Cl)OPh, Target Compound-TC1) have been determined by a conductivity method. The solvolysis rate constants of TC1 are well correlated with the extended Grunwald-Winstein equation, using the N_T solvent nucleophilicity scale and Y_{Cl} solvent ionizing scale, and sensitivity values of 0.85 ± 0.14 and 0.53 ± 0.04 for l and m , respectively. These l and m values were similar to those obtained previously for the complex chemical substances dimethyl thiophosphorochloridate; *N,N,N',N'*-tetramethyldiamidophosphorochloridate; 2-phenyl-2-ketoethyl tosylate; diphenyl thiophosphinyl chloride; and 9-fluorenyl chloroformate. As with the five previously studied solvolyses, an S_N2 pathway is proposed for the solvolyses of TC1. For four representative solvents, the rate constants were measured at several temperatures, and activation parameters (ΔH^\ddagger and ΔS^\ddagger) were estimated. These activation parameters are also in line with the values expected for an S_N2 reaction.

Key Words : Phenyl *N*-phenyl phosphoramidochloridate, Extended Grunwald-Winstein equation, S_N2 mechanism, Activation parameters

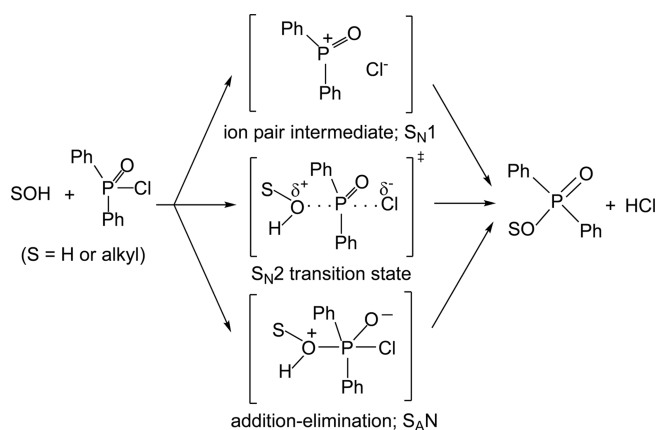
Introduction

Phosphoryl transfer is an important aspect of biological chemistry and organic synthesis. The mechanism of phosphoryl transfer from phosphate monoesters and diesters has been the subject of many recent investigations.¹ The reactions of phosphinyl chloride derivatives with binary solvent mixtures have been reported to proceed through an S_N1 (ion pair) and S_N2 pathway with addition-elimination ($S_A N$) processes depending on the reaction conditions. These possible pathways for a solvolysis reaction are presented in Scheme 1.

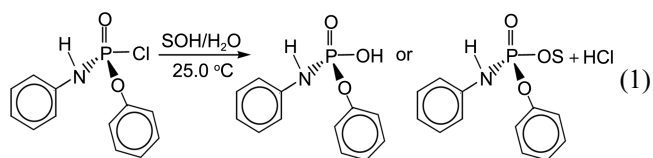
In particular, a considerable amount of work has been devoted to elucidating the question of whether the reaction proceeds through a pentacoordinate phosphorane inter-

mediate or is the result of a single transition state (TS).² The reaction mechanism of phosphoryl compounds, such as that of 'phenyl *N*-phenyl phosphoramidochloridate' (PhNHPO(Cl)OPh – Target Compound 1 or TC1), has been less studied, in spite of their importance as highly reactive chemical intermediates.

Considering our previous works on the solvolytic reactions of dimethyl thiophosphorochloridate³ ((MeO)₂PSCl); *N,N,N',N'*-tetramethyldiamidophosphorochloridate⁴ ((Me₂N)₂-POCl); 2-phenyl-2-ketoethyl tosylate⁵ (PhCOCH₂OTs); diphenyl thiophosphinyl chloride⁶ (Ph₂PSCl); and 9-fluorenyl chloroformate⁷ (9-fluorenyl-OCOCl), an S_N2 pathway based on the sensitivity values ($l = 0.95$ -1.16 and $m = 0.39$ -0.64) is proposed.



Scheme 1



Extensive experimental studies on the phosphoryl and thiophosphoryl transfer reactions of various substrates have been carried out by our group. In this work, we have attempted to investigate the reaction mechanism involved in the solvolysis of TC1, with a variety of pure and mixed solvents at 25.0 °C (Eq. 1), by determining the magnitudes of variables l and m of the extended Grunwald-Winstein equation. Further evidence was obtained from the activation parameters. This study can be used to help to clarify the phosphoryl transfer mechanism, and to compare the reac-

tivity of the first target compound with that of diphenyl phosphorochloridate⁸ ((PhO)₂POCl, TC2).

Experimental

The solvents were purified as previously described.^{7,9} Phenyl *N*-phenyl phosphoramidochloridate (TC1, 98%) was used as received. All reactions obeyed first-order rate constants (k_{obsd}) and were calculated using Eq. (2), along with the three-parameters curve-fitting method in origin programs (where, λ_t = conductivity value at any time, λ_{∞} = conductivity value at infinity, λ_0 = initial conductivity value).

$$\lambda_t = \lambda_{\infty} - (\lambda_{\infty} - \lambda_0)\exp(-k_{\text{obsd}} \times t) \quad (2)$$

Multiple regression analyses were performed using commercially available packages.¹⁰ The rate constants values (k_{obsd}) were the average of at least three runs which were reproducible within $\pm 3\%$. Kinetic runs were performed with 10 μL of the stock solution of the substrate (1 M) and 5 mL of the reaction solvent. 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 in a constant temperature bath until it reached temperature equilibrium. A 10 μL portion of the stock solution in acetonitrile was then added and the reaction cell was shaken vigorously. The change in the conductance in the reaction over time was saved in the computer as a data file. The solvolyses product was identified by ¹H, ¹³C, and ³¹P NMR spectrum.

Results and Discussion

The rate constants (k) of solvolysis were determined at 25.0 °C by the conductivity technique for 32 solvents of TC1. The solvents included ethanol, methanol, and water; as well as binary mixtures of water with ethanol, methanol, acetone, and 2,2,2-trifluoroethanol (TFE). The rate constants and the relevant N_T ¹¹ and Y_{Cl} ¹² values are reported in Table 1.

In the present paper, we are concerned with the rate constants of the solvolyses represented in Eq. (1). In most solvents the reactions were fast, and the use of an apparatus allowing a rapid response to changes in conductivity was a convenient way of following the extent of reaction as a function of time. To promote 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 rate constants increased in the order: acetone-water < ethanol-water < methanol-water, and the rate increased rapidly as the water content of the binary-solvent systems increased (Table 1). This phenomenon supports an interpretation that the solvolysis of TC1 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.¹²

The rate constant of ethanolysis of TC1 was lower ($k =$

Table 1. Rate constants (k) of solvolyses of **1** at 25.0 °C and the N_T and the Y_{Cl} values

Solvent (%) ^a	N_T ^b	Y_{Cl} ^c	k (s ⁻¹)
100EtOH	0.37	-2.52	9.00×10^{-6}
90EtOH	0.16	-0.94	3.41×10^{-5}
80EtOH	0.00	0.00	5.46×10^{-5}
70EtOH	-0.20	0.78	7.74×10^{-5}
60EtOH	-0.39	1.38	1.08×10^{-4}
50EtOH	-0.59	2.02	1.63×10^{-4}
40EtOH	-0.74	2.75	3.34×10^{-4}
30EtOH	-0.93	3.53	7.66×10^{-4}
20EtOH	-1.16	4.09	2.16×10^{-3}
100MeOH	0.17	-1.17	4.75×10^{-5}
90MeOH	-0.01	-0.18	1.30×10^{-4}
80MeOH	-0.06	0.67	1.95×10^{-4}
70MeOH	-0.40	1.46	2.73×10^{-4}
60MeOH	-0.54	2.07	3.87×10^{-4}
50MeOH	-0.75	2.70	6.47×10^{-4}
40MeOH	-0.87	3.25	1.05×10^{-3}
30MeOH	-1.06	3.73	1.86×10^{-3}
20MeOH	-1.23	4.10	3.35×10^{-3}
10MeOH	-1.36	4.39	4.72×10^{-3}
90Acetone	-0.35	-2.39	1.14×10^{-5}
80Acetone	-0.37	-0.83	3.18×10^{-5}
70Acetone	-0.42	0.17	5.86×10^{-5}
60Acetone	-0.52	1.00	9.37×10^{-5}
50Acetone	-0.70	1.73	1.71×10^{-4}
40Acetone	-0.83	2.46	3.28×10^{-4}
30Acetone	-0.96	3.21	6.81×10^{-4}
20Acetone	-1.11	3.77	1.53×10^{-3}
10Acetone	-1.23	4.28	3.56×10^{-3}
H ₂ O	-1.38	4.57	8.34×10^{-3}
80TFE ^d	-2.19	2.90	1.95×10^{-5}
70TFE	-1.98	2.96	4.46×10^{-5}
50TFE	-1.73	3.16	1.35×10^{-4}

^aOn a volume-volume content at 25.0 °C, and the other component is water. ^bValues from ref. 11. ^cValues from ref. 12. ^dSolvent prepared on a weight-weight basis at 25.0 °C, and the other component is water.

$9.00 \times 10^{-6}\text{s}^{-1}$ at 25.0 °C) than the rate constant of ethanolysis of diphenyl phosphinylchloridate (TC2)⁸ ($k = 4.97 \times 10^{-5}\text{s}^{-1}$ at 0.0 °C). The difference in the magnitude (*i.e.*, a lower rate of solvolysis for TC1 than of solvolysis for TC2) reflects that, under similar conditions, the PhNH group favours the Cl-bonded nucleofuge-(Cl⁻) expulsion less than the PhO group. The PhNH systems might be less reactive than their PhO counterparts for the difference in electronegativity between the PhNH and PhO group, which in this reaction, favors PhO over PhNH.

For ten solvents, the rate constants of solvolysis were measured at two additional temperatures. These values are reported in Table 2 and, together with the values at 25.0 °C from Table 1, they are used to estimate the enthalpies and entropies of activation, also reported in Table 2. (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, and these are consistent with an S_N2 mechanism.¹³

The linear free energy relationship developed by Grunwald and Winstein has become accepted as a useful tool to describe the correlation of rate constants of solvolysis. The initial Grunwald-Winstein equation¹⁴ considered the sensitivity to change in only one parameter, the solvent ionizing power (Y). In this equation (Eq. 3), m is sensitivity to changes in the solvent ionizing power (Y), and it can be determined by studying the rates of solvolysis reaction of a standard substrate ($m = 1$). Thus c is a constant (residual) term. The k and k_0 values are the rate constants of the solvolysis in the solvent under consideration and in the standard solvent

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 (kcal/mol) ^d	$-\Delta S^\ddagger$ (cal/mol·K) ^d
80EtOH	25	5.46×10^{-5}	16.1 ± 0.5	23.9 ± 1.5
	35	1.31×10^{-4}		
	45	3.22×10^{-4}		
60EtOH	25	1.08×10^{-4}	16.5 ± 0.0	21.3 ± 0.1
	35	2.76×10^{-4}		
	45	6.66×10^{-4}		
40EtOH	25	3.46×10^{-4}	14.1 ± 0.2	27.1 ± 0.5
	35	7.84×10^{-4}		
	45	1.64×10^{-4}		
100MeOH	25	4.81×10^{-5}	14.9 ± 1.0	28.4 ± 3.4
	35	1.23×10^{-4}		
	45	2.47×10^{-4}		
80MeOH	25	1.95×10^{-4}	14.7 ± 0.3	26.2 ± 0.9
	35	4.40×10^{-4}		
	45	9.89×10^{-4}		
60MeOH	25	3.87×10^{-4}	14.6 ± 0.2	25.3 ± 0.7
	35	9.05×10^{-4}		
	45	1.93×10^{-3}		
70Acetone	25	5.86×10^{-5}	13.9 ± 1.6	31.4 ± 5.5
	35	1.11×10^{-4}		
	45	2.72×10^{-4}		
50Acetone	25	1.71×10^{-4}	15.1 ± 0.8	25.2 ± 2.7
	35	3.76×10^{-4}		
	45	9.05×10^{-4}		
30Acetone	25	6.81×10^{-4}	13.4 ± 0.3	28.0 ± 1.0
	35	1.51×10^{-3}		
	45	3.01×10^{-3}		
50TFE ^e	25	1.35×10^{-4}	15.9 ± 0.0	22.8 ± 0.2
	35	3.36×10^{-4}		
	45	7.82×10^{-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. ^eSolvent prepared on a weight-weight basis at 25.0 °C, and the other component is water.

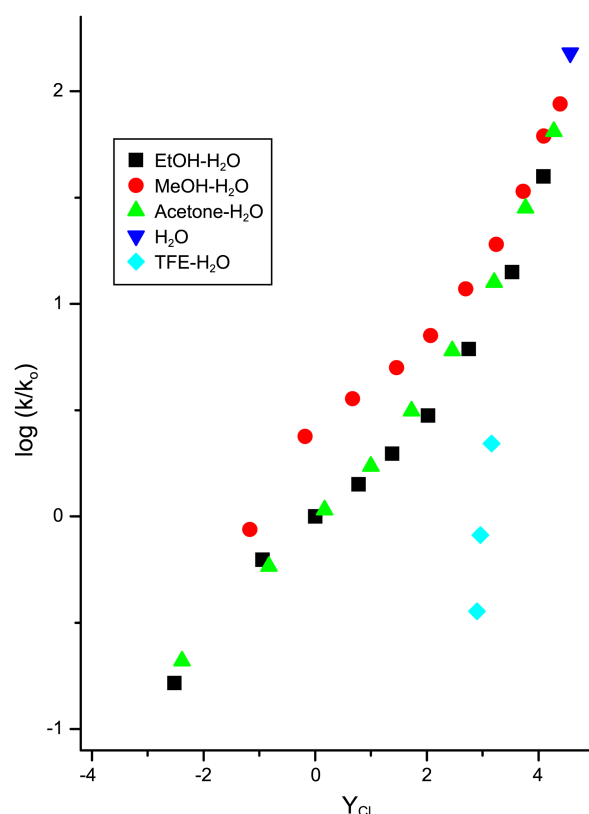


Figure 1. Plot of $\log(k/k_0)$ for solvolyses **1** against Y_{Cl} at 25.0 °C.

(80% ethanol).

$$\log(k/k_0) = mY + c \quad (3)$$

The Grunwald-Winstein plots (Eq. 3) of the rate constants in Table 1 are presented in Figure 1, using the solvent ionizing power scale Y_{Cl} . In Figure 1, the plots for the three aqueous mixtures exhibit dispersions into three separate lines, even though each individual binary solvent system exhibited a linear relationship. Furthermore, the low nucleophilicity and high ionizing power of the fluorinated alcohol, CF₃CH₂OH, showed a large deviation from Figure 1. This strongly suggests that the solvolysis of this compound is sensitive to both solvent nucleophilicity and solvent ionizing power.

A second term was suggested, which would be governed by the solvent nucleophilicity. In this equation, l represents the sensitivity to change in the solvent nucleophilicity (N) and the other terms are the same as in Eq. (3). The resulting Eq. (4) is often referred to as an extended Grunwald-Winstein equation.¹⁵ Initially applied to unimolecular and bimolecular solvolytic substitution reactions at a saturated carbon atom, the equation has also been applied, with considerable success to solvolytic substitution at the sulfur of sulfonyl chlorides¹⁶ and at the phosphorus of phosphoryl compounds.⁹

$$\log(k/k_0) = lN + mY + c \quad (4)$$

The extended Grunwald-Winstein equation, is useful for determining the extent of nucleophilic participation using the solvent, because the magnitudes of l and m in Eq. (4) are

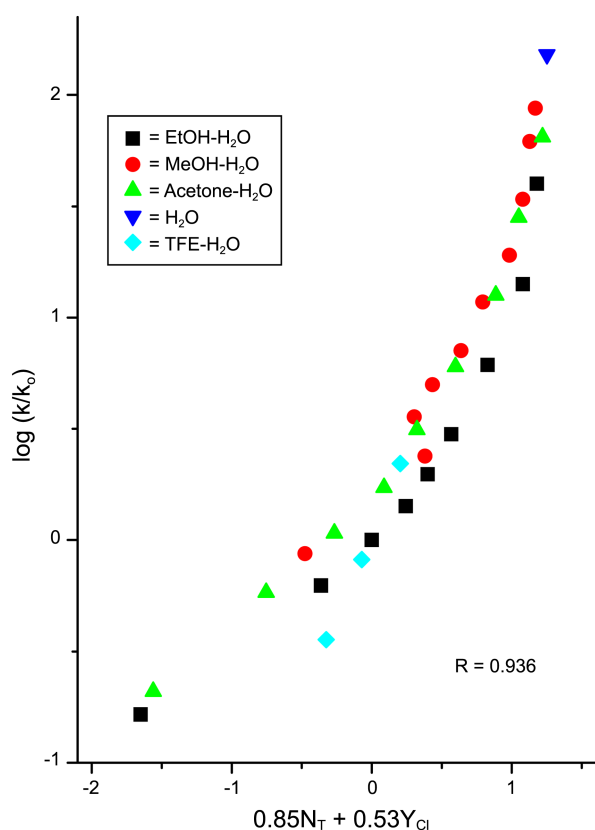


Figure 2. The plot of $\log(k/k_o)$ for solvolyses of **1** against $0.85N_T + 0.53Y_{Cl}$ at 25.0 °C.

the indicators used to determine whether a nucleophilic substitution reaction proceeds through an unimolecular (S_N1 , *i.e.*, $l \approx 0$ and $m \approx 1$) or a bimolecular (S_N2 , *i.e.*, $l \approx 1.0$ and $m \approx 0.5$) reaction, and an addition-elimination mechanism (*i.e.*, $l \geq 1.5$ and $m \approx 0.6$). Therefore, the determination of the l and m values would provide valuable information concerning the structure of the TS for the solvolyses.^{11b,17}

The analysis in terms of Eq. (4) (for the full 32 solvents for which rate constants of solvolysis of TC1 at 25.0 °C have

been determined by the conductivity technique) leads to values for l of 0.85, for m of 0.53 and for c of 0.4, with a satisfactory correlation coefficient of 0.936. The plot in terms of Eq. (3) is shown in Figure 2. The l value of 0.85 was smaller than those recently reported for reactions proceeding through an addition-elimination mechanism ($l \geq 1.5$), whereas these values were similar to those previously reported for the bimolecular (S_N2) solvolyses of the complex substances dimethyl thiophosphorochloridate³ ($l = 1.16$); N,N,N',N' -tetramethyldiamidophosphorochloridate⁴ ($l = 1.14$); 2-phenyl-2-ketoethyl tosylate⁵ ($l = 1.03$); diphenyl thiophosphinyl chloride⁶ ($l = 0.96$); and 9-fluorenyl chloroformate⁷ ($l = 0.95$). This suggests an S_N2 mechanism involving nucleophilic attack by the solvent at the phosphorus atoms of TC1. The solvolysis of TC1, where bond formation ($l = 0.85$) exceeds bond breaking ($m = 0.53$), and the values are still in the range of the S_N2 mechanism, reflects the degree of nucleophilic assistance based on the measure of the solvent nucleophile.^{4,7,17}

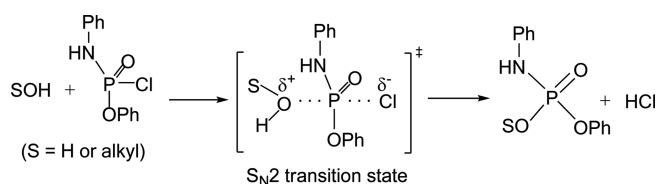
A fairly recent review¹⁰ favored an interpretation in terms of a concerted bimolecular displacement (S_N2) mechanism, involving a solvent attack at the phosphorus. Our analyses of the solvolysis of TC1 are considered to be consistent with such an explanation. The close similarity of both the l and the m values for attack at the carbonyl carbon to those for the attack at the phosphorus of TC1 gives an indication that the solvolyses of TC1 could also be concerted. The solvolysis of TC1 is best considered in terms of a concerted S_N2 reaction (Scheme 2), possibly with general-base catalysis by a second solvent molecule. Catalysis of this type has previously been proposed for solvolyses in hydroxylic solvents at phosphorus.

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 rate constants of solvolysis for other entries within Table 3. The mechanism of solvolysis, 1-adamantyl chloroformate¹⁸ (1-AdOCOCI); 2-adamantyl chloroformate^{17b} (2-AdOCOCI); N,N -diphenyl carbamoyl chloride¹⁹ (Ph_2NCOCl); and isopropyl chloride²⁰ (*i*-PrOCOCI) are known to proceed by an S_N1 pathway. In

Table 3. Coefficients from extended Grunwald-Winstein treatments [equation (4)] for the solvolysis of **1** and a comparison with values for other solvolytic displacements at phosphorus (V) and carbonyl carbon.

Substrate	Reaction Type	n^a	l^b	m^b	l/m	R^c
1-AdOCOCI ^d	S_N1	15	~ 0	0.47 ± 0.03	~ 0	0.985
2-AdOCOCI ^e	S_N1	19	0.03 ± 0.07	0.48 ± 0.04	0.06	0.971
Ph_2NCOCl^f	S_N1	33	0.23 ± 0.04	0.58 ± 0.03	0.40	0.969
<i>i</i> -PrOCOCI ^g	S_N1	20	0.28 ± 0.05	0.52 ± 0.03	0.54	0.979
$(MeO)_2PSCl^h$	S_N2	28	1.16 ± 0.08	0.55 ± 0.03	2.1	0.966
$(Me_2N)_2POCl^i$	S_N2	31	1.14 ± 0.05	0.63 ± 0.04	1.8	0.982
$PhCOCH_2OTs^j$	S_N2	24	1.03 ± 0.04	0.56 ± 0.04	1.8	0.990
Ph_2PSCl^k	S_N2	25	1.00 ± 0.04	0.64 ± 0.03	1.6	0.983
9-Fluorenyl-OCOCI ^l	S_N2	30	0.95 ± 0.07	0.39 ± 0.04	2.4	0.941
$PhNHP(O)ClOPh^m$	S_N2	32	0.85 ± 0.14	0.53 ± 0.04	1.6	0.936
$(PhO)_2POCl^n$	S_{AN}	27	1.87 ± 0.09	0.85 ± 0.04	2.2	0.973

^aNumber of data points. ^bFrom eqn. (4). ^cCorrelation coefficient. ^dFrom ref. 18. ^eFrom ref. 17. ^fFrom ref. 19. ^gFrom ref. 20. ^hFrom ref. 3. ⁱFrom ref. 4. ^jFrom ref. 5. ^kFrom ref. 6. ^lFrom ref. 7. ^mThis work. ⁿFrom ref. 8.



Scheme 2

contrast, the reactions in our earlier work with the solvolysis of dimethyl thiophosphorochloridate³ ((MeO)₂PSCl); *N,N,N',N'*-tetramethyldiamidophosphorochloridate⁴ ((Me₂N)₂-POCl); 2-phenyl-2-ketoethyl tosylate⁵ (PhCOCH₂OTs); diphenyl thiophosphinyl chloride⁶ (Ph₂PSCl); and 9-fluorenyl chloroformate¹⁰ (9-Fluorenyl-OCOCl), were believed to proceed through an S_N2 mechanism.

Also the solvolysis of TC2 ((PhO)₂POCl) was previously found to proceed by addition-elimination reaction.⁸ The *l* and *m* values of TC1 are consistent with a S_N2 mechanism for the solvolyses TC1 in Table 3. The major difference (*l*) is that the value of solvolysis of TC1 is smaller than for diphenyl phosphinylchloridate (TC2, Table 3). Possibly, this reflects decreased nucleophilic participation at the TS due to reduced interaction involving the PhNH group, relative to the PhO bond, which features more electronegative oxygen.

The ratios of *l* and *m* values (*l/m*) have 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 (Table 3): *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 (S_N1).¹⁸⁻²⁰

The solvolyses of 1-adamantyl chloroformate¹⁸ (*l/m* = ~0); 2-adamantyl chloroformate^{17b} (*l/m* = ~0.6); *N,N*-diphenyl carbamoyl chloride¹⁹ (*l/m* = 0.40); and isopropyl chloride²⁰ (*l/m* = 0.54), are indicated to proceed by the ionization pathway (S_N1). In the reactions of dimethyl thiophosphorochloridate³ (*l/m* = 2.1); *N,N,N',N'*-tetramethyl diamidophosphorochloridate⁴ (*l/m* = 1.8); 2-phenyl-2-ketoethyl tosylate⁵ (*l/m* = 1.8); diphenyl thiophosphinyl chloride⁶ (*l/m* = 1.6); and 9-fluorenyl chloroformate⁷ (*l/m* = 2.2) solvolysis, an S_N2 or an addition-elimination pathway is dominant (Table 3).

The *l/m* value was 1.6 for the solvolysis of TC1. This result suggests that the solvolysis reactions of this compound in the more nucleophilic solvent systems are very sensitive toward changes in solvent nucleophilicity. The result also suggest that we can assign a bimolecular mechanism (S_N2), or a fast addition-elimination pathway (A-E) pathway dominated by the bond formation between the reaction center of phosphorus in TC1 and the solvent, as the rate-determining step.⁹

Conclusion

The solvolyses of phenyl *N*-phenyl phosphoramidochloridate (TC1) proceeded rather rapidly and the progress of the reaction as a function of time could be conveniently monitored using a rapid-response conductivity technique. Appli-

cation of the extended Grunwald-Winstein equation (Eq. (4)) in 32 solvents led to an *l* value of 0.85 and an *m* value of 0.53, with a correlation coefficient of 0.936. These values are shown (Table 3) to be similar to previously determined values for nucleophilic attack by solvent at phosphorus (V) and at carbonyl carbons. Previously studied solvolytic displacements at phosphorus have usually been proposed to follow an S_N2 pathway, and such a pathway is also proposed for the solvolyses of TC1. The activation parameters of the typical solvents were determined and the large negative entropies of activation observed were consistent with a bimolecular process.

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