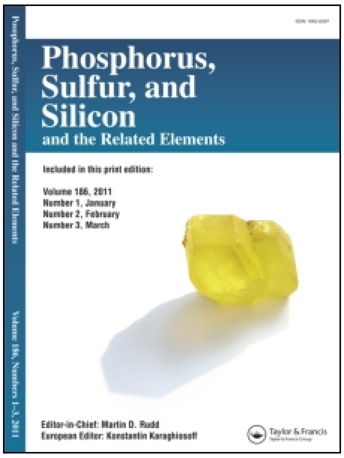

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Reaction Mechanism Studies of Solvolytic Displacement of Chloride from Phosphorus

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The extended Grunwald-Winstein equation is applied to solvolytic displacement at phosphorus. Previous studies of the solvolyses of phosphorochloridates $(RO)_2POCl$, Ph_2POCl *and* $[(CH_3)_2N]_2POCl$ *are extended to cyclic phosphorochloridates, with five and six membered rings. Both kinetic and product ratio measurements are made. The equation is also applied to kinetic studies of the solvolyses of* Ph_2PCl. *The* l *and* m *sensitivity values are compared with previous values and with values for attack at sulfur, to give useful mechanistic information.*

Keywords Chlorodiphenylphosphine; cyclic phosphorochloridates; extended Grunwald-Winstein equation; solvolysis

INTRODUCTION

The extended Grunwald-Winstein[1] equation is used to correlate the specific rates of solvolysis reactions in terms of solvent ionizing power[2]and solvent nucleophilicity[3]. In Equation (1), k and k_0 represent the specific rates of solvolysis in a given solvent and in the

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

standard solvent (80% ethanol), respectively; l represents the sensitivity to changes in solvent nucleophilicity (N_T); m represents the

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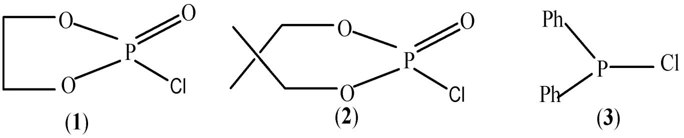
sensitivity to changes in solvent ionizing power (Y_X for a leaving group X); c represents a constant (residual) term.

The scale was initially developed for nucleophilic attack at sp^3-carbon but it has been successfully applied to attack at sp^2-carbon[4] and at phosphorus[5–7] and sulfur.[8] The solvolyses at phosphorus have included rate and product studies with dimethyl phosphorochloridate as substrate, and a direct displacement (S_N2) reaction was proposed as the pathway.[6] In the present paper, the study is extended to the solvolyses of two cyclic phosphorochloridate esters, 2-chloro-1,3,2-dioxaphospholane-2-oxide (**1**) and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane-2-oxide (**2**). The study of diphenylphosphinyl chloride[7] was also explained in terms of S_N2 attack and this has been extended to the phosphorus(III)-containing chlorodiphenylphosphine (**3**) (Scheme 1).



SCHEME 1

KINETIC STUDIES AND CORRELATION OF THE SPECIFIC RATES

The specific rates of solvolysis of **1** and **2** have been measured using a rapid response conductivity apparatus, in a wide range of solvents, including binary mixtures of water with 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The values at 25.0°C for **1** and the values at 50.0°C for **2** are determined using ethanol and methanol and their aqueous binary mixtures plus mixtures of water with acetone, TFE, and HFIP. These values are used in correlations using eqn. 1 against literature values for N_T^3 and Y_{Cl}.[2,9] The sensitivity values together with measures of the goodness-of-fit are reported in Table I, where they are compared with literature values for solvolytic displacements of chloride from sulfur (VI) or phosphorus (V).

There have been strong indications[10] that nucleophilic attack at a phosphorus within a 5-membered ring shows significant pathway differences to other situations. A large[11,12] (sometimes enormous[11]) rate acceleration is frequently observed and, whereas inversion is normally observed, reactions of 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholane-2-oxide give predominantly retention of configuration.[12] The present analyses give no support for any special effects during solvolyses, with

TABLE I Grunwald-Winstein Correlations for Attack at Phosphorus and Sulfur

Substrate	n^a	T °C	l^b	m^b	R^c
$(Me_2N)_2POCl^d$	31	25.0	1.20 ± 0.07	0.69 ± 0.04	0.958
$(MeO)_2POCl^d$	18	25.0	1.27 ± 0.14	0.47 ± 0.08	0.941
$(MeO)_2PSCl^d$	28	25.0	1.17 ± 0.07	0.56 ± 0.03	0.966
Ph_2POCl^d	27	25.0	1.42 ± 0.10	0.54 ± 0.07	0.956
1	28	25.0	1.16 ± 0.06	0.60 ± 0.03	0.974
2	27	50.0	1.03 ± 0.05	0.43 ± 0.02	0.974
3	25	25.0	1.25 ± 0.09	0.46 ± 0.06	0.954
$p\text{-}MeOC_6H_4SO_2Cl^e$	37	25.0	1.10 ± 0.17	0.61 ± 0.04	0.959
$i\text{-}PrSO_2Cl^e$	19	25.0	1.28 ± 0.05	0.64 ± 0.03	0.988
$Me_2NSO_2Cl^e$	26	25.0	1.17 ± 0.06	0.70 ± 0.04	0.975

[a]Number of data points; [b]from Eq. (1); [c]correlation coefficient; [d]from Ref. 7; and [e]from Ref. 8.

the l and m values for **1** being similar to those for other entries within Table I. Also, a comparison of the specific rates (Table II) shows **1** only modestly more reactive than the open-chain analog.

The phosphorus(III)- containing compound Ph_2PCl (**3**) not only shows l and m values very similar to the phosphorus(V)- containing compound Ph_2POCl[7]but the actual specific rates in a given solvent are very similar. For example, at 25.0°C, the specific rates in ethanol are $8.09 \times 10^{-3}s^{-1}$ and $7.02 \times 10^{-3}s^{-1}$ and, in 97% HFIP, they are $6.16 \times 10^{-6}s^{-1}$ and $5.91 \times 10^{-6}s^{-1}$, respectively. Studies with the replacement of phenyl by other groupings are needed to explore the generality of this

TABLE II Specific Rates of Solvolysis at 25.0°C, in a Few Typical Solvents, for Dimethyl Phosphorochloridate, 1 and 2

Solvent	$10^4k[(CH_3O)_2POCl]^a$	$10^4k(\mathbf{1})^b$	$10^4k(\mathbf{2})^b$
100%EtOH	2.96	37.8	0.13^c
80%EtOH	28.5	328	0.27^c
100%MeOH	11.3	48.7	0.12^c
80%MeOH	49.6	480	—
97%TFE	0.036	1.13	—
50%TFE	18.6	259	—
70%HFIP	0.71	55.4	—

[a]From ref. 6; [b]this Work; and [c]extrapolated using 3 or 4 values determined at higher temperatures.

TABLE III Selectivity Values (S)[a] in Solvolyses of 2 at 50.0°C

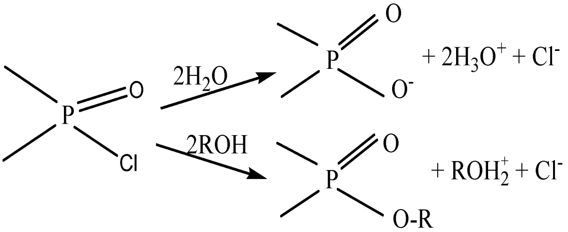
Solvent[b]:	90E	70E	50E	20E	90M	70M	40M	20M	80T	70T	50T
S(2):	1.97	1.43	1.37	2.01	2.20	1.91	1.32	1.66	0.23	0.09	0.07
S[$(CH_3O)_2POCl$]:	0.36[c]	0.56[c]	0.85[c]								

[a]From Eq.. (3); [b]E, M, T represent ethanol, methanol, and TFE, with its percentage component given (remainder water); ethanol-water and methanol-water on volume-volume basis at 25.0°C and TFE-water on weight-weight basis; [c]at 25.0°C.

observation. The acid catalysis frequently observed in substitutions at phosphorus (III)[13] appears not to operate.

PRODUCT SELECTIVITY

The reactions of **1** were sufficiently fast for appreciable reaction to occur during mixing. For **2** infinity titers could be used to determine the product partitioning [Equation (2)]. These values can be used in conjuction with the composition of a water-alcohol mixture to



(2)

arrive at selectivity values (*S*) defined as in Equation 3. Values for the selectivity are

$$S = \frac{[\text{ester in product}][H_2O\text{ in solvent}]}{[\text{acid in product}][ROH\text{ in solvent}]} \tag{3}$$

compared to those previously observed for dimethyl phosphorochloridate in Table III. The values in aqueous ethanol and aqueous methanol for the open-chain compound are slightly below unity as opposed to slightly above unity for **2**. However, the variation in the energy difference between the two pathways of Equation 2 would only have to be small to account for these changes in *S* value. As expected, TFE does not compete effectively against water.

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