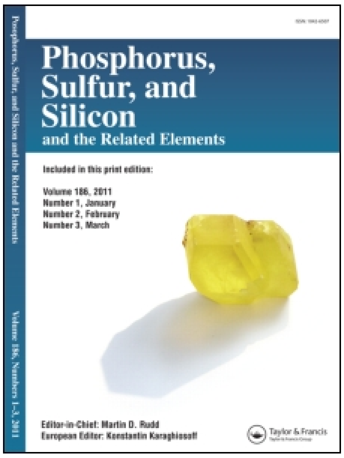

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Correlation of the Rates of Solvolysis of Chlorodiphenylphosphine Using the Extended Grunwald-Winstein Equation

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CORRELATION OF THE RATES OF SOLVOLYSIS OF CHLORODIPHENYLPHOSPHINE USING THE EXTENDED GRUNWALD–WINSTEIN EQUATION

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Specific rates of solvolysis involving displacement of chloride from the trivalent phosphorus of chlorodiphenylphosphine (Ph_2PCl, 1) are reported for ethanol, methanol, and aqueous binary mixtures incorporating ethanol, methanol, acetone, 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The 25 solvents give an extended Grunwald–Winstein correlation with an l value of 1.25 ± 0.09, m value of 0.46 ± 0.06, and correlation coefficient (R) of 0.954. The reactions in aqueous acetone were unusually fast, and these data points lie above the plot. Specific rate values are also reported for TFE–ethanol mixtures. For five representative solvents, values were obtained at three additional temperatures and activation parameters are presented. Rather low enthalpies of activation (8.4 to 11.8 kcal mol^{-1}) are accompanied by very negative entropies of activation (−33 to −46 cal mol^{-1}K^{-1}). The kinetic features observed are consistent with an S_N2 reaction incorporating appreciable bond formation and bond breaking at the transition state, and they are very similar to those previously observed for diphenylphosphinyl chloride (Ph_2POCl).

Keywords Chlorodiphenylphosphine; solvent ionizing power; solvent nucleophilicity; solvolysis

INTRODUCTION

There have been several studies of the kinetics of nucleophilic substitution reaction at a tetrahedral phosphorus atom,[1–4] and an S_N2 displacement at phosphorus [S_N2(P)] is the usually proposed mechanism. Many of the studies have involved solvolysis reactions, and we have previously reported kinetic studies of the solvolyses of diaryl,[5] dimethyl,[6] and cyclic[7] phosphorochloridates [$(RO)_2POCl$], N,N,N′,N′-tetramethyldiamidophosphorochloridate [$(Me_2N)_2POCl$],[8] and diphenylphosphinyl

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chloride [Ph_2POCl].[9] Bentley and Ebdon[10] have reported on the kinetics of the solvolysis of ethyl phenylphosphonochloridate [Ph(EtO)POCl]. Our studies have incorporated correlations of the specific rates (first-order rate coefficients) using an extended form of the Grunwald–Winstein equation[11–13] (Equation 1).

$$\log (k/k_0) = lN_T + mY_{Cl} + c \tag{1}$$

In Equation (1), k and k_0 represent the specific rates of solvolysis of a substrate in the solvent under consideration and in the standard solvent (80% ethanol), respectively, l is the sensitivity towards changes in solvent nucleophilicity (N_T),[12–14] m is the sensitivity towards changes in solvent ionizing power (Y_{Cl}, for a chloride-ion leaving group),[15,16] and c is a constant (residual) term.

There have been far fewer studies of the rates of nucleophilic substitution reactions at tricoordinated phosphorus. This is largely due to a tendency towards a fast reaction. In particular, phosphorochloridite esters [$(RO)_2PCl$] react extremely rapidly, and, for example, the ethanolysis of diethyl phosphorochloridite could be followed only at −65°C.[17] Reactions of chlorodialkylphosphines and chlorodiarylphosphines, although still fast, react considerably slower, and Halmann[17] has studied the ethanolyses of the diethyl, dipropyl, and diphenyl derivatives.

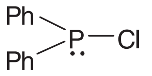
Halmann experienced several difficulties in his studies. In the ethanolyses, both chlorodiethylphosphine and chlorodiphenylphosphine exhibited a rapid increase in conductivity followed by a slower subsequent increase. On rather indirect grounds, it was assumed that the true solvolysis rate was the subsequent slow increase for the diethyl derivative but the initial fast reaction for the diphenyl derivative.

In individual runs, the dipropyl derivative reacted with good first-order kinetics, but the value for the rate coefficient was found to increase with increasing initial substrate concentration. The addition of sulfuric or perchloric acid caused considerable rate increases, and it was suggested that this acid catalysis was one cause for the dependence of the specific rate of solvolysis on the substrate concentration. A very important observation[17] with the dipropyl derivative was that contrary to what one might intuitively expect, based on substitutions at carbon, increasing the proportion of acetone in ethanol–acetone mixtures led to *increases* in reaction rate. After several half-lives, the conductivity level started to drop, and it was found that eventually the chloride-ion concentration was very low. It was suggested that a product, initially formed from the attack of acetone on the chlorophosphine, slowly incorporated the ejected chloride ion.

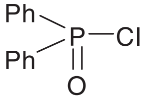
In the ethanolysis of chlorodiethylphosphine, it was suggested[17] that an initial formation of Et_2POEt was followed by an Arbusov-type rearrangement[18] to triethylphosphine oxide (Et_3PO). The replacement of chloride by hydroxide is also followed by a rearrangement to the isomeric phosphine oxide (Equation 2):[1]

(2)

For the present study, we have chosen chlorodiphenylphosphine (**1**) as the substrate. Using a rapid-response conductivity technique, the kinetics of solvolysis can be conveniently followed using a low concentration of substrate, thus avoiding the dependence on substrate concentration observed for the dipropyl derivative by Halmann.[17] This choice has the advantage of allowing a comparison with the previously reported[9] solvolyses of diphenylphosphinyl chloride **2**, a substrate which has a double bond to an oxygen rather than the lone pair of electrons of chlorodiphenylphosphine.



(**1**)



(**2**)

RESULTS

The specific rates of solvolysis of **1** were determined at 25.0°C in 29 solvents. The solvents consisted of ethanol, 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 I, together with the solvent nucleophilicity (N_T)[12,14] and solvent ionizing power (Y_{Cl})[15,16] values. For comparison purposes, the specific rates, at 25.0°C, for the corresponding solvolyses of diphenylphosphinyl chloride (**2**) are also reported in Table I.

Reported in Table II are specific rate values for **1** recorded over a fourfold variation in initial substrate concentration, at 25.0°C, for ethanol, 80% ethanol, and 50% ethanol. In Table III are the specific rate values at three additional temperatures for five of the solvolyses reported in Table I and the enthalpies and entropies of activation, calculated from the data at all four temperatures.

DISCUSSION

Since Halmann[17] found unusual kinetics, with a fast phase followed by a slow phase in the ethanolyses of chlorodiphenylphosphine (**1**), the substrate of this investigation, and chlorodiethylphosphine, we were pleased to see that, over the full range of 29 solvents, good first-order kinetics were obtained throughout each run. Since the reactions are quite fast, an initial perturbation, which is completed before the kinetic study can begin, cannot be rigorously excluded. However, after homogeneity was established, we found no evidence for the two regions of very different kinetic behavior described by Halmann.

Another observation by Halmann[17] was that in the ethanolysis of chlorodipropylphosphine at 0.0°C, the specific rate increased by a factor of five when the concentration increased from 0.8×10^{-3} M to 46×10^{-3} M (a factor of 60). Similar results, but with reduced increases in specific rate, were observed with 1M water within the ethanol. Accordingly, we felt it necessary to check for the operation of this effect in our studies with **1**. Since the runs were usually carried out with a 6.5×10^{-3} M concentration of substrate, we carried out (Table II) three determinations (each in duplicate) with the concentration also halved and doubled. Within this range, no substrate concentration dependence of the specific rates was observed in ethanol, 80% ethanol, or 50% ethanol.

An extremely surprising aspect of the present study can be seen in Table I, where at 25.0°C, the specific rate of solvolysis of **1** in a given solvent is, across the full range

Table I Specific rates of solvolysis of chlorodiphenylphosphine (Ph_2PC1)[a] in a variety of pure and mixed solvents at 25.0°C, the N_T and Y_{C1} values for the solvents, and (for comparison) the corresponding specific rate values (k') for diphenylphosphinyl chloride (Ph_2POC1)

Solvent[b]	10^2k, s^{-1}[c]	N_T[d]	Y_{C1}[e]	$10^2k'$, s^{-1}[f]
100% EtOH	0.809 ± 0.005	0.37	−2.52	0.702
90% EtOH	11.0 ± 0.1	0.16	−0.94	11.2
80% EtOH	20.2 ± 0.4	0.00	0.00	21.6
70% EtOH	30.0 ± 0.3	−0.20	0.78	30.9
60% EtOH	43.0 ± 0.2	−0.38	1.38	43.8
50% EtOH	55.2 ± 0.6	−0.58	2.02	62.6
100%MeOH	6.24 ± 0.04	0.17	−1.17	6.78
90% MeOH	29.1 ± 0.2	−0.01	−0.18	28.4
80% MeOH	50.8 ± 1.3	−0.06	0.67	51.6
70% MeOH	68.3 ± 0.5	−0.40	1.46	70.0
60% MeOH	82.5 ± 1.2	−0.54	2.07	102
95%Acetone	1.05 ± 0.01	−0.49	−3.19	0.833
90%Acetone	4.97 ± 0.06	−0.35	−2.39	4.15
80%Acetone	15.8 ± 0.2	−0.37	−0.83	14.8
70% Acetone	33.8 ± 0.1	−0.42	0.17	29.8
60% Acetone	52.8 ± 0.9	−0.52	0.95	51.4
97% TFE[g]	0.0280 ± 0.0062	−3.30	2.83	0.0233
90% TFE[g]	0.322 ± 0.005	−2.55	2.85	0.275
80% TFE[g]	1.54 ± 0.01	−2.19	2.90	1.50
70% TFE[g]	3.96 ± 0.01	−1.98	2.96	3.97
50% TFE[g]	16.7 ± 0.6	−1.73	3.16	16.5
97% HFIP[g]	0.000616 ± 0.000006	−5.26	5.17	0.000591
90% HFIP[g]	0.0296 ± 0.0002	−3.84	4.31	0.0365
70% HFIP[g]	1.04 ± 0.01	−2.94	3.83	1.48
50% HFIP[g]	3.74 ± 0.01	−2.49	3.80	3.59
80T-20E[h]	0.0721 ± 0.0013	−1.76	1.89	0.0689
60T-40E[h]	0.327 ± 0.002	−0.94	0.63	0.321
40T-60E[h]	0.722 ± 0.002	−0.34	−0.48	0.706
20T-80E[h]	1.00 ± 0.03	0.08	−1.42	0.954

[a] Substrate concentration of 0.0065 mol dm^{-3}.
[b] Unless otherwise indicated, on a vol/vol basis, at 25.0°C, with the other component water.
[c] With associated standard deviations.
[d] From refs. 12 and 14.
[e] From refs. 15 and 16.
[f] From ref. 9.
[g] Solvent prepared on weight/weight basis.
[h] T-E represent 2,2,2-trifluoroethanol-ethanol mixtures.

of solvents, very similar to that for **2**. When the specific rate values in Table III for five solvents at temperatures in the 0°C to 55°C range are compared with the corresponding values[9] for **2**, the similarity remains, and, accordingly for each solvent, the entropies and enthalpies of activation are also very similar for solvolyses of **1** and **2**.

Although a labeling error by the supplier is highly unlikely, so also is the probability very low for two substrates to show the same kinetic reactivity values over the full range of solvents usually used in solvolysis studies. Accordingly, we checked the samples of **1** used in the present study and the sample of **2** that was previously used[9] in the study of its solvolyses. This can very easily be done qualitatively by infrared spectroscopy and,

Table II Specific rates of solvolysis of chlorodiphenylphosphine (Ph_2PC1) in ethanol and ethanol–water mixtures (v/v) at 25.0°C

Solvent	$[Ph_2PC1]$, M^a	10^2k, s^{-1b}
100% EtOH	0.541	0.818 ± 0.017
	1.013	0.809 ± 0.005
	2.178	0.818 ± 0.005
80% EtOH	0.541	19.9 ± 0.4
	1.013	20.2 ± 0.4
	2.178	20.7 ± 0.1
50% EtOH	0.541	56.5 ± 0.8
	1.013	55.2 ± 0.6
	2.178	56.5 ± 1.6

[a] Concentration of stock solution in MeCN, in solution: $3{\cdot}5 \times 10^{-3}$M, $6{\cdot}6 \times 10^{-3}M$, and 14.2×10^{-3}M.

[b] The k values are the averages of three or more runs, and with associated standard deviation.

indeed, **2** showed a strong absorption at 1250 cm^{-1} due to the stretching vibration of the phosphorus–oxygen bond, and this absorption was absent in the spectrum of **1**. Also, although both **1** and **2** were only guaranteed to 98% purity, both gave C, H elemental analyses in excellent agreement with the theoretical values. Further, a sample of **1** from a second commercial source gave specific rates of solvolysis in ethanol and 80% ethanol essentially identical to those obtained using the original sample.

Table III Specific rates of solvolysis of chlorodiphenylphosphine (Ph_2PC1) in pure and mixed solvents at various temperatures and the calculated enthalpies ($\Delta H^{\neq}$) and entropies ($\Delta S^{\neq}$) of activation

Solvent	Temp. °C	$10^2k, s^{-1a}$	$\Delta H^{\neq}{}_{298}{}^{b}$ Kcal mol^{-1}	$\Delta S^{\neq}{}_{298}{}^{b}$ cal mol^{-1} K^{-1}
100% EtOH	0.0	0.207 ± 0.006		
	15.0	0.464 ± 0.002	8.8 ± 0.1	-38.6 ± 0.3
	35.0	1.50 ± 0.02		
80% EtOH[c]	0.0	4.90 ± 0.05		
	15.0	10.9 ± 0.2	8.4 ± 0.1	-33.6 ± 0.4
	35.0	30.2 ± 0.3		
100% MeOH	0.0	1.56 ± 0.01	8.4 ± 0.1	-35.8 ± 0.2
	15.0	3.93 ± 0.03		
	35.0	10.4 ± 0.1		
97% TFE[d]	35.0	0.0405 ± 0.0006	8.8 ± 0.2	-45.3 ± 0.6
	45.0	0.0761 ± 0.0007		
	55.0	0.114 ± 0.007		
97% HFIP[d]	35.0	0.00146 ± 0.00007	11.8 ± 0.2	-42.7 ± 0.6
	45.0	0.00244 ± 0.00004		
	55.0	0.00431 ± 0.00015		

[a] Averages of three or more runs, with standard deviation.

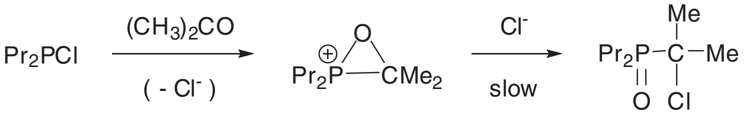
[b] Values at 25.0°C, from Table I, are also used in the calculation; the activation parameter values are accompanied by the standard error.

[c] On a volume–volume basis at 25.0°C, other component is water.

[d] On a weight–weight basis, the other component is water.

The similarity of the specific rates, independent of whether the phosphorus is trivalent with a lone pair of electrons on the phosphorus or tetrahedral with the lone pair replaced by a (essentially double) bond to oxygen, does not seem to be a general phenomenon in such a comparison. Dostrovsky and Halmann[19] found that, at 0.0°C, the tetrahedral diethyl phosphorochloridate [$(EtO)_2POCl$] solvolyses in ethanol with a specific rate of 2.3×10^{-5} s^{-1}. Halmann[17] subsequently reported that the trivalent diethyl phosphorochloridite [chlorodiethoxyphosphine, $(EtO)_2$ PCl] underwent ethanolysis at −65°C with a specific rate of 2×10^{-4} s^{-1}, an order of magnitude faster at a 65°C lower temperature.

In a study of the solvolysis of chlorodipropylphosphine at 0°C, Halmann found that the specific rate in 100% ethanol was about doubled upon addition of 5% acetone, and this value doubled again upon increasing the acetone content to 16%. The chloride ion initially liberated was found to have been consumed after several half lives for disappearance of substrate. Halmann suggested the pathway shown in Equation (3):



(3)

The rate increases upon adding acetone were contrary to what would have been predicted based on nucleophilic substitution at carbon, where dilution of water or an alcohol with acetone is a standard procedure for moderating the rates of solvolysis. It has been estimated[20] that both S_N1 and S_N2 solvolyses would decrease in rate by 10^4 to 10^6 upon moving from water to moist acetone. We find in the present study, consistent with Halmann,[17] that the solvolysis rates in aqueous acetone are faster than one would predict. Indeed, the specific rate in 95% acetone (5% water) is comparable to that in 100% ethanol. This observation applies to the solvolyses of both **1** and **2**, with the close similarity in specific rate values continuing to apply for the 95–60% aqueous acetone solvents. The initial interaction with acetone appears to be independent of whether a lone-pair of electrons or a double bond to oxygen is present at the reaction site.

The enthalpies of activation are at quite low values, in the range of 8.4 to 8.8 kcal mol^{-1}, in ethanol, methanol, 80% ethanol, and 97% TFE, with a somewhat higher value of 11.8 kcal mol^{-1} in 97% HFIP. In all five solvents, a very negative entropy of activation (−33 to −46 cal $mol^{-1}K^{-1}$) is observed, consistent with the proposed bimolecular nature of the substitution process (Table III).

Application of the extended Grunwald–Winstein equation [Equation (1)] to the data leads to values for all of the 29 solvents of Table I of 1.31 ± 0.14 for l and 0.51 ± 0.09 for m, with a rather poor multiple correlation coefficient of 0.899. Omission of the four TFE–ethanol points, often falling below the correlation line in application of Equation (1),[8] improved the multiple correlation coefficient to 0.954, and the sensitivity values are now at values of 1.25 ± 0.09 for l and 0.46 ± 0.06 for m (Figure 1).

In Table IV, these values are compared to those for several solvolytic displacements of chloride ion from tetrahedral phosphorus, including solvolyses of **2**, of dimethyl phosphorochloridate [$(MeO)_2POCl$] and phosphorochloridothionate [$(MeO)_2PSCl$],[6] of diphenyl phosphorochloridothionate [$(PhO)_2PSCl$],[21] and of diphenylthiophosphinyl chloride [Ph_2PSCl].[22] The l and m values are similar in all cases, and they and the l/m ratio

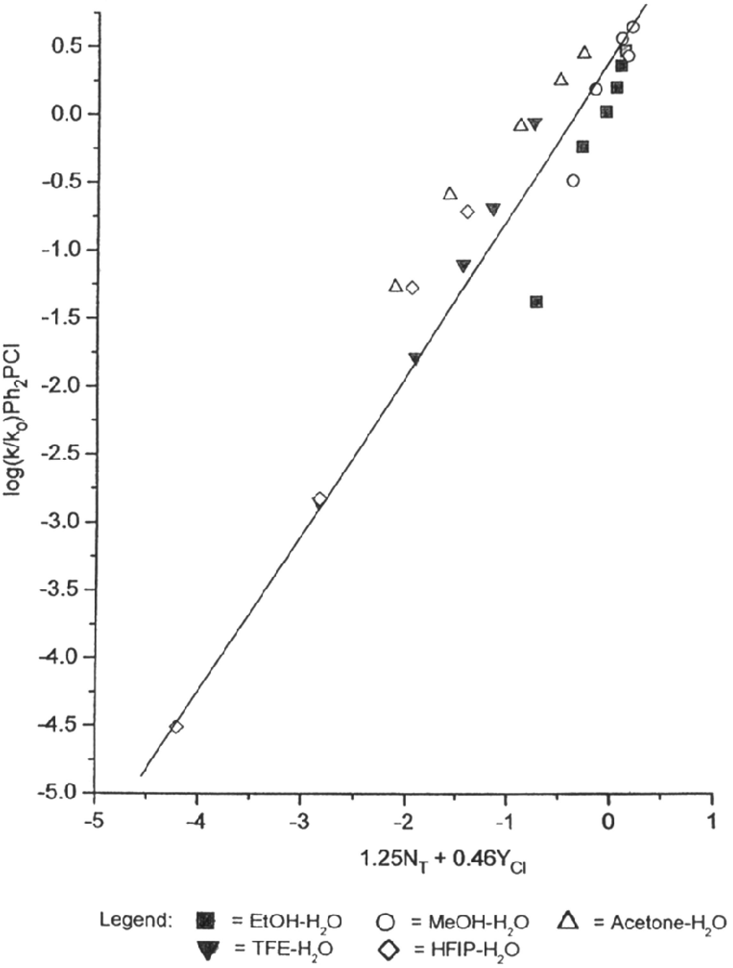


Figure 1 Plot of log (k/k_o) for solvolyses of **1** at 25.0°C against ($1.25N_T+0.46Y_{Cl}$).

are consistent with a direct displacement (S_N2) pathway across the full range of solvents included in the studies.

When the phosphorus is bonded to sulfur, rather than bonded to oxygen or carrying a lone pair of elections, the correlation coefficients tend to be higher, suggesting that the perturbations involving the electrophilic center of the solvent molecules and the lone pair, oxygen, or sulfur are least for sulfur. The presence of sulfur also leads to slightly lower l values and slightly elevated m values, such that the l/m ratios of 2.6 to 2.7 for **1**, **2**, and $(MeO)_2$ POCl decrease to 1.6 to 2.1 for the three sulfur-containing substrates of Table IV. This indicates that the introduction of sulfur results in an S_N2 transition state with increased bond-breaking and reduced bond-forming characteristics.

Table IV Extended Grunwald–Winstein correlations of the kinetics of solvolytic displacement of chloride from phosphorus

Substrate	n^a	Temp. °C	l^b	m^b	R^c	l/m
1	29	25.0	1.31 ± 0.14	0.51 ± 0.09	0.899	2.57
$\mathbf{1}^{d}$	25	25.0	1.25 ± 0.09	0.46 ± 0.06	0.954	2.72
$\mathbf{2}^{d,e}$	27	25.0	1.42 ± 0.10	0.54 ± 0.07	0.956	2.63
$(MeO)_2POC1^{d,f}$	18	25.0	1.27 ± 0.14	0.47 ± 0.08	0.941	2.70
$(MeO)_2PSC1^{d,f}$	28	25.0	1.17 ± 0.07	0.56 ± 0.03	0.966	2.09
$(PhO)_2PSC1^{g}$	30	55.0	1.29 ± 0.07	0.64 ± 0.02	0.989	2.02
$Ph_2PSC1^{d,h}$	25	55.0	1.00 ± 0.04	0.64 ± 0.03	0.983	1.56

[a] Number of solvents.

[b] From Equation (1) and with associated standard error.

[c] Multiple correlation coefficient.

[d] With the TFE–EtOH data points excluded from the correlation.

[e] From ref. 9.

[f] From ref. 6.

[g] From ref. 21.

[h] From ref. 22.

CONCLUSIONS

The irregularities in the kinetics found by Halmann,[17] in the form of the existence of two regions of different kinetic behavior for each run and a substrate concentration dependence for the observed specific rate of solvolysis, were not found in the present study. Good first-order kinetics were observed throughout each run for a wide range of solvents at 25.0°C and in runs at 0–55°C for five selected solvents. The enthalpies of activation were low (8.4 to 11.8 kcal mol^{-1}), but this effect was countered by very negative entropies of activation (−33 to −46 cal $mol^{-1}K^{-1}$). The highly negative entropies of activation suggest a bimolecular (or higher molecularity) process.

A surprising feature was that the specific rates of solvolysis of **1** were extremely similar to those previously measured for **2**, despite **1** having a lone pair of electrons on the phosphorus and the tetrahedral **2** having a double bond to oxygen at that position. Careful checks were made (infrared spectra and elemental analyses) to firmly establish the identities of **1** and **2**. This is not a general phenomenon for compounds related in this way, however, since studies of the ethanolyses of $(EtO)_2PCl$ and $(EtO)_2POCl$, with the identical structural relationship, showed the trivalent species to react by an order of magnitude faster at a 65°C lower temperature,[17] with a very rough estimate, suggesting a difference of about three orders of magnitude at a common temperature.

Since the specific rates of solvolysis of **1** and **2** are extremely similar, so also are the activation parameters and the sensitivities obtained from an extended Grunwald–Winstein equation treatment of the data. The values for l of 1.25 ± 0.09 and for m of 0.46 ± 0.06 (l/m ratio of 2.72) are very similar to those previously reported[9] for solvolyses of **2** and for other solvolyses in which a chloride ion is displaced from phosphorus. If a double bond to sulfur replaces that to oxygen, a slightly lower l value and slightly higher m value results in the l/m ratio falling to 1.6 to 2.1 (Table IV), suggesting a looser, but still bimolecular, transition state.

An earlier surprising feature was the observation by Halmann[17] that, unlike for solvolyses involving displacement at carbon, addition of acetone to ethanol accelerated rather than reduced the rates of solvolysis of the trivalent chlorodipropylphosphine. Similarly, we find that the rates of solvolysis of **1** are faster than one would anticipate in the aqueous-acetone solvents. This can be readily seen by the acetone–water points lying above the best fit plot of Figure 1.

The overall situation that extended Grunwald–Winstein equation treatments of several kinetic studies involving displacement of chloride from phosphorus, across the full range of solvents, strongly suggests a bimolecular process with both bond formation and bond breaking having progressed appreciably at the transition state remains unaltered, with the solvolyses of **1**, the first trivalent phosphorus substrate to be included in the study, conforming to this pattern.

EXPERIMENTAL

The chlorodiphenylphosphine (Aldrich 98% or TCI 98%) was used as received. Solvents were purified as previously described.[14]

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.[23] The stability (lack of any appreciable perturbation due to reaction of the substrate with the solvent) of the concentrated stock solution of **1** in acetonitrile was checked by showing, for solvolyses in 100% ethanol at 25.0°C, that identical specific rates were obtained when the stock solution was allowed to stand for 0.5, 30, 75, or 375 minutes prior to the addition of a 12 μL portion to the ethanol.

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

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