

Kinetic Studies of the Solvolyses of Phenyl 4-Methylphenoxy Thiophosphinyl Chloride

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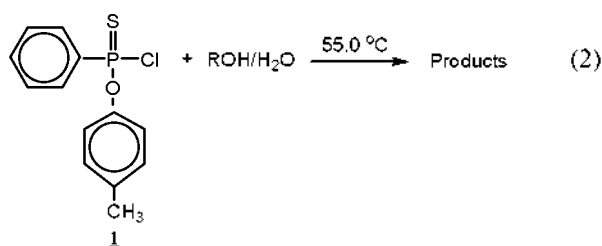
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The extended Grunwald-Winstein equation can be expressed as in equation (1); k and k_0 represent the specific rates of solvolysis of a substrate RX in a given solvent and in the standard solvent (80% ethanol), respectively; l is the sensitivity of the solvolysis towards changes in solvent nucleophilicity (N_T);¹ m is the sensitivity of the solvolysis towards changes in solvent ionizing power (Y_X , for a leaving group X);² and c is a constant (residual) term.

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

A considerable recent effort has been to study the extent to which the solvent nucleophilicity and solvent ionizing power scales, developed for nucleophilic attack at sp² carbon³ and at phosphorus⁴ and at sulfur.⁵ There have been several studies of the kinetics of nucleophilic substitution reaction at a tetrahedral phosphorus atom⁶ and a S_N2 displacement at phosphorus is the usually proposed mechanism.

In this work, we investigated the solvolyses of phenyl 4-methylphenoxy thiophosphinyl chloride (**1**) in pure solvents and mixed binary solvents to obtain an exact kinetic information in various solvents at 55.0 °C, equation (2).



In addition to the application of the extended Grunwald-Winstein equation to the specific rates, the influence of temperature on the specific rate in the three solvents has been discussed by calculated activation enthalpies and entropies. For understanding a further exact mechanistic information, the kinetic solvent isotope effect (KSIE), the kinetic run was performed in deuterated methanol (MeOD).

Results and Discussion

The specific rates of solvolysis of **1** were determined at 55.0 °C in 29 solvents. Used solvents are consisted of ethanol, methanol, and binary mixtures of water with ethanol, methanol,

acetone and 2,2,2-trifluoroethanol (TFE). The rate constants are summarized in Table 1, together with the solvent nucleophilicity (N_T)¹ and solvent ionizing power (Y_{Cl})² values.

The activation parameters for solvolysis of **1** are shown in Table 2. The values of ΔH^\ddagger (= 12.8 ~ 13.9 kcal·mol⁻¹) are relatively low, whereas the values of ΔS^\ddagger (= -32.3 ~ -34.6 cal·mol⁻¹·K⁻¹) are large and negative. This observation lies in the

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

Solvent ^b	10 ³ k ^c (s ⁻¹)	N_T ^d	Y_{Cl} ^e
100% EtOH	0.229 ± 0.002	0.37	-2.52
90% EtOH	0.407 ± 0.003	0.16	-0.94
80% EtOH	0.676 ± 0.007	0.00	0.00
70% EtOH	0.933 ± 0.006	-0.20	0.78
60% EtOH	1.10 ± 0.03	-0.38	1.38
50% EtOH	1.70 ± 0.04	-0.58	2.02
40% EtOH	3.16 ± 0.04	-0.74	2.75
20% EtOH	3.55 ± 0.03	-1.16	4.09
100% MeOH ^f	0.427 ± 0.004	0.17	-1.20
90% MeOH	1.05 ± 0.02	-0.01	-0.20
80% MeOH	2.82 ± 0.05	-0.06	0.67
70% MeOH	4.47 ± 0.06	-0.40	1.46
60% MeOH	7.08 ± 0.06	-0.54	2.07
50% MeOH	13.0 ± 0.3	-0.75	2.70
40% MeOH	19.2 ± 0.3	-0.87	3.25
95% Acetone	0.0162 ± 0.0002	-0.49	-3.19
90% Acetone	0.0324 ± 0.0003	-0.35	-2.39
80% Acetone	0.195 ± 0.002	-0.37	-0.83
70% Acetone	0.457 ± 0.004	-0.42	0.17
60% Acetone	1.23 ± 0.02	-0.52	1.00
50% Acetone	1.82 ± 0.02	-0.70	1.73
40% Acetone	3.89 ± 0.03	-0.83	2.46
30% Acetone	7.41 ± 0.06	-0.96	3.21
20% Acetone	15.6 ± 0.3	-1.11	3.77
97% TFE ^g	0.00309 ± 0.00003	-3.30	2.53
90% TFE	0.0562 ± 0.0004	-2.55	2.85
80% TFE	0.155 ± 0.002	-2.19	2.90
70% TFE	0.204 ± 0.002	-1.98	2.96
50% TFE	0.977 ± 0.005	-1.73	3.16

^aUnless otherwise indicated, a 10⁻³ M solution of the substrate in the indicated solvent, also containing 0.1% CH₃CN within the solvent. ^bOn a volume-volume content at 25.0 °C. ^cWith associated standard deviations. ^dValues from ref. 1. ^eValues from ref. 2. ^fValue for k of 2.15 (± 0.02) · 10³ s⁻¹ in methanol-*d* (MeOD), corresponding to k_{MeOH}/k_{MeOD} value of 1.99 ± 0.04. ^gOn a weight-weight basis at 25.0 °C.

Table 2. Specific rates and activation parameters for the solvolysis of **1**^a in pure and aqueous solvents at various temperatures.

Solvent	Temperature (°C)	$10^3 k^b$ (s ⁻¹)	ΔH^\ddagger (kcal·mol ⁻¹) ^c	$-\Delta S^\ddagger$ (cal·mol ⁻¹ ·K ⁻¹) ^c
100% EtOH	25	0.301 ± 0.002	12.8 ± 0.5	34.6 ± 1.8
	35	0.573 ± 0.003		
	45	1.15 ± 0.002		
	55	2.29 ± 0.002		
80% EtOH	25	0.890 ± 0.003	12.8 ± 0.3	32.3 ± 0.9
	35	1.72 ± 0.02		
	45	3.56 ± 0.04		
	55	6.76 ± 0.07		
90% TFE	25	0.0639 ± 0.0002	13.9 ± 0.4	34.3 ± 1.4
	35	0.128 ± 0.002		
	45	0.281 ± 0.003		
	55	0.562 ± 0.004		

^aA 10⁻³ M solution of the substrate in the indicated solvent, also containing 0.1% CH₃CN. ^bWith associated standard deviation. ^cThe activation parameters are accompanied by the standard error.

range of those for a S_N2 reactions.⁷

The extended Grunwald-Winstein equation is a very useful indicator of the extent of nucleophilic participation by the solvent, as indicated by the magnitude of the parameter, *l*, which, in turn, is directly related to whether a substitution reaction follows a unimolecular or bimolecular pathway.¹ In general, for an ionization reaction without any nucleophilic assistance, *l* will be zero and *m* close to unity. Whereas for a reaction proceeding with extensive nucleophilic assistance, the *l* value

will be in the region of 0.7 to 1.7 and the *m* value in the region of 0.3 to 0.5.⁵

Therefore, determination of these values will be a valuable source of information concerning the structure of the transition state for these solvolyses.⁹ Application of equation (1) to the solvolyses of **1** led to 1.08 ± 0.08 for *l*, 0.53 ± 0.03 for *m*, and 0.19 for *c*; the standard error of the estimate was 0.07 and the R value was 0.958. Figure 1. The *l* and *m* values for the solvolysis of **1** were compared with recently reported results for the specific rates of solvolysis of diphenyl thiophosphorochloridate (*l* = 1.29, *m* = 0.64),¹⁰ diphenyl phosphorochloridate (*l* = 1.31, *m* = 0.61),¹¹ diphenylphosphinyl chloride (*l* = 1.42, *m* = 0.54)^{4c} and diphenylthiophosphinyl chloride (*l* = 1.00, *m* = 0.64),¹² isopropylsulfonyl chloride (*l* = 1.28 ± 0.05, *m* = 0.64 ± 0.03),⁵ N,N-dimethylsulfonyl chloride (*l* = 1.20 ± 0.04, *m* = 0.72 ± 0.03),⁵ 2-phenyl-2-ketoethyl tosylate (*l* = 1.03 ± 0.04, *m* = 0.56 ± 0.04),¹³ dimethyl thiophosphorochloridate (*l* = 1.16 ± 0.08, *m* = 0.55 ± 0.03),^{4a} and N,N,N',N'-tetramethyl dimidophosphorochloridate (*l* = 1.14 ± 0.05, *m* = 0.63 ± 0.04).^{4h} The *l* value of 1.08 and the *m* value of 0.53 for the solvolysis of **1** were consistent with the reported works^{4,5,10-13} which indicates a S_N2 mechanism involving an attack by the solvent at phosphorus of **1**. The solvolysis of **1**, where bond making (*l* = 1.08) is more progressed than bond breaking (*m* = 0.53), and the values are still in the range of S_N2 mechanism, reflecting on the degree of the nucleophilic assistance based on the measure of solvent nucleophile.^{9c}

The *l/m* values from the extended Grunwald-Winstein equation could be classified into three classes of mechanism: *l/m* values of 1.2 to 2.0 for bimolecular mechanism (S_N2), 2.3 to 3.5 for an addition-elimination pathway, and below 0.7 for an ionization pathway.¹⁴ For the solvolysis of **1**, the *l/m* value was calculated as 2.0 which is very similar to those of diphenyl thiophosphorochloridate (*l/m* = 2.0),¹⁰ diphenyl phosphorochloridate (*l/m* = 2.1),¹¹ diphenylphosphinyl chloride (*l/m* = 2.6)^{4c} and diphenylthiophosphinyl chloride (*l/m* = 1.60),¹² isopropylsulfonyl chloride (*l/m* = 2.0),⁵ N,N-dimethyl sulfonyl chloride (*l/m* = 1.7),⁵ 2-phenyl-2-ketoethyl-tosylate (*l/m* = 1.8),¹³ dimethyl thiophosphorochloridate (*l/m* = 2.1),^{4a} and

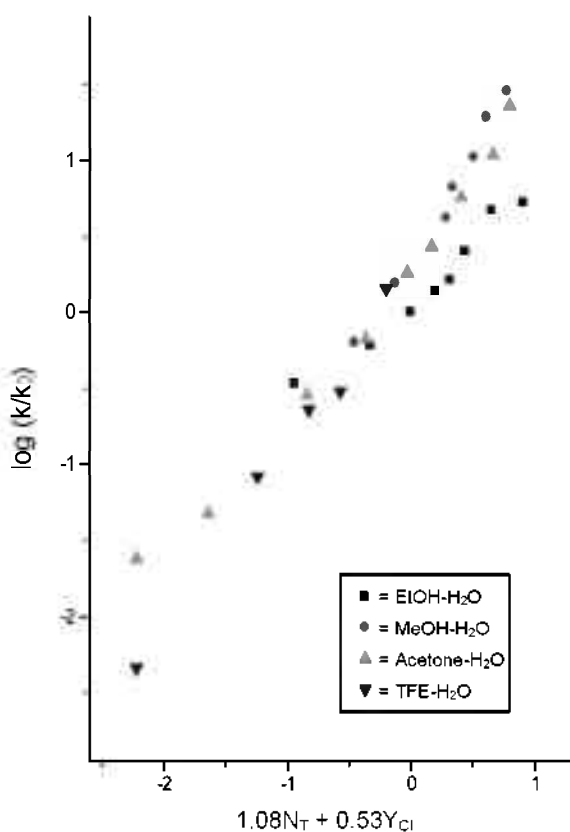
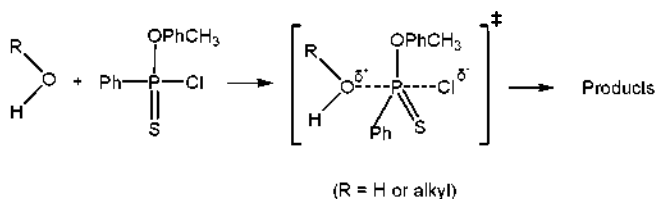


Figure 1. Plot of log (*k*/*k*₀) for solvolyses of **1** at 55.0 °C against (1.08 N_T + 0.53 Y_{Cl}).



Scheme 1

N,N,N',N'-tetramethyldiamido-phosphorochloridate ($l/m = 1.8$),^{4b} and these similarities suggest the S_N2 mechanism.

Bentley, Jones, and Koo^{9d} suggested that the concerted mechanism being favored in more polar solvents. A fairly recent review¹⁵ has suggested an interpretation in terms of the S_N2 mechanism, involving an attack at sulfur by solvent. Our results also seem to be consistent with such an explanation. Scheme 1.

In methanol and methanol-*d* (MeOD), a KSIE ($k_{\text{MeOH}}/k_{\text{MeOD}}$) of 1.99 ± 0.05 at 55.0°C is observed ($k_{\text{MeOD}} = 2.15 (\pm 0.20) \times 10^{-3} \text{ s}^{-1}$). This result is in the range of values from 1.58 ± 0.05 to 2.31 ± 0.07 which have been observed¹⁶ for the corresponding methanolyses of a series of phosphorus,⁴ benzyl³ and benzenesulfonyl compounds in which the reactions are believed to be a S_N2 in character.

The sensitivity values ($l = 1.08$ and $m = 0.53$) of **1** were similar to those obtained for diphenyl thiophosphorochloridate ((PhO)₂PSCl, **2**),¹⁰ diphenyl phosphorochloridate ((PhO)₂POCl, **3**),¹¹ diphenylphosphinyl chloride (Ph₂POCl, **4**)^{4c} and diphenylthio-phosphinyl chloride (Ph₂PSCl, **5**).¹² As with the previously studied of **2** ~ **5** solvolyses, a S_N2 pathway is proposed for the solvolyses of **1**. The activation parameters, ΔH^\ddagger ($= 12.8 \sim 13.9 \text{ kcal}\cdot\text{mol}^{-1}$) and ΔS^\ddagger ($= -32.3 \sim -34.6 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), were in line with values expected for a S_N2 reaction.⁷ Kinetic solvent isotope effect is accord with a S_N2 mechanism as shown in the range of 1.99 in MeOH/MeOD.¹⁶

Experimental

Substrate (**1**) was prepared by reacting phenyl thiophosphonic dichloride (Sigma-Aldrich's Rare Chemical Library) with 4-methylphenol. The purification of acetone, methanol, ethanol and TFE were carried out as previously described.¹⁷ The substrate did not react with the pure acetonitrile within the stock solution. (Ph-4-CH₃PhO)PSCl : Calc. for C₁₃H₁₂OPSCl : C, 62.15; H, 4.78. Found : C, 62.11; H, 4.80%.

The kinetic experiments were carried out by allowing a conductivity cell containing 12.5 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. A 12 μL portion of a 1.0 mol dm⁻³ stock solution of **1** in acetonitrile was then added. The monitoring of increases in conductivity with time and the calculation of the specific rates (first-order rate coefficients) were as previously reported.⁹

The multiple regression analyses were performed using commercially available statistical packages.

References

- (a) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1991**, *56*, 1845. (b) Kevill, D. N. In *Advances in Quantitative Structure-Property Relationships*; Charton, M., ed.; JAI Press: Greenwich, CT, 1996; Vol. 1, pp 81-115.
- (a) Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846. (b) Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121. (c) Kevill, D. N.; D'Souza, M. J. *J. Chem. Res. Synop.* **1993**, 174. (d) Bentley, T. W.; Carter, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 5741. (e) Koo, I. S.; Bentley, T. W.; Kang, D. H.; Lee, I. *J. Chem. Soc. Perkin Trans. 2* **1991**, 296.
- (a) Kevill, D. N.; D'Souza, M. J. *J. Chem. Soc. Perkin Trans. 2* **1997**, 1721. (b) Koh, H. J.; Kang, S. J.; Kim, C. J. *Bull. Korean Chem. Soc.* **2009**, *30*, 378.
- (a) Kevill, D. N.; Carver, J. S. *Org. Biomol. Chem.* **2004**, *2*, 2040. (b) Kevill, D. N.; Miller, B. J. *Org. Chem.* **2002**, *67*, 7399. (c) Kevill, D. N.; Koh, H. J. *J. Phys. Org. Chem.* **2007**, *20*, 88.
- Kevill, D. N.; Park, B. C.; Park, K. H.; D'Souza, M. J.; Yaakoubd, L.; Mlynarski, S. L.; Kyong, J. B. *Org. Biomol. Chem.* **2006**, *4*, 1580.
- (a) Kirby, A. J.; Varroglis, A. G. *J. Am. Chem. Soc.* **1967**, *89*, 415. (b) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper and Row: New York, 1976. (c) Edmundson, R. S. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1996; Vol. IV, pp 598-630. (d) Hoque, Md. E. U.; Dey, N. K.; Guha, A. K.; Kim, C. K.; Lee, B.-S.; Lee, H. W. *Bull. Korean Chem. Soc.* **2007**, *28*, 1797. (e) Koh, H. J.; Kang, S. J.; Kevill, D. N. *Phosphorus, Sulfur, and Silicon* **2008**, *183*, 364.
- (a) Lee, I.; Sung, D. D.; Uhm, T. S.; Ryu, Z. H. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1697. (b) Yew, K. H.; Koh, H. J.; Lee, H. W.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2263.
- Lee, S. H.; Rhu, C. J.; Kyong, J. B.; Kim, D. K.; Kevill, D. N. *Bull. Korean Chem. Soc.* **2007**, *28*, 657.
- (a) Kevill, D. N.; D'Souza, M. J. *J. Org. Chem.* **1998**, *63*, 2120. (b) Kyong, J. B.; Park, B. C.; Kim, C. B.; Kevill, D. N. *J. Org. Chem.* **2000**, *65*, 8051. (c) Kevill, D. N.; D'Souza, M. J. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1790. (d) Bentley, T. W.; Jones, R. O.; Koo, I. S. *J. Chem. Soc. Perkin Trans. 2* **1994**, 753. (e) Kevill, D. N.; D'Souza, M. J. *J. Phys. Org. Chem.* **2002**, *15*, 881. (f) Kyong, J. B.; Won, H. S.; Lee, Y. H.; Kevill, D. N. *Bull. Korean Chem. Soc.* **2005**, *26*, 661.
- Koh, H. J.; Kang, S. J.; Kevill, D. N. *Bull. Korean Chem. Soc.* **2009**, *30*, 383.
- Koh, H. J.; Kevill, D. N. Preparing the paper.
- Koh, H. J.; Kang, S. J.; Kevill, D. N. *Bull. Korean Chem. Soc.* **2008**, *10*, 1927.
- Kevill, D. N.; Kim, C. B. *J. Org. Chem.* **2005**, *70*, 1490.
- (a) Kyong, J. B.; Kim, Y. G.; Kim, D. K.; Kevill, D. N. *Bull. Korean Chem. Soc.* **2000**, *21*, 662. (b) Kevill, D. N.; Kyong, J. B.; Weitz, F. L. *J. Org. Chem.* **1990**, *55*, 4304. (c) Kyong, J. B.; Ryu, S. H.; Kevill, D. N. *Int. J. Mol. Sci.* **2006**, *7*, 186. (d) Kevill, D. N.; D'Souza, M. J. *J. Org. Chem.* **2004**, *69*, 7044. (e) Kyong, J. B.; Won, H. S.; Kevill, D. N. *Int. J. Mol. Sci.* **2005**, *6*, 87.
- Gordon, I. M.; Maskill, H.; Ruasse, M.-F. *Chem. Soc. Rev.* **1989**, *18*, 123.
- Koo, I. S.; Lee, I.; Oh, J. U.; Yang, K. Y.; Bentley, T. W. *J. Phys. Org. Chem.* **1993**, *6*, 223.
- Lee, I.; Koh, H. J.; Park, Y. S.; Lee, H. W. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1575.