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Product selectivities and third-order rate laws for solvolyses of ethyl phenylphosphonochloridate in aqueous alcohols[†]

T. William Bentley* and David N. Ebdon

Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea SA2 8PP, UK

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ABSTRACT: Rate constants and product selectivities (S) for solvolyses of ethyl phenylphosphonochloridate [PhP(=O)OEtCl] in aqueous ethanol and methanol at 0 °C are reported; S = ([ester product]/[acid product]) × ([water]/[alcohol solvent]). The results show trends very similar to those previously reported for solvolyses of diphenyl phosphorochloridate [$(PhO)_2P(=O)Cl$] and p,p'-dichlorodiphenyl phosphorochloridate, much more hydrophobic substrates. Implications of these results are as follows: (i) as S increases about threefold from 99.8 to 90% alcohol–water and only about the same amount from 90 to 40% alcohol–water, the main cause of variations in S does not appear to be medium effects of the solvents; (ii) contrary to the general trend to increase, values of S may decrease slightly (ca 15%) in highly aqueous alcohol–water mixtures, even when (as in this case) there is no evidence for mechanistic changes; (iii) the deviations from expected third-order rate product correlations previously reported for solvolyses of diphenyl phosphorochloridate and the p,p'-dichloro derivative do not appear to be due solely to their high hydrophobicity. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: phosphonochloridate; acid choride; kinetics; solvolysis; selectivity

INTRODUCTION

Studies of rates and products of solvolyses in alcohol–water mixtures can provide useful insights into solvolyses,[1,2] and recent progress has been made particularly for reactions of acid halides. Reactions proceeding via cationic intermediates may be ca 10^7 times slower in ethanol than in water (based on solvolysis rates for 1-adamantyl chloride, a model compound for S_N1 reactions used to define the Y_{Cl} scale of solvent ionizing power).[3] Consequently, an alternative mechanism may be favoured in ethanol and in other less aqueous media, e.g. evidence for a mechanistic change can be seen from the two distinct linear regions of the rate-rate profiles observed by comparing rates of solvolyses of p-dimethylaminobenzoyl fluoride in ethanol–water mixtures with Y_{Cl}.[4]

Because evidence for mechanistic changes from 'breaks' in rate rate profiles for solvolyses of other acid chlorides in ethanol–water mixtures may not always be clear,[5] additional evidence was obtained from kinetic studies in a wider range of solvents[6–8] and/or by studies of product selectivities [S, Eqn. (1)].[8] Rates of solvolyses of benzoyl chloride can be explained by two competing mechanisms, and substituents (e.g. p-Cl and p-Me) alter the solvent composition at which the mechanistic change occurs. Independent supporting evidence is provided by values of S [Eqn. (1)] in alcohol–water mixtures, which reach maxima for the solvent compositions very close to those predicted from rate-rate profiles as the positions of mechanistic change.[8]

$$S = ([\text{ester product}]/[\text{acid product}]) \times ([\text{water}]/[\text{alcohol solvent}]) \qquad (1)$$

Solvolyses of electron-rich benzenesulfonyl chlorides were interpreted similarly in terms of two competing mechanisms,[9–11] but the effect of substituents is smaller than for benzoyl chlorides. There appears to be general agreement that less electron-rich sulfonyl chlorides including p-methylbenzenesulfonyl chloride solvolyse via a single reaction channel, probably via an S_N2 mechanism.[10,12–15] However, recent alternative proposals for solvolyses of electron-rich sulfonyl chlorides are (i) that there is only one mechanism, and the non-linear rate–rate profiles[10] {and by implication possibly also the

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*Correspondence to: T. W. Bentley, Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea SA2 8PP, UK.
E-mail: cmsolvol@swan.ac.uk

[†] Dedicated to Dr John Shorter on the occasion of his 75th birthday.

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decrease in S [Eqn. (1)] in more aqueous alcohols} is due to a non-linear dependence of solvent nucleophilicity on Y_{Cl};[14] and (ii) that solvolyses occur by S_N2 mechanisms with 'exploded' transition states having both bond formation to the incoming nucleophile and extensive cleavage of the S—Cl bond.[16,17]

Solvolyses of the chlorophosphate diphenyl phosphorochloridate [$(PhO)_2P(=O)Cl$] in alcohol–water mixtures react via an $S_N2(P)$ mechanism;[18] although there is no evidence for mechanistic changes, S decreases slightly for solvolyses in 30% methanol–or ethanol–water and 'pure' water.[18] However, the diphenyl substrate is not readily soluble in highly aqueous mixtures, and values of S are dependent on the efficiency of mixing.[5,18] To investigate this problem further, and also aspects of our third-order treatment[18] of observed first-order rate constants (see Discussion), we now report rate and product data for solvolyses of ethyl phenylphosphonochloridate (**1**) in ethanol–and methanol–water mixtures.

Table 1. First order rate constants (k) for solvolyses of ethyl phenylphosphonochloridate (**1**) in aqueous ethanol and methanol at 0 °C[a,b]

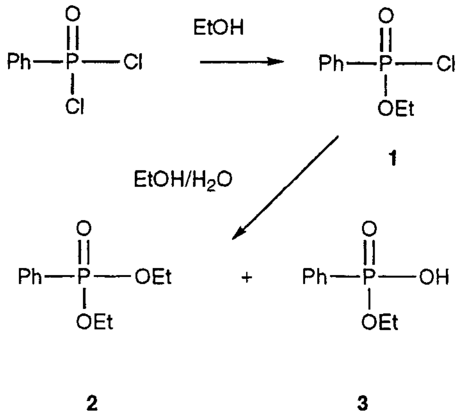
	k (10^{-3} s^{-1})	
Solvent (%, v/v)	Ethanol	Methanol
100	0.86 ± 0.03	5.65 ± 0.15
90	6.00 ± 0.02	17.9 ± 0.3
80	10.1 ± 0.1	31.0 ± 1.0
70	13.0 ± 0.1	41.4 ± 0.8
60	18.6 ± 0.3	55.3 ± 1.1
50	27.0 ± 0.2	76.2 ± 0.2
40	51.7 ± 0.2	117 ± 3
30	123 ± 1	183 ± 4
20	220 ± 4	244 ± 3
10	350 ± 4	363 ± 2
Water	430 ± 10	430 ± 10

[a] Determined conductimetrically at least in duplicate; errors shown are average deviations.
[b] Injected 3–15 µl of freshly prepared 1% solutions of ethyl phenylphosphonochloridate in acetonitrile into 5 ml of solvent.

RESULTS

The substrate **1**, prepared by reacting phenylphosphonic dichloride with 1.1 equiv. of ethanol at 0 °C,[19] was further solvolysed in alcohol and in alcohol–water mixtures at 0 °C to give an ester (**2**) and an acid (**3**) as shown in Scheme 1. Reaction rates were monitored from the change in conductivity due to **3** and to the HCl by-product, and first-order rate constants were calculated by standard methods (Table 1).

Product ratios were determined using freshly distilled substrate **1** by ion pair reversed-phase high-performance liquid chromatography (HPLC) as before,[18] except that instead of acetic acid in the eluent, triethylamine and a higher concentration of ion-pairing reagent were added to the eluent to give pH ≈10. Corrections were made for the small percentage of ester (**2**) in the starting material, and control experiments showed that the products were stable under the acidic reaction conditions and under the basic chromatographic conditions.[20] Product selectivities (S) are given in Table 2; because values of S are low, and the HPLC conditions were investigated in detail, it was



Scheme 1

Table 2. Product selectivities, S [Eqn. (1)] for solvolyses of ethyl phenylphosphonochloridate (**1**) in aqueous ethanol and methanol at 0 °C[a]

	S	
Solvent (%, v/v)	Ethanol	Methanol
99.8	0.052^b, 0.048^c	0.129^b, 0.151^c
99.5	0.063^b, 0.058^c	0.193^b, 0.190^c
99	0.066^b, 0.065^c	0.197^b, 0.211^c
98	0.089^b, 0.084^c	0.229^b, 0.229^c
95	0.135^b, 0.131^c	0.313^b, 0.301^c
92	0.179^b, 0.174^c	0.434^b, 0.411^c
90	0.19^b, 0.19^c, 0.21^d	0.44^b, 0.43^c, 0.44^d
80	0.33^d	0.68^d
70	0.44^d	0.88^d
60	0.57^d	1.07^d
50	0.68^d	1.21^d
40	0.72^d	1.28^d
30	$0.7^{d,e}$	1.15^d
20	$0.6^{d,e}$	1.11^d
10	$—^e$	1.10^d

[a] All values calculated from the ester:acid molar product ratio determined by duplicate HPLC analyses on at least two independent samples. Typical errors 1–5%. Exact concentrations of water in 95–99.8% alcohol were determined by Karl Fischer titration.
[b] Typical injection: 2 µl of neat ethyl phenylphosphonochloridate into rapidly stirred solvent (5 ml).
[c] Solvolyses repeated using the same conditions as in footnote b.
[d] Typical injection: 20 µl of a 5% solution in acetonitrile into rapidly stirred solvent (5 ml).
[e] Additional experimental uncertainty due to the presence of diester (**2**) in the starting phosphonochloridate (**1**).

possible to obtain reliable values of *S* for 99.5% alcohol–water mixtures, and even for 99.8% ethanol–water.

DISCUSSION

The substrate **1** was selected because it contained one aromatic ring, a suitable chromophore for UV detection in HPLC, and reacted by a single nucleophilic substitution mechanism at a convenient rate.[19] Preliminary conductimetric measurements in 95% (v/v) acetone–water at 0 °C gave a rate constant of $(7.63 \pm 0.14) \times 10^{-4}$ s^{-1}, in only fair agreement with the published titrimetric value of 9.9×10^{-4} s^{-1}.[19] Solvolyses of phosphonochloridates having OMe, OEt or OPh groups occur at very similar rates in 95% (v/v) acetone–water at 0 °C (within a factor of two),[19] and in general are much less sensitive to substituent effects than solvolyses of corresponding carbonyl compounds.[19,21] Even replacing an alkyl group by an *O*-alkyl group only results in a ca 15-fold rate decrease, whereas ethyl chloroformate (EtOCOCl) solvolyses about 10^4 times more slowly than acetyl chloride.[21]

Rate constants for solvolyses of the chlorophosphonate **1** (Table 1) are close to 10-fold faster than those for corresponding solvolyses of $[(PhO)_2P(=O)Cl]$[18] over the full range of alcohol–water mixtures. Hence, there is no evidence for significant differences in initial state or other effects for solvolyses of the more hydrophobic diphenyl ester in more aqueous solvents.[18] The additional *O*-aryl group in the phosphorochloridate $[(PhO)_2P(=O)Cl]$ is the main factor lowering the reactivity.[19,21]

Product selectivities for **1** (Table 2) are greater than but very similar to (within a factor of two) those for $[(PhO)_2P(=O)Cl]$.[17] For both substrates, *S* increases about three fold from 99.8 to 90% alcohol–water and only about the same amount from 90 to 40% alcohol–water. Consequently, the main cause of variations in *S* does not appear to be medium effects of the solvents, because medium effects usually change more gradually with variations in solvent composition.[3] The similar trends for both substrates also confirm that *S* may decrease slightly in more aqueous media (from ca 40% alcohol–water towards water), even when there is no evidence for mechanistic changes.[19]

An explanation of the ca 10-fold increase in *S* from 99.8% alcohol to 10% alcohol–water solvents (Table 2) cannot be achieved if the reactions simply involved second-order reactions, in which either alcohol or water attacked the substrate, because *S* would then be expected to be constant.[2] The results can be explained by third-order processes, in which one molecule of solvent acts as a nucleophile and the other acts as a general base. According to this theory, *S* should reach a maximum (plateau) value in highly aqueous media, when water dominates as the general base;[22] another factor such as mechanistic change was previously thought to be required to explain any decrease in *S* in highly aqueous media.[23]

Selectivities for carboxylic acid chorides are complicated by mechanistic changes,[8,23] but solvolyses of *p*-nitrobenzenesulfonyl chloride strongly support the theory that values of S may reach a plateau in highly aqueous media.[24] Selectivities for *p*-nitrobenzoyl chloroformate in methanol–water also increase as water is added, but in ethanol–water there is a decrease from 5.2 in 40% to 4.7 in 10% ethanol–water.[25] Solvolyses of **1** (Table 2) and $(PhO)_2P(=O)Cl$[18] confirm that *S* values may decrease slightly (ca 15%) in highly aqueous media, even when a mechanistic change is unlikely.

To analyse the results (Tables 1 and 2) in more detail, we follow previous work[18,22–25] and assume that the pseudo-first-order reactions occur by a combination of four third-order processes in which one molecule of solvent (water, w, or alcohol, a) acts as a nucleophile and the other acts as a general base: see Eqn. (2), in which the first letter of the subscript denotes the nucleophile and the second letter denotes the general base:

$$k_{obs} = k_{ww}[\text{water}]^2 + (k_{aw} + k_{wa})\{[\text{alcohol}][\text{water}] + k_{aa}[\text{alcohol}]^2\} \qquad (2)$$

The third-order rate constant for hydrolysis, k_{ww} and k_{aa}, can be calculated from the rate constants in pure solvents, and the other two rate constants can be obtained from the product selectivities as described below.

When the k_{aa} term ($k_{aa}[\text{alcohol}]^2$) is unimportant, *S* [Eqn. (1)] simplifies to Eqn. (3), and when $k_{ww}[\text{water}]^2$ is negligible *S* is given by Eqn. (4):[23]

$$1/S = (k_{wa}/k_{aw})([\text{alcohol}]/[\text{water}]) + k_{ww}/k_{aw} \qquad (3)$$

$$S = (k_{aw}/k_{wa})([\text{water}]/[\text{alcohol}]) + k_{aa}/k_{wa} \qquad (4)$$

Two independent measurements of the ratios of the

Table 3. Ratios k_{aw}/k_{wa} derived from $1/S$ and S plots [Eqns (3) and (4)] for solvolyses of ethyl phenylphosphonochloridate (**1**) in alcohol–water mixtures

Plot	Solvent range	Slope	k_{aw}/k_{wa}
$1/S^a$	30–80% EtOH	1.61 ± 0.07	0.62 ± 0.03
S^b	98–99.8% EtOH	0.60 ± 0.04	0.60 ± 0.04
$1/S^c$	40–80% MeOH	0.47 ± 0.01	2.13 ± 0.05
S^d	92–99.8% MeOH	1.24 ± 0.06	1.24 ± 0.06

[a] Eqn. (3): slope = 1.606 ± 0.070, intercept = 1.053 ± 0.044, $r = 0.996$.

[b] Eqn. (4): slope = 0.601 ± 0.042, intercept = 0.047 ± 0.002, $r = 0.995$.

[c] Eqn. (3): slope = 0.474 ± 0.012, intercept = 0.631 ± 0.012, $r = 0.999$.

[d] Eqn. (4): slope = 1.235 ± 0.056, intercept = 0.173 ± 0.006, $r = 0.997$.

Table 4. Calculated third-order rate constants ($\text{M}^{-2}\ \text{dm}^6\ \text{s}^{-1}$) for solvolyses of ethyl phenylphosphonochloridate (**1**) in alcohol–water mixtures at 0 °C

	Ethanol–water		Methanol–water	
Rate constant	$1/S$, Eqn. (3)	S, Eqn. (4)	$1/S$, Eqn. (3)	S, Eqn. (4)
k_{ww}[a]	1.4×10^{-4}	1.4×10^{-4}	1.4×10^{-4}	1.4×10^{-4}
k_{wa}	2.1×10^{-4}	6.3×10^{-5}	1.1×10^{-4}	5.4×10^{-5}
k_{aw}	1.3×10^{-4}	3.8×10^{-5}	2.2×10^{-4}	6.6×10^{-5}
k_{aa}[b]	3.0×10^{-6}	3.0×10^{-6}	9.3×10^{-6}	9.3×10^{-6}

[a] From $k_{obs}/[H_2O]^2$.
[b] From $k_{obs}/[ROH]^2$.

third-order rate constants k_{aw}/k_{wa} can been obtained from the slopes of $1/S$ plots [Eqn. (3)] and S plots [Eqn. (4)]. The two measurements of the ratios of k_{aw}/k_{wa} show excellent agreement for solvolyses in ethanol–water ($k_{aw}/k_{wa} = 0.61 \pm 0.01$) (see Table 3); this is the best agreement obtained so far for investigations of this type.[18,23–25] The ratio for methanol–water mixtures covers a larger range ($k_{aw}/k_{wa} = 1.7 \pm 0.4$), continuing a general trend that there is better agreement of these ratios in ethanol–water than in methanol–water (possibly the k_{aw}/k_{wa} ratios are slightly solvent dependent in methanol–water mixtures[24]).

Absolute values for each of the third-order rate constants, k_{ww}, k_{wa}, k_{aw} and k_{aa}, are listed in Table 4; the third-order rate constants k_{wa} and k_{aw} calculated from $1/S$ plots [Eqn. (3)] are approximately 2–3-fold larger than those calculated from S plots [Eqn. (4)]. This difference is very similar to that for $(PhO)_2P({=}O)Cl$ where the k_{aw} and k_{wa} values calculated from the $1/S$ and S plots vary by 2–4-fold.[18] Substitution of the values of third-order rate constants (Table 4) into Eqn. (2) leads erroneously high predictions for observed first-order rate constants,[20] suggesting that solvolyses of ethyl phenylphosphonochloridate (**1**) may be affected by additional solvation effects such as variations in ground-state stabilization in aqueous organic solvents.[18]

Solvation effects might also explain the sinuosoidal plots of log$k$ vs Y_{Cl} for solvolyses of $(PhO)_2P({=}O)Cl$ [see Figs 1 and 2 of Ref. 18; plots for solvolyses of ethyl phenylphosphonochloridate (**1**) are very similar[20]]. Consequently, a non-linear plot of log$k$ vs Y_{Cl} is not 'proof' of a mechanistic change, and (as usual) evidence should ideally be based on several criteria, e.g. (i) for solvolyses of benzoyl chlorides and substituted derivatives, breaks in rate–rate profiles such as plots of log$k$ vs Y_{Cl}, marked maxima in S and a clear dependence on substituents strongly support the case for mechanistic changes;[8] (ii) in contrast, solvolyses of p-toluenesulfonyl chloride do not show breaks in plots of log$k$ vs Y_{Cl}, or clear maxima in S,[10] consistent with the absence of mechanistic changes.

CONCLUSIONS

For solvolyses of phosphorochloridates and phosphonochloridates, values of S [Eqn. (1)] decrease slightly (ca 15%) in highly aqueous media (see Ref. 18 and Table 2), for reasons unlikely to be due to mechanistic changes. Consequently, the decrease in S observed for solvolyses of electron-rich sulfonyl chlorides is not necessarily associated with mechanistic changes (as originally proposed[10]). However, electron-rich sulfonyl chlorides show larger (ca 50%) changes in S than the phosphorus substrates, and the solvent composition for a maximum in S depends on the structure of the sulfonyl chloride.[10] If there are two reaction channels, both are expected to be nucleophilically assisted[16,17] and they may respond similarly to changes in solvent nucleophilicity.[14]

EXPERIMENTAL

Materials. Ethyl phenylphosphonochloridate (**1**), prepared from phenylphosphonic dichloride (Lancaster) and ethanol (1.1 equiv.) in diethylether at 0 °C in the presence of triethylamine (1.1 equiv.),[19] was distilled prior to use (b.p. 82 °C at 0.01 mmHg; lit.[19] 103 °C at 0.3 mmHg and lit.[26] 120 °C at 2 mmHg), and was shown by HPLC analysis of the ethanolysis product to contain <0.1% of acid (**3**), 2.4% of diester (**2**) and 1% of the dichloride starting material. Standard solutions for response calibration of the HPLC system were obtained by reaction of the acid chloride (**1**) at 0 °C for 10 half-lives with ethanol to give the diester (**2**) or with acetonitrile–water to give the acid (**3**); acid/ester peak areas were 0.48 ± 0.03; similarly, methanolysis of **1** gave a methyl ester with acid/ester peak area = 0.51 ± 0.01.

Solvents for kinetics were dried and distilled and solvolysis media were prepared as described elsewhere.[27] The accurate water contents of the low-percentage water–alcohol mixtures, determined by Karl Fischer titration using a Mettler Toledo DL18 apparatus and Hydranal titrant (2), were usually within ±0.2% of the nominal values given in Table 2 (except the 98% methanol–water was actually 97.52%); the more exact compositions were used for calculations.

Materials for chromatography were AR grade methanol and acetic acid, distilled water and tetrabutylammonium bromide (TBAB), (Lancaster).

Kinetic methods. Conductimetric measurements were made by the rapid injection method,[23] and calculations were performed on a PC version of LSKIN.

Analytical methods. Four sets of HPLC conditions were used for product studies; separate methods were used for solvolyses in aqueous ethanol and methanol. All chromatography was performed on 10 μl aliquots using a 15 cm × 1/4 in Spherisorb ODS 2 column, eluted at a flow-rate of 1 ml min^{-1}, with UV detection at 265 nm. For solvolysis mixtures containing up to 90% ethanol–water, the absorbance range (AUFS) was 0.01, and the eluent, 40% (v/v) methanol–water, contained 0.07 M TBAB and 0.15% (v/v) triethylamine; corresponding figures for solvolyses up to 90% methanol were 0.03 M TBAB and 0.1% (v/v) triethylamine. Solvolyses in more alcoholic media were analysed using 30% methanol–water as eluent with AUFS = 0.05.[20] The HPLC equipment was as described earlier.[18]

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