relative importance of inductive electronic effects is substantial even in the distant ring. This is shown in the values of $\lambda = \rho_R/\rho_I$ for the carbons in this ring; even at C-4″, λ is only 1.70.

Since the response of the electronic system to the perturbation of the substituent is the common factor between NMR chemical shifts and σ values, changes in electronic charge densities at the particular carbons are important influences in these correlations. The nonlinearity of the Δδ vs. σ relationship at C-1′ and C-4′, both para-type positions in the central ring, may well reflect the decreased sensitivity of these carbons to substituent effects because of the moderation of the π-electron density changes at C-1′ and C-4′ by the terminal phenyl group. This effect is similar to the decreased sensitivity of the para carbon to mesomeric substituents observed by Bromilow and coworkers[17] in 1,4-disubstituted benzenes.

Since the ground and very low-lying excited states play a major role in determining ^{13}C NMR chemical shifts, the best σ_R parameter should be σ_R^0, which is more characteristic of the electronic ground state than, for example, σ_p^+. This is indeed the case for the resonance terms in the H, DSP, and DSP-NLR calculations, except at C-2,6. At C-2,6, the resonance and inductive effects have opposite signs, and σ_R^- gives the best correlations.

The positive signs of the coefficients are as expected: electron-withdrawing substituents lead to decreased shielding of the molecule, and electron-releasing substituents lead to increased shielding. At C-1′ and C-1″, however, these signs are negative, indicating the resonance-modified redistribution of π-electron density that is especially effective along the long molecular axis.

An interesting aspect of the substituent effects in the terphenyls is that the transmission of these effects is quite similar to that in 4-substituted styrenes. The λ values obtained in this work for analogous positions are nearly identical with those calculated by Reynolds and co-workers.[15] The mean λ in this work is 1.46 with a 1.48 standard deviation, which is statistically indistinguishable from the mean λ in Reynolds' work of λ = 1.48 with a standard deviation of 1.82. Since the values of λ cannot be the same at all positions, the results rigorously support the necessity of a dual substituent scale.[15] The results also show that even for long-range effects of substituents on carbon chemical shifts, both inductive and resonance transmission of these effects are important in terphenyls.

Acknowledgment. We thank John T. Wilson, Steven T. Maher, Dolores James, and Ronald E. Block for valuable technical assistance and Victor Hasselblad for useful advice on statistics.

Registry No. 1 (R = NO_2), 10355-53-0; 1 (R = $COOCH_3$), 51166-76-8; 1 (R = CN), 17799-51-8; 1 (R = H), 92-94-4; 1 (R = CH_3), 28952-41-2; 1 (R = I), 1762-85-2; 1 (R = Br), 1762-84-1; 1 (R = Cl), 1762-83-0; 1 (R = NH_2), 7293-45-0; 1 (R = $N(CH_3)_2$), 80583-47-7.

Solvent Effect on the Kinetics of the Chlorine Isotopic Exchange Reaction between Chloride Ion and *O,O*-Diphenyl Phosphorochloridate or *O,O*-Diphenyl Phosphorochloridothioate

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The effect of solvent on the kinetics of the chlorine isotopic exchange reaction between $^{36}Cl^-$ ions and *O,O*-diphenyl phosphorochloridate [$(PhO)_2POCl$, 1] or *O,O*-diphenyl phosphorochloridothioate [$(PhO)_2PSCl$, 2] has been investigated in nitromethane, acetonitrile, propylene carbonate, benzonitrile, nitrobenzene, and hexamethylphosphoric triamide. The rate constants decrease with increasing electrophilicity of the solvent. A good correlation between the logarithm of the rate constants and acceptor number (AN) of the solvent was obtained with identical slopes for reactions with phosphoryl and thiophosporyl compounds. The slopes for the dependences of $\Delta H^{\ddagger}$ or $T\Delta S^{\ddagger}$ vs. AN for chlorine isotopic exchange in 1 are opposite those for the exchange reaction in 2, so a constant ratio of $k_{P=O}/k_{P=S}$ is observed, resulting from compensation of $\Delta H^{\ddagger}$ by $\Delta S^{\ddagger}$. The effect of solvent on the initial state (from solubility measurements) and the transition state of the reaction between $(PhO)_2PSCl$ and the Cl^- ion was evaluated. Changes of solvation of 2 have practically no effect on the kinetics of the reaction. Changes of solvation of the chloride ion and of the transition state primarily influence the rate constants and activation parameters of the investigated isotopic-exchange reaction.

Recently we found[1] that the reactivity decrease related to the substitution of oxygen by sulfur in the phosphoryl group of *O,O*-diaryl phosphorochloridates depends on the decrease of the positive charge on the phosphorus atom. This conclusion was based on the kinetic substituent effects of para-substituted benzene rings on the rate constants of the chlorine isotopic-exchange reaction between $(p\text{-}RC_6H_4O)_2POCl$ or $(p\text{-}RC_6H_4O)_2PSCl$ and chloride ion in acetonitrile. Good Hammett correlations of the rate constants with the Taft's σ^0 constants were obtained, and the values of the reaction constants ρ were found to be

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[1] W. Reimschüssel, M. Mikołajczyk, H. Slebocka-Tilk, and M. Gajl, *Int. J. Chem. Kinet.*, 12, 979 (1980).

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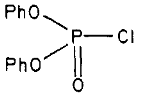
identical for phosphoryl and thiophosphoryl compounds.



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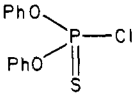

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It was interesting to us to determine whether the reactivity, related to the positive charge on phosphorus, is decreased by the intramolecular substituent effect and/or the intermolecular interactions, namely, solvent effects. Isotopic exchange is a good model reaction for studying solvent effects. Since the substrates and products are the same, the effect of the solvent in relation to the initial and transition states emerges most clearly for consideration. Moreover, on the basis of our results[2] we can note that in the reaction of the chloride 2 with Cl⁻ the cation added to the solution with chloride ion does not take part in the elementary reaction event because the nature of the cation (Me_4N^+, Et_4N^+, n-Bu_4N^+) has no effect on the rate constants and activation parameters of the reaction.

The present work is concerned with the effect of the solvent on the reaction of the $^{36}Cl^-$ ion with phosphorus chlorides 1 and 2. The protic solvents, and such aprotic solvents as Me_2SO, DMF, or DMA, were excluded because of their reactivity toward the phosphorus chlorides. Consequently, six dipolar aprotic solvents, nitromethane (NM), acetonitrile (ANT), propylene carbonate (PC), benzonitrile (BN), nitrobenzene (NB), and hexamethylphosphoric triamide (HMPT), were chosen for our studies. The dielectric constants of the solvents investigated by us vary in the wide range from 25.2 for BN to 65.0 for PC. Three solvents have similar values of dielectric constant (NM 36.7; ANT, 36.0; NB 34.9), but their molecular structures and electrophilic and ionizing properties are quite different. In all chosen solvents $Et_4N^+Cl^-$ is completely dissociated. It is important because in such a case the results might be interpreted by using data for the free energies of transfer, $\Delta^0G^s{}_{Cl^-}$, determined by Parker and others,[3-5] and only in such a case are experimental rate constants independent of the salt concentration[2].

Experimental Section

Materials. The solvents nitromethane,[6] acetonitrile,[1] propylene carbonate,[7] benzonitrile,[8] nitrobenzene,[9] and hexamethylphosphoric triamide[10] were purified by standard procedures. Dry solvents were protected from moisture. *O,O*-Diphenyl phosphorochloridate [$(PhO)_2POCl$, 1] and *O,O*-diphenyl phosphorochloridothionate [$(PhO)_2PSCl$, 2] were prepared and purified as described in our earlier paper.[1]

Kinetic Procedure. The kinetic procedure was the same as that reported earlier.[1] The isotopic-exchange experiments were carried out in sealed ampules containing solutions of $Et_4N^{36}Cl$ and the chloride 1 or 2. The reaction temperature was maintained with an accuracy of ±0.1 °C. The reactants were separated by extraction with a mixture of water and carbon tetrachloride (1:5). The radioactivity of the water phase was measured with a liquid scintillation counter (Intertechnique SL-30) by using scintillation solutions of *p*-terphenyl (6 g L⁻¹) and naphthalene (50 g L⁻¹) in dioxane. The second-order rate constants were calculated from the eq 1, where k_{ex} is the isotopic exchange rate constant and a

$$k = k_{ex}/(a + b) \qquad (1)$$

and b are the concentrations of 1 or 2 and $Et_4N^{36}Cl$, respectively. The value of k_{ex} was determined from the plot of log $(I - I_\infty)$ against time, where I and I_∞ are the counting rates for the sample at times t and t_∞, respectively. The value of I_∞ was calculated from the concentration of the reagents and the initial counting rate I_0 for $t = 0$.

Table I. Solubility and Density of $(PhO)_2PSCl$ in Dipolar Aprotic Solvents at 25 °C and the Acceptor Number of the Solvents

solvent[a]	C,[b] mol L⁻¹	d,[c] g cm⁻³	AN[12]
NM	0.65 ± 0.02	1.209 ± 0.001	20.5
ANT	0.92 ± 0.01	0.915 ± 0.001	18.9
PC	0.63 ± 0.04	1.269 ± 0.001	18.3
BN	1.95 ± 0.07	1.175 ± 0.001	15.5
NB	2.12 ± 0.05	1.592 ± 0.001	14.8
HMPT	5.30 ± 0.09	1.823 ± 0.001	10.6

[a] Abbreviations are as follows: NM, nitromethane; ANT, acetonitrile; PC, propylene carbonate; BN, benzonitrile; NB, nitrobenzene; HMPT, hexamethylphosphoric triamide. [b] Solubility. [c] Density of the saturated solution.

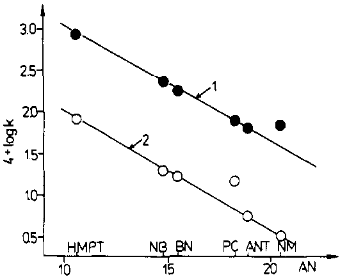

Figure 1. Correlation of the second-order rate constants with AN of the solvents for the reaction between $Et_4N^{36}Cl$ and $(PhO)_2POCl$ (1) or $(PhO)_2PSCl$ (2) at 25 °C.

Calculations of k_{ex} and the statistical error Δk_{ex} were carried out by using the method of least squares.[11] Calculations of the Arrhenius activation parameters log A and B were carried out by using the statistical weight $k^2/(\Delta k)^2$. The errors were quoted on the 0.95 confidence level. The enthalpy and entropy of activation were calculated for 25 °C according to Eyring theory.

Solubility Measurements. The solubility of chloride 2 in all solvents under investigation was determined in the manner described below. An excess of powdered 2 was added to the appropriate solvent and shaken. Then, the flask was placed into a thermostat in which a temperature of 25 °C was maintained with an accuracy of ±0.002 °C. The first samples of the solution were collected after 72 h and the following samples at 24-h intervals. The last samples were collected after 120 h. It has been found that equilibrium is achieved in the flask after 72 h under these conditions. The samples were weighed before and after removal of the solvent. The density of the saturated solutions were determined pycnometrically in the usual manner. The solubilities determined in this way are listed in Table I.

Results and Discussion

The rate constants of the chlorine isotopic-exchange reaction between chloride 1 or 2 and $^{36}Cl^-$ in six dipolar aprotic solvents are collected in Tables II and III. The activation parameters for the above-mentioned reactions are shown in Tables IV and V.

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(2) W. Reimschüssel, S. Tilk, M. Mikołajczyk, and H. Slebocka-Tilk, *Int. J. Chem. Kinet.*, 13, 417 (1981).

(3) A. J. Parker, *Chem. Rev.*, 69, 1 (1969).

(4) R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Am. Chem. Soc.*, 94, 1148 (1972).

(5) A. J. Parker, U. Mayer, R. Schmid, and V. Gutmann, *J. Org. Chem.*, 43, 1843 (1978).

(6) C. P. Smyth and W. S. Walls, *J. Chem. Phys.*, 3, 557 (1935); R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, 41, 2875 (1949).

(7) M. J. Jansen and H. L. J. Yeager, *J. Phys. Chem.*, 77, 3089 (1973).

(8) R. S. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.*, 82, 3239 (1960).

(9) K. B. McAlpine and C. P. Smyth, *J. Chem. Phys.*, 3, 55 (1935).

(10) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, 87, 2372 (1965).

(11) D. Margerison in "Comprehensive Chemical Kinetics", Vol. 1, S. H. Bamford and C. F. H. Tipper, Eds., Elsevier, Amsterdam, London, New York, 1972, Chapter 5.

Table II. Second-Order Rate Constants (10^4k, L mol^{-1} s^{-1}) for the Chlorine Isotopic-Exchange Reaction between $(PhO)_2POCl$ and $Et_4N^{36}Cl$

	temp, °C				
solvent[a]	0	20	25	30	35
NM[b]	4.91 ± 0.18, 5.76 ± 0.10	39.7 ± 3.3	70.4 ± 4.3	88.0 ± 5.0	
ANT[c]	4.00 ± 0.03, 4.18 ± 0.04	40.2 ± 1.0, 42.7 ± 0.9	66.3 ± 1.9, 64.8 ± 1.1	119.5 ± 3.3, 120.9 ± 2.8	
PC[d]	5.90 ± 0.08	53.5 ± 0.7	79.3 ± 0.7	120.7 ± 1.5	207 ± 3
BN	14.0 ± 0.2		183 ± 3		473 ± 6
NB[e]		138 ± 7	235 ± 6	343 ± 16	565 ± 9
HMPT	86.9 ± 1.5		851 ± 9		1897 ± 25

[a] Abbreviations as in Table I. [b] At 15 °C, $10^4k = 23.9 \pm 1.8$. [c] At 5.5 °C, $10^4k = 8.41 \pm 0.12$. [d] At 10 °C, $10_4k = 18.2 \pm 0.2$. [e] At 15 °C, $10^4k = 96.2 \pm 1.4$.

Table III. Second-Order Rate Constants (10^4k, L mol^{-1} s^{-1}) for the Chlorine Isotopic-Exchange Reaction between $(PhO)_2PSCl$ and $Et_4N^{36}Cl$

	temp, °C				
solvent[a]	0	20	25	30	35
NM	0.398 ± 0.008	2.54 ± 0.03	3.21 ± 0.09	4.93 ± 0.05	7.55 ± 0.16
ANT	0.312 ± 0.004, 0.314 ± 0.002, 0.315 ± 0.004	3.66 ± 0.16, 3.54 ± 0.05	5.55 ± 0.06, 5.64 ± 0.06	8.33 ± 0.25, 8.86 ± 0.12	
PC[b]	1.05 ± 0.02	9.08 ± 0.09	14.8 ± 0.1	21.9 ± 0.2	38.3 ± 0.3
BN	0.91 ± 0.02		16.8 ± 0.9		45.2 ± 0.5
NB[c]		10.3 ± 0.5[d]	20.3 ± 1.6,[e] 20.8 ± 1.9,[e] 20.6 ± 1.5[e]	32.4 ± 1.5, 31.0 ± 1.7	
HMPT	3.82 ± 0.04		79.4 ± 2.2		235 ± 3

[a] Abbreviations as in Table I. [b] At 9 °C, $10^4k = 4.89 \pm 0.06$. [c] At 15 °C, $10^4k = 6.60 \pm 0.86$. [d] At 19.6 °C. [e] At 25.5 °C.

Table IV. Activation Parameters for the Chlorine Isotopic-Exchange Reaction between $(PhO)_2POCl$ and $Et_4N^{36}Cl$

solvent[a]	E, kcal mol^{-1}	log A, L mol^{-1} s^{-1}	$\Delta H^{\ddagger}_{25}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25}$, cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{25}$, kcal mol^{-1}
NM	15.3 ± 0.3	9.1 ± 0.2	14.7	−19.0	20.4
ANT	18.3 ± 0.1	11.2 ± 0.3	17.7	−9.0	20.4
PC	16.7 ± 0.2	10.2 ± 0.1	16.1	−13.9	20.2
BN	16.8 ± 0.2	10.6 ± 0.2	16.2	−12.0	19.8
NB	13.6 ± 0.6	9.9 ± 0.3	15.0	−15.4	19.6
HMPT	14.7 ± 0.2	9.7 ± 0.1	14.0	−16.0	18.8

[a] Abbreviations as in Table I.

Table V. Activation Parameters for the Chlorine Isotopic-Exchange Reaction between $(PhO)_2PSCl$ and $Et_4N^{36}Cl$

solvent[a]	E, kcal mol^{-1}	log A, L mol^{-1} s^{-1}	$\Delta H^{\ddagger}_{25}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{25}$, cal K mol^{-1}	$\Delta G^{\ddagger}_{25}$, kcal mol^{-1}
NM	13.8 ± 0.4	6.7 ± 0.3	13.1	−29.9	22.2
ANT	18.5 ± 0.1	10.3 ± 0.3	17.9	−13.3	21.9
PC	17.0 ± 0.3	9.6 ± 0.2	16.4	−16.5	21.3
BN	18.7 ± 0.3	10.9 ± 0.2	18.1	−10.5	21.2
NB	19.4 ± 0.4	11.5 ± 0.3	18.8	−7.7	21.1
HMPT	19.7 ± 0.3	12.3 ± 0.2	19.1	−4.1	20.2

[a] Abbreviations as in Table I.

Table VI. Values of a_k for $\log k_{25} = a_kX + b$, where X = AN, DN, Z, or E_T[a]

reaction	AN[b]	DN	Z[c]	E_T[d]
$(PhO)_2POCl + {}^{36}Cl^-$	−0.134 ± 0.001	0.024 ± 0.032	−0.113 ± 0.123	−0.151 ± 0.095
$(PhO)_2PSCl + {}^{36}Cl^-$	−0.140 ± 0.003	0.029 ± 0.033	−0.135 ± 0.133	−0.150 ± 0.155

[a] The data of AN, DN, Z, and E_T were taken from ref 12. [b] The data for the reaction of $(PhO)_2POCl$ in NM and for $(PhO)_2PSCl$ in PC were omitted. [c] Kosover parameter; the Z parameters for PC and NB are not available. [d] Reichardt parameter.

In order to compare our kinetic data with the properties of the solvents, we have tested the linear correlation of log k and activation parameters with solvent empirical parameters[12] X such as the acceptor number (AN), characterizing electrophilic properties, the donor number (DN), describing nucleophilic properties, and the Kosower (Z) and the Reichard (E_T) parameters, which characterize the ionizing properties of the solvent. From the plot of log k against X one can see (Table VI) that there is no correlation with DN as well as with Z or E_T. However, a good linear relationship of log k with AN exists (Figure 1) for the reactions involving chlorides 1 and 2, if the data for 1 in nitromethane and for 2 in propylene carbonate were omitted.

When ΔH^{*} or $T\Delta S^{*}$ is plotted vs. AN (Figure 2) straight lines for reactions of both phosphoryl and thiophosphoryl

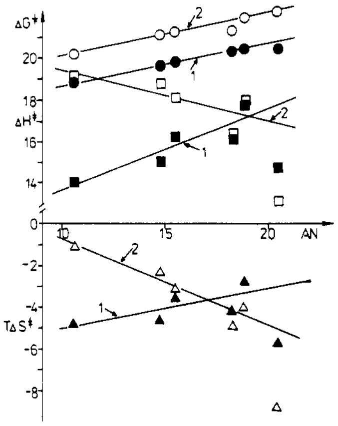

Figure 2. Correlation of the activation parameters $\Delta G^{\ddagger}$ (●, ○), $\Delta H^{\ddagger}$ (■, □), and $T\Delta S^{\ddagger}$ (▲, △) with AN of the solvents for reaction between $Et_4N^{36}Cl$ and $(PhO)_2POCl$ (1) or $(PhO)_2PSCl$ (2) at 25 °C.

compounds are obtained (without data for nitromethane), but the slopes for **1** ($a_{\Delta H^{\ddagger}} = 0.38 \pm 0.11$, $a_{T\Delta S^{\ddagger}} = -0.19 \pm 0.09$) are opposite to those for **2** ($a_{\Delta H^{\ddagger}} = -0.25 \pm 0.11$, $a_{T\Delta S^{\ddagger}} = 0.42 \pm 0.08$).

In our opinion the observed best correlation of our experimental results with AN is most probably due to the similar solvation of the phosphoryl and thiophosphoryl groups in our substrates to that of the P=O group of Et_3PO used as a standard to define the acceptor number.[12] The identical (within the limits of error) a_k values for the reaction of phosphoryl and thiophorsphoryl compounds indicate that the accepting effect of the solvents is transmitted indiscriminantly to the reaction center regardless of whether it is a phosphoryl or thiophosphoryl group. The constant ratio obtained, $k_{P=O}/k_{P=S} = 11.3 \pm 0.7$, at 25 °C is similar to that reported earlier, $k_{P=O}/k_{P=S} = 12.3 \pm 0.8$, for the same chlorine isotopic-exchange reaction of $(p\text{-}RC_6H_4O)_2POCl$ and $(p\text{-}RC_6H_4O)_2PSCl$ (R = MeO, Me, H, Cl, Br, NO_2). Thus, the nonspecific interactions, the intermolecular solvent effect or the intramolecular substituent effect, give the same result, namely, the constant reactivity decrease of thiophosphoryl compounds in comparison with their phosphoryl analogues.

According to Mayer et al.[12] increasing the acceptor number leads to an increase of the positive charge of the phosphorus atom. The influence of solvent on the ^{31}P chemical shifts results from the polarization of the P=O bond induced by the interactions of the electrophile with the phosphoryl oxygen atom. Reduction of π bond character is probably accompanied by polarization of the δ bond. Both effects lead to a decrease of electron density at the phosphorus atom. However, we found that increasing the acceptor number causes a decrease in the rate constants for both reactions (Figure 1). Therefore, there is no simple relation between the rate constant of the reaction and the positive charge on the phosphorus atom. Comparison of changes in the positive charge on the phosphorus atom caused by solvent effects and substituent effects suggests that solvent electrophilicity and the electron-accepting capabilities of substituents should induce the same result, thereby increasing the positive-charge on the phosphorus atom. But the changes of the rate of the reaction are different. Increasing solvent electrophilicity decreases the rate constant while increasing the accepting abilities of the substituents increases it.

Comparison of the activation parameters with AN (Figure 2) shows that identical slopes of the plots of log k (or $\Delta G^{\ddagger}$) vs. AN are obtained as a result of compensation between $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$. The change of $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ with AN indicates that the solvent interaction, with regard to the reaction of phosphoryl and thiophosphoryl compounds, causes different structural changes ($\Delta S^{\ddagger}$) and different changes of energy ($\Delta H^{\ddagger}$) required for the reaction to proceed. Changes of energy with the electrophilic properties of the solvent are more significant for the reaction with $(PhO)_2POCl$ while greater structural changes accompany the reaction of $(PhO)_2PSCl$. The observed differences are probably caused by the various interactions of the solvent with respect to the initial and transition states of the investigated reaction.

Approximately the same tetrahedral structure of the initial state, which is generally accepted for molecules of tetracoordinate phosphorus compounds, can be discussed for molecules **1** and **2**, taking into consideration the difference in the positive charge of the phosphorus and the different polarizability of the P=O and P=S bonds. The transition state is represented as a trigonal bipyramid with the centrally situated phosphorus atom and the entering and leaving chlorine atoms in apical positions. The oxygen or sulfur atoms and phenoxy groups are in equatorial positions. Although the symmetrical distribution of the negative charge between the chlorine atoms in the apical positions seems to be the most reasonable for the investigated isotopic-exchange reaction, the extent of the charge at the phosphorus atom and the distribution of the negative charge between the equatorial groups will be different. As for the possibility of the transient phosphorane formation, we may say that if the phosphorane intermediate were formed, it cannot undergo permutational isomerization (pseudorotation). This statement is based on the results of our previous work[13] dealing with the isotopic chlorine exchange at phosphorus and racemization of chiral thiophosphoryl chloride. It has been shown that the ratio k_{rac}/k_{exch} is practically equal to 2, thus providing evidence for the inversion of configuration at P during exchange and against pseudorotation of the transient dichlorophosphorane formed. Moreover, the phosphorane structure with the two chlorine atoms occupying apical positions seems to be the most convenient structure from the point of apicophilicity of the substituents at phosphorus, and there is no need for pseudorotation in this particular case. In other words, the decomposition of such a phosphorane should be faster than pseudorotation.[14]

It can be expected that the solvent molecules will be more rigidly ordered about the more polar phoshoryl transition state. On the other hand, taking into account the solvation of the phosphoryl and thiophosphoryl groups, initial-state participation of the solvent molecules in the activation process will be greater for the reaction of **2** than that for the reaction of **1**. This can account for the opposite effect of the AN on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ and is also consistent with a greater polarizability of the P=S bond in comparison with the P=O bond.

The solvent acceptor number is an excellent quantitative empirical solvent parameter, but only for expressing all types of solvent interactions in relation to the entire chemical phenomena. The correlation of acceptor number

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[12] U. Mayer, V. Gutmann, and W. Gerger, *Monatsh. Chem.*, **106**, 1235 (1975).

[13] J. Michalski, M. Mikołajczyk, A. Halpern, and K. Proszynska, *Tetrahedron Lett.*, 1919 (1966).

[14] For a more extensive discussion on the mechanism of nucleophilic substituion at phosphorus see: F. H. Westheimer, *Acc. Chem. Res.*, 1, 70 (1968); R. F. Hudson and C. Brown, *ibid.*, 5, 204 (1972); S. J. Benkovic and K. J. Schray, "The Enzymes", Vol. 8 P. A. Boyer, Ed. 3rd ed., Academic Press, New York and London 1973, p 201.

Table VII. Free-Energy of Transfer from Acetonitrile (Index 0) to Another Solvent (Index s)[a]

solvent[b]	$\log k^s/k^0$	$\Delta^0G^s_{Cl^-}$, kcal mol^{-1}	$\Delta^0G^s_{\phi}$, kcal mol^{-1}	$\Delta^0G^s_{\ddagger}$, kcal mol^{-1}
NM	−0.205	+3.14	−0.20	+2.66
ANT	0.0	0.0	0.0	0.0
PC	+0.422	+0.14	−0.22	+0.49
BN	+0.477	−1.39	+0.45	−0.29
NB	+0.567	−1.77[c]	+0.49	−0.51
HMPT	+1.152	−4.09	+1.03	−1.49

[a] For chloride ion, $\Delta^0G^s_{Cl^-}$; for $(PhO)_2PSCl$, $\Delta^0G^s_{\phi}$; for transition state, $\Delta^0G^s_{\ddagger}$. [b] Abbreviations as in Table I. [c] Value of $\Delta^0G^s_{Cl^-}$ estimated from dependence of $\Delta^0G^s_{Cl^-}$ on AN.

with kinetic data gives no information about the interaction of the solvent with substrates and the transition state of the reaction. The thermodynamic quantities which represent a measure of the solvent effects toward substrates, ions, or molecules and toward the transition state of S_N2 reactions are free energies of transfer[3], $\Delta^0G^s_i$, from the reference (index 0) to the other solvent (index s). The values of $\Delta^0G^s_{Cl^-}$ for chloride ion are available[4] for all the solvents investigated with acetonitrile as a reference solvent. The free energies of transfer, $\Delta^0G^s_{\phi}$, for chloride **2** were calculated (Table VII) from the solubility measurements (Table I). Unfortunately, these values cannot be determined for the phosphoryl analogue because the liquid chloride **1** mixes in every ratio with the solvents used. The free energy of transfer, $\Delta^0G^s_{\ddagger}$, for the transition state was calculated by using eq 2, where k^0 and k^s are the rate

$$-RT \ln k^s/k^0 = \Delta^0G^s_{Cl^-} + \Delta^0G^s_{\phi} - \Delta^0G^s_{\ddagger} \qquad (2)$$

constants of the isotopic exchange reaction in acetonitrile (index 0) and the investigated (index s) solvent. The values of $\Delta^0G^s_i$ are given in Table VII. Parker, Gutmann, et al.[5] showed that the effect of solvent transfer on the rates of S_N2 reactions depends on the anion-solvating properties of the solvents, as measured either by $\Delta^0G^s_{Cl^-}$ or by the changes in the solvent acceptor number. They found the approximate linear free-energy relationship $n\Delta^0G^s_{Cl^-} = -n'\Delta$ (AN). Similar dependences were obtained for solvents investigated in this work (Figure 3). With increasing AN, $\Delta^0G^s_{Cl^-}$, $\Delta^0G^s_{\ddagger}$, and, consequently, the solvation of the chloride ion and the transition state are increased. However, an increase of solvation for the chloride ion is more significant than that for the transition state (the slopes of the straight lines in Figure 3 are 0.51 ± 0.07 and 0.21 ± 0.10, respectively). This can be related to the change of negative charge distribution in the transition state.

Data for experiments conducted in nitromethane were omitted because this solvent interacts more strongly than other solvents with the chloride ion and the transition state while its interactions with chlorine **2** are normal. This is reflected in the values of $\Delta^0G^s_{\ddagger}$, $\Delta^0G^s_{Cl^-}$, and $\Delta^0G^s_{\phi}$ shown in Figure 3, indicating that the smaller values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reaction in nitromethane (Figure 2) are connected with stronger solvation of the chloride ion and the transition state. Our data clearly demonstrate that there is no good correlation with AN in nitromethane as solvent. Most probably the solvation of the Cl^- ion and the transition state in nitromethane is different in character as compared with other solvents. The nature of the Cl^-–nitromethane interaction is not known. van der Heijde and Dahmen[15] suggested that nitromethane may be classified as a weak protic solvent.

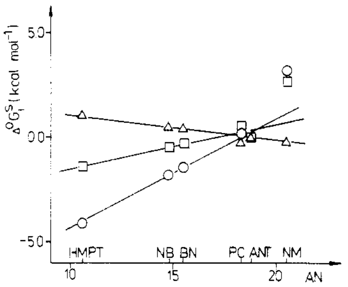

Figure 3. Relationship between $\Delta^0G^s_{Cl^-}$ (○), $\Delta^0G^s_{\ddagger}$ (□), $\Delta^0G^s_{\phi}$ (△) and AN of the solvent for reaction of $(PhO)_2PSCl$ with $Et_4N^{36}Cl$ at 25 °C.

The plot of $\Delta^0G^s_{\phi}$ vs. AN has a negative slope: −0.10 ± 0.06. Increasing AN leads to a slight decrease of the solvation of **2** and to an increase of positive charge on the phosphorus atom. If solvation of the molecules of **2** were responsible for the rate of reaction, one should observe increasing rate constants, which is contrary to the result obtained. Therefore, solvation of the free chloride ion and the polar transition state mainly influences the course of the reaction and finally results in decreasing rate constants as the accepting properties of the solvents are increased.

The results obtained permit the conclusion that the reactivity of organic disubstituted phosphoryl and thiophosphoryl chlorides depends on the accepting properties of the solvent as well as on intramolecular substituent effects. The constant reactivity decrease of the thiophosphoryl compounds in comparison to their phosphoryl analogues is maintained, regardless of whether the effect of the substituent or the properties of the solvent are changed.

Registry No. 1, 2524-64-3; **2**, 22077-44-7; Cl^-, 16887-00-6.

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(15) H. B. van der Heijde and E. A. M. F. Dahmen, *Anal. Chim. Acta*, 16, 378 (1957).