

Correlation of the rates of solvolysis of diphenylphosphinyl chloride using an extended form of the Grunwald–Winstein equation

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ABSTRACT: The specific rates of solvolysis of diphenylphosphinyl chloride (**1**) have been measured at 25.0 °C in 30 solvents. For six representative solvents, studies were made at several temperatures and activation parameters determined. These were used to calculate a value at 25.0 °C in 100% 2,2,2-trifluoroethanol (TFE) from values at higher temperatures. The 31 solvents gave a reasonable extended Grunwald–Winstein plot, correlation coefficient (*R*) of 0.920, which improved to 0.956 when the four TFE–ethanol points were excluded. The sensitivities (*l* and *m*) were similar to those obtained for dimethyl phosphorochloridate and phosphorochloridothionate and for *N,N,N',N'*-tetramethyldiamidophosphorochloridate. As with the three previously studied solvolyses, an S_N2 pathway is proposed for the solvolyses of **1**. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: extended Grunwald–Winstein equation; solvolysis; diphenylphosphinyl chloride; kinetics

INTRODUCTION

As a continuation of our kinetic studies of solvolytic displacements involving loss of chloride ion from phosphorus, we now report a study with diphenylphosphinyl chloride (Ph₂POCl, **1**) as the substrate. This compound is a very useful reagent in organophosphorus chemistry. For example, it is reacted with pentafluorophenol to give pentafluorophenyl diphenylphosphinate, recommended as a coupling reagent in dipeptide synthesis.^{1,2}

Previous studies from our laboratory have been of diaryl (**2**)³ and dimethyl (**3**)⁴ phosphorochloridates, (RO)₂POCl, and the sulfur-for-oxygen substituted dimethyl phosphorochloridothionate, (MeO)₂PSCl, **4**.⁴ A study has also been reported for the solvolyses of *N,N,N',N'*-tetramethyldiamidophosphorochloridate, (Me₂N)₂POCl, **5**.⁵ Linear free energy relationship (LFER) treatments in terms of the extended Grunwald–Winstein equation [Eqn (1)] led, except for the poorly correlated solvolyses of **2** with phenyl (**2a**)

$$\log\left(\frac{k}{k_0}\right) = lN_T + mY_{Cl} + c \quad (1)$$

or *p*-chlorophenyl (**2b**) as the aryl group,³ to acceptable correlations, with very similar *l* and *m* values. In Eqn (1), *k* and *k*₀ are the specific rates of solvolysis of the substrate in the solvent under consideration and in the standard solvent (80% ethanol), respectively; *l* is the sensitivity to changes in the solvent nucleophilicity value (*N*_T);^{6,7} *m* is the sensitivity to changes in the solvent ionizing power (*Y*_{Cl});^{8,9} and *c* is a constant (residual) term.

The studies of (ArO)₂POCl compounds³ were extended by Bentley and Ebdon¹⁰ to the solvolyses in aqueous ethanol and aqueous methanol of ethyl phenylphosphonochloridate, Ph(EtO)POCl, **6**. The variations in rate and the product selectivities over a range of mixed solvent composition showed trends similar to those reported earlier. The fact that the rates were approximately one order of magnitude faster than those for **2a** is considered to be primarily due to the removal of one of the RO-type groups. In the present study of the solvolyses of **1**, we also replace the second RO-type group and, assuming that no change in mechanism results, one would again anticipate an increase in the rates of solvolysis. The specific rate of the ethanolysis of **1** has been determined previously at two temperatures¹¹ and the values were found to be about 25 times higher than for (PhO)₂POCl.^{11,12}

RESULTS

The specific rates of solvolysis were determined at 25.0 °C in 30 solvents. The solvents consisted of ethanol,

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methanol, binary mixtures of 2,2,2-trifluoroethanol (TFE) with ethanol, and binary mixtures of water with ethanol, methanol, acetone, TFE, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). These values are reported in Table 1, together with the solvent nucleophilicity (N_T)^{6,7} and solvent ionizing power (Y_{Cl})^{8,9} values. Also shown in

Table 1 is a value for 100% TFE, extrapolated from studies of the solvolysis at three higher temperatures, reported in Table 2. Also reported in Table 2 are specific rate values at three additional temperatures for five of the solvents of Table 1 and activation parameters calculated from data at all four temperatures for solvolyses of **1** in those five solvents, and from the three temperatures of Table 2 for solvolyses in 100% TFE.

Table 1. Specific rates of solvolysis (k) of diphenylphosphinyl chloride (**1**)^a at 25.0 °C and N_T and Y_{Cl} values of the solvents

Solvent ^b	10^2k (s ⁻¹) ^c	N_T ^d	Y_{Cl} ^e
100% EtOH	0.702 ± 0.010 ^f 0.801 ± 0.006 ^{g,h}	0.37	-2.52
90% EtOH	11.2 ± 0.3	0.16	-0.94
80% EtOH	21.6 ± 1.6 ⁱ 20.8 ± 0.4 ^g	0.00	0.00
70% EtOH	30.9 ± 0.9	-0.20	0.78
60% EtOH	43.8 ± 1.5	-0.38	1.38
50% EtOH	62.6 ± 2.3 ^j	-0.58	2.02
100% MeOH	6.78 ± 0.24 6.06 ± 0.10 ^g	0.17	-1.17
90% MeOH	28.4 ± 0.1	-0.01	-0.18
80% MeOH	51.6 ± 1.0 50.2 ± 1.2 ^g	-0.06	0.67
70% MeOH	70.0 ± 3.2	-0.40	1.46
60% MeOH	102 ± 2	-0.54	2.07
95% Acetone	0.833 ± 0.009	-0.49	-3.19
90% Acetone	4.15 ± 0.08	-0.35	-2.39
80% Acetone	14.8 ± 0.2 15.2 ± 0.5 ^g	-0.37	-0.83
70% Acetone	29.8 ± 0.9	-0.42	0.17
60% Acetone	51.4 ± 1.8	-0.52	0.95
50% Acetone	82.7 ± 2.3	-0.70	1.73
100% TFE	4.22 × 10 ^{-4k}	-3.93	2.81
97% TFE	0.0233 ± 0.0003	-3.30	2.83
90% TFE	0.275 ± 0.003	-2.55	2.85
80% TFE	1.50 ± 0.04	-2.19	2.90
70% TFE	3.97 ± 0.08	-1.98	2.96
50% TFE	16.5 ± 0.4	-1.73	3.16
97% HFIP	5.91 (± 0.40) × 10 ⁻⁴	-5.26	5.17
90% HFIP	0.0365 ± 0.0009	-3.84	4.31
70% HFIP	1.48 ± 0.04	-2.94	3.83
50% HFIP	3.59 ± 0.03	-2.49	3.80
80T-20E ^l	0.0689 ± 0.0031	-1.76	1.89
60T-40E ^l	0.321 ± 0.007	-0.94	0.63
40T-60E ^l	0.706 ± 0.021	-0.34	-0.48
20T-80E ^l	0.954 ± 0.012	0.08	-1.42

^a Unless otherwise indicated, a 10⁻³ M solution of the substrate in the indicated solvent, also containing 0.1% CH₃CN.

^b On a volume–volume basis at 25.0 °C, except for TFE–H₂O and HFIP–H₂O mixtures, which are on a weight–weight basis.

^c With associated standard deviations.

^d Values from Refs. 6 and 7.

^e Values from Refs. 8 and 9.

^f With half and double concentrations of substrate, values obtained of 0.714 ± 0.010 and 0.702 ± 0.007, respectively.

^g With direct addition of 0.4–0.5 μL of substrate to 5 mL of solvent.

^h A value of 0.73 ± 0.07 has been reported at 25.2 °C (Ref. 11).

ⁱ With half and double concentrations of substrate, values of 21.6 ± 1.2 and 22.3 ± 0.9, respectively.

^j With half and double concentrations of substrate, values of 64.9 ± 3.5 and 64.1 ± 3.5, respectively.

^k By extrapolation, using values from Table 2.

^l T–E indicates TFE–EtOH mixtures.

DISCUSSION

In most solvents, the reactions were rather fast, and use of an apparatus allowing rapid response to changes in conductivity^{10,13} 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 amount of a concentrated stock solution in acetonitrile, such that the reaction solution contained about 0.1% acetonitrile. Halmann¹² found for the ethanolysis of the related diethylphosphinyl chloride 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 fourfold variation at our lower concentrations (0.5–2 × 10⁻³ M) of **1** in ethanol and in 50% or 80% ethanol (Table 1).

In ethanol, methanol, and 80% ethanol at 0 °C, the specific rates for solvolyses of **1** are, respectively, 2.0, 3.0, and 4.4 times greater than for **6** under identical conditions.¹⁰ A comparison can also be made with the specific rates of solvolysis of dimethylphosphinyl chloride. Halmann¹² reported a value of 60 × 10⁻⁴ s⁻¹ at -8.5 °C for the ethanolysis in 100% ethanol. Using the data from Tables 1 and 2, we can extrapolate using the Arrhenius equation to a value of 10.1 × 10⁻⁴ s⁻¹ for **1** at this temperature, corresponding to a reduction in rate by a factor of six on replacing the two methyl groups by phenyl groups. Extrapolating values for **1** at two temperatures, a specific rate at -8.5 °C of 6.8 × 10⁻⁴ s⁻¹, and a corresponding reduction by a factor of nine have been reported.¹⁴ We have determined¹⁵ specific rates for solvolysis of dimethylphosphinyl chloride at 0.0 °C of 18.8 (± 0.9) × 10⁻³ s⁻¹ in ethanol and 54.1 (± 0.5) × 10⁻³ s⁻¹ in methanol, corresponding to reductions in rate on replacing methyl by phenyl (Table 2) of 11 and 3, respectively. Accordingly, although in ethanol or methanol replacement of methyl groups by phenyl groups consistently leads to reductions in the rate of solvolysis, the effect is rather modest. Modest effects of this magnitude, while not rigidly requiring a concerted mechanism, are readily rationalized by electronic effects having opposing influences as regards the bond-making and bond-breaking processes, coupled with a larger steric hindrance to approach of a solvent molecule toward the phosphorus reaction center of **1**. The much slower reaction of di-*t*-butylphosphinyl chloride with respect to

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

Solvent	Temperature (°C)	10^3k (s ⁻¹) ^b	$\Delta H^\ddagger_{298.2}$ (kcal mol ⁻¹) ^c	$\Delta S^\ddagger_{298.2}$ (cal mol ⁻¹ K ⁻¹) ^c
100% EtOH	0.0	1.74 ± 0.05^d		
	15.0	4.66 ± 0.10		
	35.0	13.1 ± 0.4	8.9 ± 0.1	-38.5 ± 0.4
80% EtOH ^e	0.0	44.3 ± 0.8		
	15.0	112 ± 1		
	35.0	328 ± 14	9.2 ± 0.1	-31.0 ± 0.3
100% MeOH	0.0	17.2 ± 0.1		
	15.0	35.4 ± 1.6		
	35.0	104 ± 1	8.2 ± 0.1	-36.6 ± 0.4
100% TFE ^f	35.0	0.00123 ± 0.00003		
	45.0	0.00299 ± 0.00001		
	55.0	0.00818 ± 0.00012	18.2 ± 0.1	-22.1 ± 0.3
97% TFE ^g	35.0	0.423 ± 0.015		
	45.0	0.720 ± 0.013		
	55.0	1.18 ± 0.07	9.8 ± 0.2	-42.4 ± 0.7
97% HFIP ^g	35.0	0.00119 ± 0.00001		
	45.0	0.00235 ± 0.00003		
	55.0	0.00595 ± 0.00004	14.0 ± 0.2	-35.7 ± 0.7

^a A 10^{-3} M solution of the substrate in the indicated solvent, also containing 0.1% CH₃CN.

^b With associated standard deviation.

^c Values at 25.0 °C, from Table 1, are also used in calculation (based on four values, except for those for 100% TFE); the activation parameters are accompanied by the standard error.

^d A value of 1.3 ± 0.1 has been reported at -0.2 °C (Ref. 11).

^e On a volume–volume basis at 25.0 °C.

^f Values used to calculate value at 25.0 °C (Table 1).

^g On a weight–weight basis.

diethylphosphinyl chloride¹² is consistent with such a steric effect and, also, not supportive of a claim¹⁶ of S_N1 reaction for the di-*t*-butylphosphinyl chloride.

The solvents used in the correlations include TFE and five TFE–H₂O compositions and four HFIP–H₂O compositions, two important classes of solvents for studies of the specific rates of solvolysis when correlation analyses are performed using the extended Grunwald–Winstein equation [Eqn (1)]. The data points for solvolyses in TFE–ethanol mixtures fell somewhat below the best-fit line (this behavior has been discussed previously⁵) and the correlations were carried out both with and without (Fig. 1) the inclusion of these four data points. The correlation and statistical parameters for these two correlations are presented in Table 3, together with values we have previously determined for other solvolyses which involve displacement of chloride ion from phosphorus(V).

Since the TFE–ethanol points lie toward the middle of the range of the plotted points, their omission leads primarily to an increase in the *c* (intercept) value with only very minor changes in the *l* and *m* values. An accompanying appreciable increase in the multiple correlation coefficient (*R*) and, despite fewer data points, an increase in the *F*-test value are also noted (Table 3).

For the 27-point correlation, the *m* value of 0.54 ± 0.07 is within the range of values, 0.45 ± 0.08 to 0.63 ± 0.03 ,

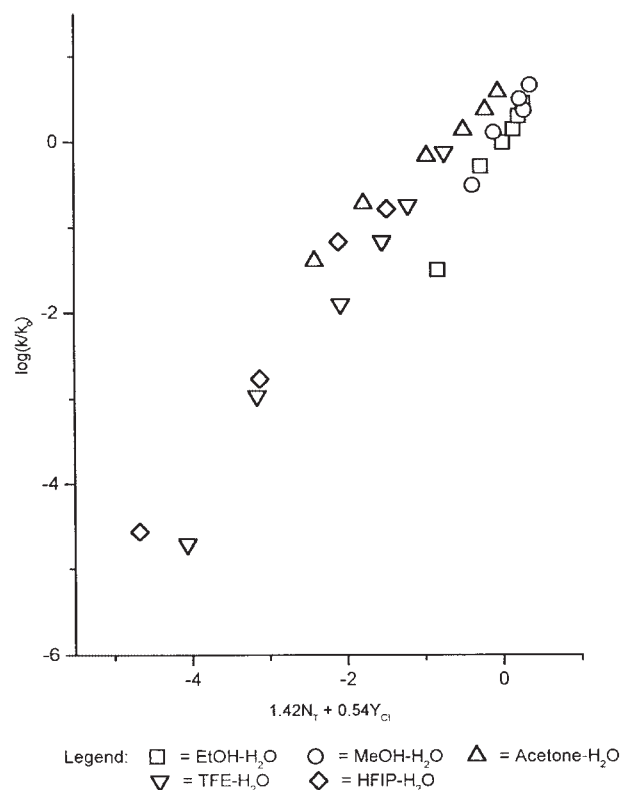


Figure 1. Plot of $\log(k/k_0)$ for solvolyses of diphenylphosphinyl chloride at 25.0 °C against $(1.42N_T + 0.54Y_{Cl})$

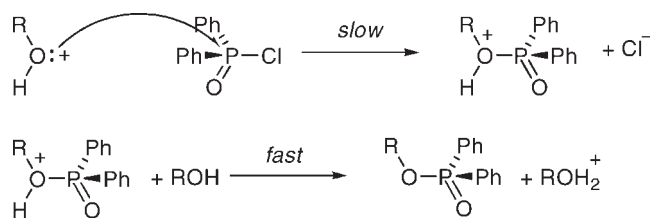
Table 3. Coefficients from the extended Grunwald–Winstein correlations of the specific rates of solvolysis of diphenylphosphinyl chloride at 25.0 °C and a comparison with corresponding values for other solvolytic displacements of chloride ion from phosphorus(V)

Substrate	<i>n</i> ^a	<i>l</i> ^b	<i>m</i> ^b	<i>c</i> ^b	<i>R</i> ^c	<i>F</i> ^d
Ph ₂ POCl	31	1.44 ± 0.13	0.58 ± 0.09	0.15 ± 0.14	0.920	77
Ph ₂ POCl ^e	27	1.42 ± 0.10	0.54 ± 0.07	0.32 ± 0.11	0.956	128
(MeO) ₂ POCl ^f	22	1.36 ± 0.23	0.54 ± 0.13	-0.02 ± 0.17	0.844	24
(MeO) ₂ POCl ^{e,f}	18	1.24 ± 0.14	0.45 ± 0.08	0.18 ± 0.11	0.941	54
(MeO) ₂ PSCl ^f	31	1.21 ± 0.10	0.60 ± 0.04	0.22 ± 0.07	0.943	112
(MeO) ₂ PSCl ^{e,f}	28	1.16 ± 0.08	0.55 ± 0.03	0.30 ± 0.06	0.966	154
(Me ₂ N) ₂ POCl ^g	31	1.20 ± 0.07	0.69 ± 0.04	0.03 ± 0.32	0.958	155
(Me ₂ N) ₂ POCl ^{e,g}	27	1.14 ± 0.05	0.63 ± 0.03	0.17 ± 0.21	0.982	320
(PhO) ₂ POCl ^h	38	1.72 ± 0.18	0.68 ± 0.06	0.42 ± 0.15	0.885	
(<i>p</i> -ClC ₆ H ₄ O) ₂ POCl ^h	31	1.79 ± 0.20	0.58 ± 0.08	0.11 ± 0.18	0.863	

^a Number of data points.^b From Eqn (1).^c Correlation coefficient.^d *F*-test value.^e Data points for TFE–ethanol mixtures excluded.^f From Ref. 4.^g From Ref. 5.^h From Ref. 3.

observed in the analysis using Eqn (1) for the other three solvolyses involving chloride-ion displacement from phosphorus(V).^{4,5} The data for the solvolyses of the two diaryl phosphorochloridates (**2a** and **2b**)³ are included in Table 3 but not in these comparisons since, for reasons which are not understood, poor correlations are obtained for these two substrates. For the solvolyses of **1**, the *l* value of 1.42 ± 0.10 is a little higher than the range of 1.14 ± 0.05 to 1.24 ± 0.14 for the three substrates studied earlier. However, when the combined standard errors are considered, it would be unwise to attempt to assign any appreciable significance to this variation.

The solvolyses of **1** are best considered in terms of a concerted S_N2 reaction (Scheme 1), possibly with general-base catalysis by a second solvent molecule. Such a catalysis has previously been proposed not only for solvolyses in hydroxylic solvents at phosphorus(V)^{3,10} but also at the sulfur(VI) of sulfonyl derivatives.^{17,18} The *l* and *m* values for solvolyses of **1** are consistent not only with the corresponding values for other solvolyses at phosphorus(V) which are believed to be S_N2 in character but, also, with values for solvolyses at sulfur(VI) believed to be S_N2 in character. For example, *l* values of 1.10 ±

**Scheme 1.**

0.07 to 1.28 ± 0.05 and *m* values of 0.61 ± 0.04 to 0.70 ± 0.03 have been reported for four solvolyses of XSO₂Cl-type compounds (with X = alkyl, aryl, or dialkylamino).¹⁹

For bimolecular solvolytic displacements at acyl carbon, such as in the solvolyses of chloroformate esters, *l* values in the range of 1.6–2.0 have been reported.²⁰ The present value of 1.42, although slightly larger than most other values for bimolecular solvolytic displacement at phosphorus, falls below this range. Although the *l* value is consistent with a concerted pathway, in the absence of a well-defined standard for addition–elimination reactions at phosphorus, one cannot use the *l* value to rigidly rule out such a pathway.

For six typical solvents, activation parameters were determined (Table 2). In all instances very negative (–22 to –42 cal mol⁻¹ K⁻¹) entropies of activation were calculated, consistent with nucleophilic attack in the rate-determining step, but not helpful in deciding between concerted and stepwise processes.

CONCLUSIONS

The solvolyses of **1** proceed rather rapidly at 25.0 °C and the progress of reaction as a function of time can be conveniently monitored using a rapid-response conductivity technique. For six typical solvents, activation parameters were determined and the large negative entropies of activation were consistent with a bimolecular process. Under identical conditions, the specific rates of solvolysis of **1** were slightly higher than for ethyl phenylphosphorochloridate (**6**) and slightly lower than for dimethylphosphinyl chloride.

Application of the extended Grunwald–Winstein equation [Eqn (1)] in 27 solvents led to an l value of 1.42 and an m value of 0.54 (correlation coefficient of 0.956). These values are shown (Table 3) 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 S_N2 pathway, and such a pathway is also proposed for the solvolyses of **1** (Scheme 1).

EXPERIMENTAL

The diphenylphosphinyl chloride (diphenylphosphinic chloride, Aldrich 98%) was used as received. Solvents were purified as previously described.⁷ The kinetic experiments were carried out by allowing the conductivity cell containing 12.5 mL of solvent to equilibrate, with stirring, in a constant-temperature water bath. A 2 μ L portion of a concentrated stock solution of **1** in acetonitrile was then added. The monitoring of increases in conductivity as a function of time and the calculation of the specific rates were as previously reported.¹³ The multiple regression analyses were performed using commercially available statistical software packages.

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