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

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The extended Grunwald-Winstein equation can be expressed as in equation (1); k and k_o 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.

$$\log (k/k_o) = l\,N_T + m\,Y_X + c \qquad (1)$$

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 sp^2 carbon[3] and at phosphorus[4] and at sulfur.[5] There have been several studies of the kinetics of nucleophilic substitution reaction at a tetrahedral phosphorus atom[6] 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).

$$(2)$$
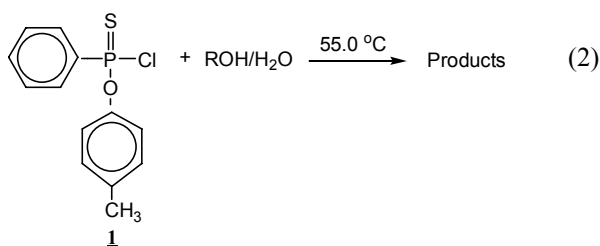
In addition to the application of the extended Grunwald-Winstein equation to the specific rates, the influence of temperature on the specific rate in the three solvents has been discussed by calculated activation enthalpies and entropies. For understanding a further exact mechanistic information, the 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-trifluroethanol (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 $\Delta H^{\neq}$ (= 12.8 ~ 13.9 kcal·mol^{-1}) are relatively low, whereas the values of $\Delta S^{\neq}$ (= −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 $\underline{\mathbf{1}}$[a] at 55.0 °C and N_T and Y_{Cl} values of the solvents.

Solvent[b]	$10^2 k$[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

[a]Unless otherwise indicated, a 10^{-3} M solution of the substrate in the indicated solvent, also containing 0.1% CH$_3$CN within the solvent. [b]On a volume-volume content at 25.0 °C. [c]With associated standard deviations. [d]Values from ref. 1. [e]Values from ref. 2. [f]Value for k of 2.15 (± 0.02) × 10^{-3} s^{-1} in methanol-*d* (MeOD), corresponding to k_{MeOH}/k_{MeOD} value of 1.99 ± 0.04. [g]On 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})	$\Delta H^{\neq}$ (kcal·mol^{-1})[c]	$-\Delta S^{\neq}$ (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		

[a]A 10^{-3} M solution of the substrate in the indicated solvent, also containing 0.1% CH_3CN. [b]With associated standard deviation. [c]The 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.[4] 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

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

will be in the region of 0.7 to 1.7 and the m value in the region of 0.3 to 0.5.[8]

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 ($l = 1.28 \pm 0.05$, $m = 0.64 \pm 0.03$),[5] N,N-dimethylsulfamoyl chloride ($l = 1.20 \pm 0.04$, $m = 0.72 \pm 0.03$),[5] 2-phenyl-2-ketoethyl tosylate ($l = 1.03 \pm 0.04$, $m = 0.56 \pm 0.04$),[13] dimethyl thiophosphorochloridate ($l = 1.16 \pm 0.08$, $m = 0.55 \pm 0.03$),[4a] and N,N,N',N'-tetramethyl dimidophosphorochloridate ($l = 1.14 \pm 0.05$, $m = 0.63 \pm 0.04$).[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 sulfamoyl chloride ($l/m = 1.7$),[5] 2-phenyl-2-ketoethyl-tosylate($l/m = 1.8$),[13] dimethyl thiophosphorochloridate ($l/m = 2.1$),[4a] and
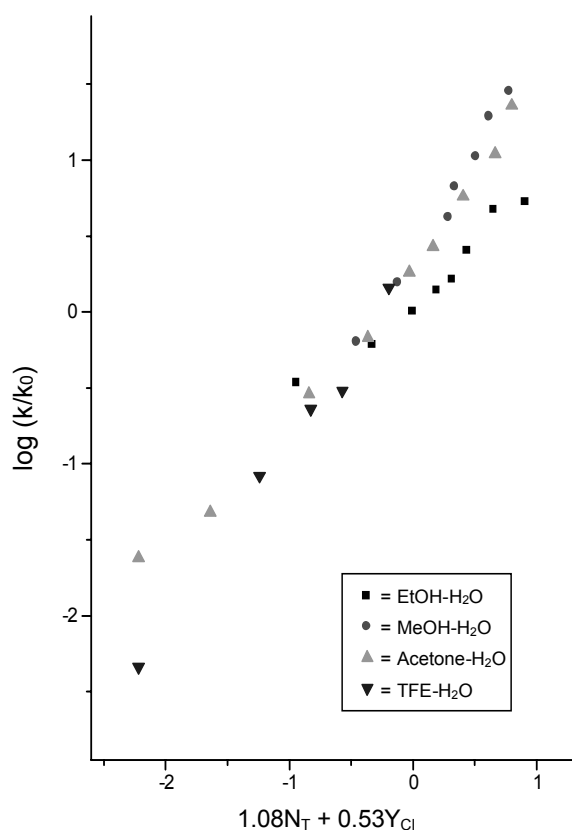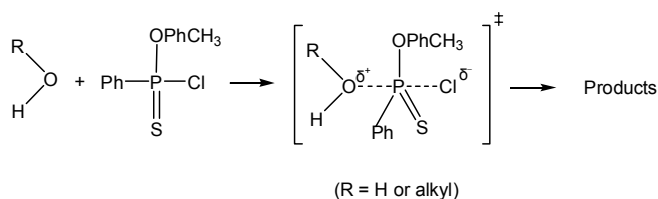
(R = H or alkyl)

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 review[15] 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_{MeOH}/k_{MeOD}) of 1.99 ± 0.05 at 55.0 °C is observed (k_{MeOD} = 2.15 (± 0.20) × $10^{-3}s^{-1}$). This result is in the range of values from 1.58 ± 0.05 to 2.31 ± 0.07 which have been observed[16] for the corresponding methanolyses of a series of phosphorus,[4] benzyl[3] 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 (($PhO)_2$ PSCl, **2**),[10] diphenyl phosphorochloridate (($PhO)_2POCl$, **3**),[11] diphenylphosphinyl chloride (Ph_2POCl, **4**)[4c] and diphenylthiophosphinyl chloride (Ph_2PSCl, **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, $\Delta H^{\neq}$ (= 12.8 ~ 13.9 kcal·mol^{-1}) and $\Delta S^{\neq}$ (= −32.3 ~ −34.6 cal·mol^{-1}·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-CH$_3$PhO)PSCl : Calc. for C$_{13}$H$_{12}$OPSCl : 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.

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