

Rate and product studies with dimethyl phosphorochloridate and phosphorochloridothionate under solvolytic conditions †

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The specific rates of solvolysis of dimethyl phosphorochloridate and of dimethyl phosphorochloridothionate are very well correlated using the extended Grunwald–Winstein equation, with incorporation of the N_T solvent nucleophilicity scale and the Y_{Cl} solvent ionizing power scale. The sensitivity parameters (l and m) are similar to each other and also similar to previously recorded values for solvolyses of arenesulfonyl chlorides, which were proposed to follow a concerted displacement mechanism. For solvolyses in aqueous ethanol or aqueous methanol the product selectivities (S) are close to unity. For solvolyses in aqueous 2,2,2-trifluoroethanol, the values are too small to accurately measure, showing a very large preference for product formation involving nucleophilic attack by the water component. It is concluded that the chloride and chloridothionate solvolyses, in common with the solvolyses of arenesulfonyl chlorides, follow a concerted displacement mechanism.

Introduction

The extended Grunwald–Winstein equation¹ [equation (1)] can give information which is very helpful in assessing the mechanism of solvolysis reactions.

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

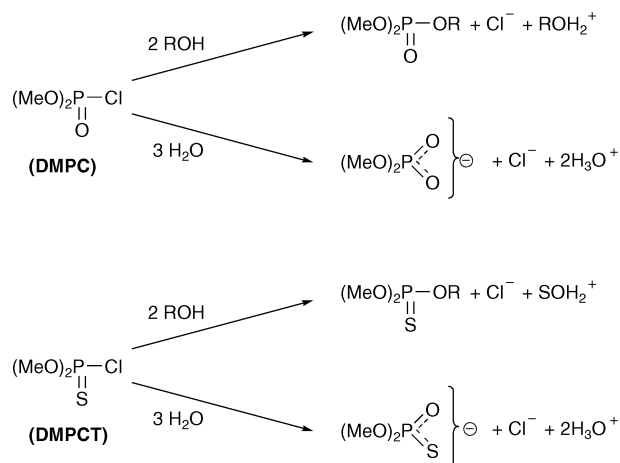
Although originally parameterized using attack at sp^3 -hybridized carbon, it has been found to also be applicable to attack at the sp^2 -hybridized carbon of acyl² and carbamoyl³ halides and chloroformate esters,⁴ and to attack at the sulfur of sulfonyl halides.⁵ In equation (1), k and k_0 are the specific rates of solvolysis in the solvent under consideration and the standard solvent (80% ethanol), respectively; l is the sensitivity to changes in the solvent nucleophilicity value (N_T); m is the sensitivity to changes in the solvent ionizing power value (Y_{Cl}); c is a constant (residual) term.

When it was applied to solvolytic displacement of chloride ion from phosphorochloridates the situation was found to be less clear cut. Initially, diaryl phosphorochloridates were studied⁶ and, while evidence for significant nucleophilic participation was provided, equation (1) was found to hold rather poorly, with significant dispersion and variation in slope for different mixed solvent systems in linear free energy relationship plots. In contrast, we found⁷ quite good correlations in a study of the solvolyses of N,N,N',N' -tetramethyldiamidophosphorochloridate (TMDAPC) in a wide variety of pure and mixed solvents, the only major deviation being the often observed lower $\log(k/k_0)$ values for 2,2,2-trifluoroethanol (TFE)–ethanol mixtures relative to those calculated based on correlation using results from the other solvents used in the study. The nature of these deviations was discussed.⁷

The cause of the differences in the quality of the correlation in the two studies^{6,7} is not clear. Further, it is not possible to know whether one of the solvolyses can be considered as typical and the other as atypical as regards analyses in terms of the extended Grunwald–Winstein equation for solvolyses involving attack at phosphorus.

Possible reasons for the difference in behavior include the substituent variation from aryloxy to amido groups in the two studies and the presence of aryl groups in just one of the studies. The influence on the goodness of fit of aryl groups can be investigated through a parallel study using the corresponding methyl derivative, dimethyl phosphorochloridate (DMPC, frequently named as dimethyl chlorophosphate).

In the recent study of TMDAPC, the hydrolysis product was neutral,⁸ and it has been proposed⁹ to exist as a zwitterion (protonation on nitrogen). Fortunately, the hydrolysis product from DMPC titrates as acid and, hence, from a study of the position of the infinity titer between one equivalent of acid (HCl), corresponding to all reaction with alcohol, and two equivalents of acid, corresponding to all reaction with water, we can indirectly and accurately determine¹⁰ the product ratio in mixed alcohol–water solvents. Accordingly, a two-part experimental study of the effect of solvent variation has been carried out involving determination of both the specific rates of solvolysis and, for aqueous alcohols, the partitioning between the two possible solvolysis products. In addition, a parallel study has been carried out using dimethyl phosphorochloridothionate (DMPCT, frequently named as dimethyl chlorothiophosphate) as the substrate. This is in response to interesting trends observed on similar sulfur for oxygen substitution during studies of chloroformate esters¹¹ and carbamoyl halides.¹² The two systems studied are outlined in Scheme 1.



Scheme 1

† Presented, in part, at the Tenth Kyushu International Symposium on Physical Organic Chemistry, Fukuoka, October 2003. Abstracted in part from the MS thesis of J. S. C., Northern Illinois University, December 1998.

Table 1 Specific rates of solvolysis (k) of dimethyl phosphorochloridate^a and dimethyl phosphorochloridodithionate^b at 25.0 °C in a variety of pure and mixed solvents and solvent nucleophilicity (N_T) and solvent ionizing power (Y_{Cl}) values

Solvent ^c	10 ⁵ k , s ⁻¹		N_T ^e	Y_{Cl} ^f
	(CH ₃ O) ₂ POCl	(CH ₃ O) ₂ PSCl		
100% EtOH	29.6 ± 1.2	0.86 ± 0.04	0.37	-2.52
90% EtOH	161 ± 3	2.90 ± 0.06	0.16	-0.94
80% EtOH	285 ± 7	5.11 ± 0.17	0.00	0.00
70% EtOH	416 ± 13	8.46 ± 0.18	-0.20	0.78
60% EtOH		12.7 ± 0.3	-0.38	1.38
50% EtOH		21.7 ± 0.5	-0.58	2.02
40% EtOH		40.1 ± 1.2	-0.74	2.75
20% EtOH		76.6 ± 3.3	-1.16	4.09
100% H ₂ O		156 ± 7	-1.38	4.57
100% MeOH	113 ± 2	3.74 ± 0.14	0.17	-1.17
90% MeOH	309 ± 10	9.17 ± 0.17	-0.01	-0.18
80% MeOH	496 ± 8	15.3 ± 0.4	-0.06	0.67
70% MeOH		25.3 ± 0.8	-0.40	1.46
60% MeOH		39.0 ± 1.3	-0.54	2.07
40% MeOH		78.1 ± 2.1	-0.87	3.25
20% MeOH		116 ± 5	-1.23	4.10
90% Acetone	49.1 ± 0.9	0.75 ± 0.03	-0.35	-2.39
80% Acetone	172 ± 2	2.32 ± 0.05	-0.37	-0.83
70% Acetone	322 ± 8	4.74 ± 0.09	-0.42	0.17
60% Acetone	506 ± 10	8.77 ± 0.09	-0.52	0.95
50% Acetone		15.1 ± 0.2	-0.70	1.73
40% Acetone		30.1 ± 0.4	-0.83	2.46
20% Acetone		96.4 ± 1.3	-1.11	3.77
90% Dioxane	67.2 ± 1.1	0.73 ± 0.02		
80% Dioxane	233 ± 10	2.78 ± 0.05	-0.46	
70% Dioxane	425 ± 23	6.54 ± 0.11	-0.37	
60% Dioxane		13.3 ± 0.2	-0.54	
50% Dioxane		24.7 ± 0.3	-0.66	
97% TFE ^g	0.36 ± 0.01		-3.30	2.83
90% TFE ^g	1.79 ± 0.06		-2.55	2.85
80% TFE ^g	11.9 ± 0.5	0.48 ± 0.01	-2.19	2.90
70% TFE ^g	34.8 ± 1.7	1.31 ± 0.02	-1.98	2.96
50% TFE ^g	186 ± 8	5.99 ± 0.07	-1.73	3.16
80T-20E ^h	0.81 ± 0.03		-1.76	1.89
60T-40E ^h	4.59 ± 0.14		-0.94	0.63
50T-50E ^h		0.36 ± 0.01	-0.64	0.16
40T-60E ^h	13.1 ± 0.6	0.51 ± 0.01	-0.34	-0.48
20T-80E ^h	25.3 ± 1.4	0.71 ± 0.01	0.08	-1.42
70% HFIP ^g	7.06 ± 0.25	0.49 ± 0.02	-2.94	3.83
50% HFIP ^g	29.5 ± 0.7	1.56 ± 0.03	-2.49	3.80

^a Concentration of ca. 0.010 mol dm⁻³. ^b Concentration of ca. 0.0070 mol dm⁻³. ^c Unless otherwise stated, on a vol-vol basis, at 25.0 °C, with the other component water. ^d With associated standard deviations. ^e From refs. 13 and 14. ^f From refs. 15 and 16. ^g Solvent prepared on weight-weight basis. ^h T-E are 2,2,2-trifluoroethanol-ethanol mixtures.

Results

The specific rates of solvolysis were determined at 25.0 °C in 25 solvents for DMPC and in 36 solvents for DMPCT. The solvents consisted of ethanol, methanol and water, binary mixtures of TFE with ethanol, and binary mixtures of water with ethanol, methanol, acetone, dioxane, TFE, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The specific rates of solvolysis are reported in Table 1, together with the available solvent nucleophilicity (N_T)^{13,14} and ionizing power (Y_{Cl})^{15,16} values.

The percentages of dimethyl hydrogen phosphate [(CH₃O)₂-P(O)OH] within the product were calculated by taking the excess titer over that for reaction in 100% alcohol, relative to the excess titer for solvolysis in 60% acetone over that for the reaction in 100% alcohol. Values for duplicate experiments were recorded at 10, 15, and 20 half lives. No trends were observed and the values reported in Table 2 are based on the averages of the six determinations for each solvent composition. The percentages of acid formation (x), resulting from hydrolysis,

Table 2 Percentages of reaction with acid as product^a and product selectivities (S) for solvolyses of dimethyl phosphorochloridate and dimethyl phosphorochloridodithionate in aqueous alcohol solvents at 25.0 °C

Solvent ^d	(CH ₃ O) ₂ POCl ^b		(CH ₃ O) ₂ PSCl ^c	
	% acid	S ^e	% acid	S ^e
90% EtOH	50.3	0.36	38.8	0.57
80% EtOH	63.6	0.46	49.4	0.83
70% EtOH	71.0	0.56	57.8	1.00
60% EtOH			64.8	1.16
40% EtOH			81.5	1.10
20% EtOH			89.1	1.59
90% MeOH	22.9	0.85	19.9	1.00
80% MeOH	40.1	0.84	30.0	1.31
70% MeOH			39.0	1.51
60% MeOH			46.8	1.70
40% MeOH			61.8	2.09
20% MeOH			82.0	1.98
90% TFE	100.0	f		
80% TFE	99.2	f		
70% TFE	102.8	f		
50% TFE	98.8	f		

^a Based on (CH₃O)₂PS(O)OH production of 0% in pure alcohol and 100% in 60% acetone. ^b Concentration of 0.0070 M. ^c Concentration of 0.0037 M. ^d Solvents contain 0.6% acetone and are on a volume-volume basis, except for the 2,2,2-trifluoroethanol-H₂O mixtures, which are on a weight-weight basis. ^e For ester formation relative to acid formation, defined as in eqn. 2. ^f Only small amounts of (CH₃O)₂P(O)OCH₂CF₃ are formed and the S value is too low to determine by this technique.

were then used to calculate product selectivity values (S) using equation (2); these values are also presented in Table 2.

$$S = \frac{(100 - x)}{x} \frac{[\text{Water in solvent}]}{[\text{Alcohol in solvent}]} \quad (2)$$

Discussion

The specific rates of solvolysis of DMPC and DMPCT were studied in a wide variety of pure and mixed solvents, including the TFE- and HFIP-containing systems, which are important components of meaningful extended Grunwald-Winstein correlations. The data points for solvolyses in TFE-ethanol mixtures fell below the best fit line, as is often observed in treatments of this type. This phenomenon was very recently discussed⁷ and it will not be considered again in this report. Correlations were carried out both with and without the TFE-ethanol data.

The results of the correlations are presented in Figs. 1 and 2 and reported in Table 3, together with the corresponding parameters obtained in the analyses of earlier kinetic studies of attack at a variety of phosphorus and sulfur centers. The specific rates measured in dioxane-water mixtures could not be included in the correlations due to a lack of Y_{Cl} values. The l and m values [equation(1)] for DMPC and DMPCT are similar to each other, with the variation within the combined standard errors. The values are also very similar to those previously derived⁷ for the solvolyses of *N,N,N',N'*-tetramethyldiamidophosphorochloridate. The values obtained⁵ from an analysis of literature values¹⁷⁻¹⁹ for the solvolyses of arenesulfonyl chlorides are also very similar. Only the l values of 1.7 to 1.8 for the solvolyses of diphenyl phosphorochloridate and the di-*para*-chloro-substituted derivative show appreciable deviation from the other values reported in Table 3; these values are in the range anticipated for an addition-elimination mechanism but, because of the poor correlations, one should not read too much into these values.

The other substrates of Table 3 all have solvolyses with l values in the 1.1 to 1.3 range and m values in the 0.45 to 0.7

Table 3 Coefficients from the extended Grunwald–Winstein correlations of the specific rates of solvolysis of dimethyl phosphorochloridate and dimethyl phosphorochloridothionate at 25.0 °C and a comparison with corresponding values for other phosphorochloridates and for arenesulfonyl chlorides

Substrate	n^a	l^b	m^b	c^b	R^c	F^d
(MeO) ₂ POCl	22	1.36 ± 0.23	0.54 ± 0.13	-0.02 ± 0.17	0.844	24
(MeO) ₂ POCl ^e	18	1.24 ± 0.14	0.45 ± 0.08	0.18 ± 0.11	0.941	54
(MeO) ₂ PSCl	31	1.21 ± 0.10	0.60 ± 0.04	0.22 ± 0.07	0.943	112
(MeO) ₂ PSCl ^e	28	1.16 ± 0.08	0.55 ± 0.03	0.30 ± 0.06	0.966	154
(Me ₂ N) ₂ POCl ^f	31	1.20 ± 0.07	0.69 ± 0.04	0.03 ± 0.32	0.958	155
(Me ₂ N) ₂ POCl ^{e,f}	27	1.14 ± 0.05	0.63 ± 0.03	0.17 ± 0.21	0.982	320
(PhO) ₂ POCl ^g	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 ^g	31	1.79 ± 0.20	0.58 ± 0.08	0.11 ± 0.18	0.863	
<i>p</i> -MeC ₆ H ₄ SO ₂ Cl ^h	33	1.25 ± 0.15	0.62 ± 0.04	0.21 ± 0.20	0.967	216
<i>p</i> -MeOC ₆ H ₄ SO ₂ Cl ^h	37	1.10 ± 0.17	0.61 ± 0.04	0.22 ± 0.23	0.959	194

^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. 7. ^g From ref. 6. ^h From ref. 5.

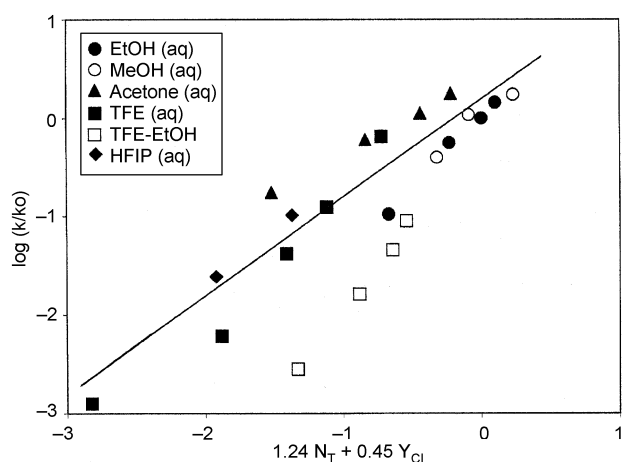


Fig. 1 Plot of $\log(k/k_0)$ for solvolyses of dimethyl phosphorochloridate at 25.0 °C against $(1.24 N_T + 0.45 Y_{Cl})$.

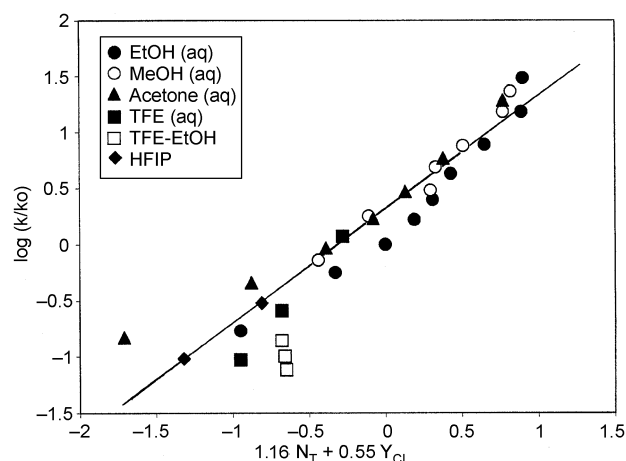


Fig. 2 Plot of $\log(k/k_0)$ for solvolyses of dimethyl phosphorochloridothionate at 25.0 °C against $(1.16 N_T + 0.55 Y_{Cl})$.

range. It is well-established that displacement at the sulfonyl group is a concerted process,²⁰ and these similarities can be considered to give indirect evidence in support of a parallel process for solvolytic displacement of chloride ion from the phosphorus of phosphorochloridates and phosphorochloridothionates.

The slower reaction with the thio-derivative is consistent with the findings for phenyl chloroformate that progressive introduction of sulfur for oxygen leads to a reduction of rate for the component of the solvolyses believed to follow a mechanism with a rate-determining bimolecular attack. However,

unlike the situation for phenyl chloroformate and its three thio-derivatives,^{4a,11,21} the similar *l* and *m* values for (MeO)₂POCl and (MeO)₂PSCl, with the values essentially constant across the full range of solvent compositions studied, give no evidence for any changeover in mechanism to one involving ionization assisted by nucleophilic solvation of the developing cation.

The selectivity values (*S*) for the solvolytic substitution of chloride ion, either by nucleophilic attack of an alcohol molecule or by nucleophilic attack of a water molecule, are presented in Table 2 for a wide range of composition of the binary solvent mixture. One must avoid a simplistic view of these values since it is well established that, for attack at carbonyl carbon,²² phosphorus,^{6,23} or sulfur,^{18,23} general-base catalysis involving both of the components of the binary mixture is frequently operative.

The values of 0.36 to 0.91 for the solvolyses of DMPC in aqueous ethanol or aqueous methanol (5 determinations) indicate only a very slight preference for a general-base catalyzed attack by water. It could well be that a slightly higher nucleophilicity for an alcohol molecule is counterbalanced by slightly less steric hindrance to nucleophilic attack by a water molecule. Some support for this view comes from a comparison with *S* values previously obtained for the same five solvent compositions for solvolyses of diphenyl phosphorochloridate [(PhO)₂POCl]⁶ and ethyl phenylphosphonochloridate [Ph(EtO)POCl].²³ The lowest set of *S* values (0.15 to 0.46) are with (PhO)₂POCl as the substrate, with the *S* values for Ph(EtO)POCl (0.20 to 0.68) intermediate in value. Values relative to (PhO)₂POCl for the 5 common solvents are from 1.3 to 1.6 for Ph(EtO)POCl and, except for a value of 3.0 for 90% MeOH, of from 1.8 to 2.4 for (MeO)₂POCl. This indicates that the *S* values fall with increased steric hindrance, with Ph(EtO)₂POCl apparently being intermediate in character.

For the thio-derivative (DMPCT), the *S* values in the five solvents are somewhat larger (0.57–1.31). The values rise with further increases in water content, reaching 1.59 for 20% ethanol and 1.98 for 20% methanol. For the five solvents used in both studies, the *S* values are about 50% higher than the values for solvolyses of DMPC. These could be coupled with a lower *l* value for DMPCT being indicative of a reduced steric hindrance effect, but it is probably best to consider the 50% difference as being too small for a detailed discussion of its source. For the solvolyses of 2,4,6-trimethylbenzenesulfonyl chloride¹⁸ in the five solvents, the *S* values of 1.9 to 3.2 are noticeably higher than for the reactions at the phosphorus of a phosphorochloridate or a phosphonochloridate.

For solvolyses of DMPC in 90%–50% TFE the percentages of (MeO)₂POOH produced were in excess of 99% of the theoretical and no appreciable amount of reaction with the TFE

component could be taking place. This is consistent with the corresponding product study with (PhO)₂POCl as the substrate, when only small amounts (<1%) of the trifluoroethyl ester were observed in the products by reversed-phase high-performance liquid chromatography.⁶

Conclusion

Unlike the previously studied solvolyses of (PhO)₂POCl, the solvolyses of (MeO)₂POCl and of (MeO)₂PSCl give good correlations when analyzed using the extended Grunwald–Winstein equation. The goodness of fit in each case is comparable to that observed previously for (Me₂N)₂POCl. As has been found to be frequently the case, the correlations are improved upon omission of the data points for TFE–ethanol mixtures. The *l* values (1.27 ± 0.14 and 1.17 ± 0.07) and *m* values (0.47 ± 0.08 and 0.55 ± 0.03) are very similar to each other, indicating that no appreciable change of mechanism occurs on the replacement of the oxygen by sulfur. The values are very similar to those previously recorded for the solvolyses of arenesulfonyl chlorides. This is taken as support for the concept of a concerted displacement reaction,²⁴ similar to that put forward^{5,20} for nucleophilic attack at the sulfur of the sulfonyl chlorides.

The selectivity values (*S*) in aqueous ethanol and aqueous methanol are similar for the two substrates and, for relatively low water content, slightly favor reaction with the water. The values are somewhat lower than those for arenesulfonyl chloride solvolyses, which moderately favor reaction with the alcohol. Comparison with values for solvolyses of Ph-(EtO)POCl and (PhO)₂POCl suggests that a balance between higher nucleophilicity for the alcohol and lower steric hindrance to water attack may be a major factor influencing the variation of the *S* values with substrate structure.

Experimental

Both of the substrates (Aldrich, 97%) were purified by distillation of 25 g under reduced pressure using a 10 cm Vigreux column. A forerun of 5 g and a pot residue of about 5 g were discarded. The distillation temperature was 40–50 °C. **CAUTION!** Dimethyl phosphorochloridithionate must be distilled under reduced pressure because it undergoes a violent autocatalytic decomposition when heated above 120 °C.²⁵ A comparison of weights of substrate taken and infinity titers after solvolysis in 60% acetone (2 equivalents of acid produced) indicated 99.3 ± 0.4% purity for (MeO)₂POCl and 100.4 ± 0.6% purity for (MeO)₂PSCl.

The solvents were purified and the kinetic runs carried out as previously described.¹⁴ The product ratios could have been determined from the infinity titers of the kinetic runs but, to maximize the accuracy, the values reported were determined independently. A 0.47 M solution of the substrate in acetone was prepared and 0.300 mL was added to 20.0 mL of the binary solvent mixture under investigation. All determinations were in duplicate at 25.0 °C and 5.00 mL portions were titrated in the usual manner¹⁴ at 10, 15, and 20 half lives.

The multiple regression analyses were performed using the ABSTAT statistical package (Anderson-Bell, Arvada, Colorado, USA).

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