Proton Acceptor Power of Diamines. Diamines exhibit more striking differences in behavior in acetonitrile and in water than those described for monoamines. The results in Table II lead to the following conclusions.

1. Diprotonated diamines are weakened less on being transferred from water to acetonitrile than is the case for the corresponding monoprotonated compounds, in agreement with the expectation that the lower dielectric constant of acetonitrile discourages higher charge type ions to a greater degree than is the case in water.

2. In acetonitrile, monoprotonated diaminopropane and diaminobutane are weaker acids than would be predicted from the strength of *n*-propyl- and *n*-butylammonium ions. This weakening is attributed to stabilization of the species $H_2N(CH_2)_nNH_3^+$ with n = 3 and 4 by intramolecular hydrogen bonding, a reaction which is largely masked in water. In going up the series of diamines, an abrupt increase in acid strength occurs with diaminopentane, which is in agreement with the foregoing, since for the species $H_2N(CH_2)_5NH_3^+$ intramolecular hydrogen bonding would require a seven-membered ring (not counting hydrogen). The same phenomenon is illustrated more strikingly in Table III. In water the difference between the two pK_a values of a given diamine decreases in going up the series and gradually approaches the statistical factor of $\log 4 = 0.60$. In acetonitrile this difference is larger and abruptly decreases at diaminopentane. It is interesting to compare values of the

"effective" dielectric constant, D_E, calculated on the basis of the Kirkwood–Westheimer model,[20] in three media for which dissociation constants are available (water, 80% (v./v.) ethanol, and acetonitrile)

$$\log \frac{K_{a_1}}{4K_{a_2}} = \Delta pK_{a, cor} = \frac{e^2}{2.303 kTR D_E}$$

where $\Delta pK_{a, cor}$ is the value of ΔpK_a corrected for the statistical factor, R represents the distance (in cm.) between the protons, and other symbols have their usual meaning. It follows that

$$D_E = \frac{2.43 \times 10^{-6}}{R \Delta pK_{a, cor}}$$

Values of D_E are listed in Table III. For acetonitrile D_E increases abruptly at diaminopentane, whereas in the isodielectric ethanol–water mixture, in which little intramolecular hydrogen bonding is to be expected; D_E smoothly approaches the bulk dielectric constant of the medium. Further calculations probably are not justified in view of the uncertainties associated with the Kirkwood–Westheimer model.[21]

(20) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 6, 506 (1938).

(21) S. Ehrenson, *Progr. Phys. Org. Chem.*, 2, 199 (1964).

Rates of Chloride Ion Exchange with Various Phosphonic Chlorides and Phosphorochloridates

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From measurements of the chloride-36 exchange rate with various $RPOCl_2$ compounds and spectroscopic determination of the donor strength of various phosphoryl compounds, it has been possible to examine the electronic effects present in bimolecular displacement reactions on four-coordinate phosphorus. The exchange reaction with $RPOCl_2$ compounds has been shown to follow second-order kinetics in the solvent 1,2-dichloroethane at $-30°$. The effect of substituent is to decrease the rate in the order $C_6H_5 > CH_3 > OCH_3 \sim Cl > OC_6H_5$. The effect of substituent on the donor strength of the phosphoryl oxygen gives rise to the order $(CH_3)_2N \sim C_6H_5 > CH_3 > OCH_3 > OC_6H_5 > Cl$. The relative importance of inductive and conjugative effects for these substituents has been discussed. These studies aid in the interpretation of some previously published n.q.r. data. Interpreting the donor strength as an indication of the formal positive charge on phosphorus, it is observed that the rate of exchange is not in direct proportion to this charge. In order to rationalize the rate data, it is necessary to consider the effect that inductive withdrawal of electron density and π bonding have on the relative energies of the ground and transition states.

Introduction

There has been considerable interest in the mechanism of substitution reactions of four-coordinate phosphorus compounds. Much of this interest has arisen from the comparison of the mechanisms of these reactions with substitution reactions on carbon. There has also been considerable interest in the behavior of phosphorus oxychlorides as nonaqueous solvents, and this has served as the motivation for kinetic studies. We report, in this article, work which is pertinent to both of these areas.

Much nonaqueous solvent work has been interpreted in terms of solvent self-ionization, for example

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^- \qquad (1)$$
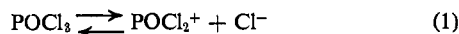
It has been shown[2] that radiochloride exchange with POCl₃ in acetonitrile is first order in both chloride ion and POCl₃. This casts considerable doubt on the importance of eq. 1 in describing reactions in POCl₃ because the dielectric constant and solvating tendency of acetonitrile is even greater than that of POCl₃. However, no other conclusions concerning the mechanism of the substitution reaction could be drawn from these early exchange studies.

For a second-order reaction in which self-ionization of the phosphorus compound is considered to be unimportant, there are three general types of possible mechanisms: (a) attack and elimination without formation of a trigonal bipyramidal transition state (or intermediate)
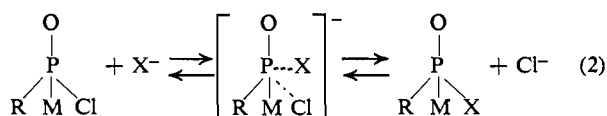
(b) attack and elimination with the formation of a trigonal bipyramidal transition state (or intermediate) without undergoing a Walden-type inversion
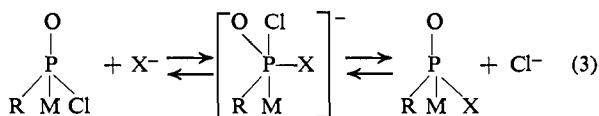
(c) attack and elimination with the formation of a trigonal bipyramidal transition state (or intermediate) with a Walden-type inversion occurring
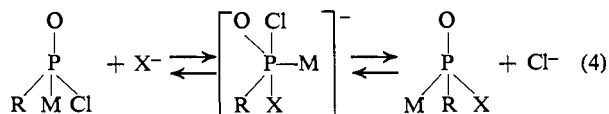
In 1959, Green and Hudson in a preliminary description of some experimental work proposed that the reaction of methoxide ions with 3-phenanthrylmethylphosphinyl chloride and fluoride is a simple bimolecular SN2 inversion reaction occurring through the formation of a five-coordinate transition state.[3] Inversion was subsequently observed for the reaction of ethoxide ions with isopropyl methylphosphorochloridate and O-isopropyl S-methyl methylphosphonothioate.[4] These reactions firmly established that inversion did occur, but did not show that inversion occurred as part of the substitution reaction. It was later shown[5] that exchange reactions and substitution proceed by the same mechanism. By studying the racemization of methyl ethylphenylphosphinate during methoxide exchange, it was found that the rate of racemization is twice the rate of exchange and that the reaction was second order just as predicted from eq. 4.

An interesting exchange experiment was carried out to test for the existence of an intermediate in the reac-

tion of R₂POF with water. In the hydrolysis of R₂POF (R = methyl or isopropoxy), no exchange of oxygen-18 between the phosphoryl group and water was observed.[6a] In a similar study,[6b] no exchange was observed between (EtO)₂POCl in H₂O¹⁸ and of (EtO)₂PO¹⁸Cl in H₂O. It was argued that if a five-coordinate intermediate did form, there should be a rapid interchange of protons resulting in oxygen-18 exchange. While this work does not define a specific transition state, it does show that an intermediate does not exist for a period long enough to allow proton interchange between the entering hydroxyl group and the phosphoryl oxygen.

There have been several reports of the effect of substitution on the rate of solvolysis of various phosphoryl compounds.[7,8] As these studies have been carried out in hydroxylic solvents, interpretation of the results is quite difficult. It is possible that large contributions from solvation of the ground and transition states could dominate the trends. Furthermore, the relative importance of bond making vs. bond breaking in the transition state cannot be ascertained from these studies.

By selecting a nonhydroxylic solvent and observing the rate of chloride exchange, it is possible to eliminate both extensive solvation and asymmetric charge distribution as factors in the formation of a transition state. For these reasons, we have studied the exchange of radiochloride with RPOCl₂ in 1,2-dichloroethane as a function of the R substituent.

Experimental Section

All phosphorus compounds used in the exchange were distilled through a micropath column just prior to use. The purified reagents were stored in desiccators containing activated alumina or "Drierite" in the absence of light.

Phosphoryl chloride (Mallinckrodt), POCl₃, was distilled from metallic sodium, b.p. 103.5°.

Methylphosphonic dichloride was prepared according to a standard synthesis.[9] *Anal.* Cacld. for CO₃POCl₂: C, 9.02; H, 2.28. Found: C, 9.23; H, 2.45.

Phenylphosphonic dichloride (Eastman) had b.p. 125.2° (4.25 mm.). *Anal.* Calcd. for C₆H₅POCl₂: C, 36.96; H, 2.59. Found: C, 37.01; H, 2.57.

Methyl phosphorodichloridate was obtained from K and K Laboratories. *Anal.* Calcd. for CH₃POCl₂: C, 8.06; H, 2.01; Cl, 47.7. Found: C, 8.27; H, 2.01; Cl, 40.0.

Phenyl phosphorodichloridate was obtained from Aldrich. *Anal.* Calcd. for C₆H₅POPCl₂: C, 34.15; H, 2.38. Found: C, 34.43; H, 2.37.

(Chloromethyl)phosphonic dichloride was purchased from Victor. *Anal.* Calcd. for CH₂ClPOCl₂: C, 7.18; H, 1.20; Cl, 63.55. Found: C, 7.21; H, 1.29; Cl, 63.38.

Thiophosphoryl chloride (Victor) had b.p. 121.8°. *Anal.* Calcd. for PSCl₃: P, 18.28; Cl, 62.79. Found: P, 18.36; Cl, 62.74.

(2) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 336 (1957).
(3) M. Green and R. F. Hudson, *Proc. Chem. Soc.*, 227 (1959).
(4) H. S. Aaron, R. T. Uyeda, H. F. Franck, and J. I. Miller, *J. Am. Chem. Soc.*, 84, 617 (1962).
(5) M. Green and R. F. Hudson, *Proc. Chem. Soc.*, 307 (1962).

(6) (a) M. Halmann, *J. Chem. Soc.*, 305 (1959); (b) I. Dostrovsky and M. Halmann, *ibid.*, 1004 (1956).
(7) B. Miller, *J. Am. Chem. Soc.*, 84, 403 (1962).
(8) R. F. Hudson and L. Keay, *J. Chem. Soc.*, 1859, 1865 (1960).
(9) A. M. Kinnear and E. A. Perren, *ibid.*, 3437 (1952).

Methyl sulfinyl chloride was prepared by a standard synthesis,[10] b.p. 56.0° (2 mm.). *Anal.* Calcd. for CH₃SOCl: C, 12.18; H, 3.07; S, 32.54; Cl, 35.97. Found: C, 12.25; H, 3.09; S, 32.45; Cl, 35.94.

Phosphorus trichloride was Baker and Adamson "Reagent" grade. *Anal.* Calcd. for PCl₃: Cl, 77.50. Found: Cl, 77.66.

Arsenic trichloride was Baker and Adamson "Reagent" grade, b.p. 129.6°.

1,2-Dichloroethane and tetraethylammonium chloride were purified as previously described.[11]

The required phosphorodiamines were prepared by mixing the phosphorochlorides and dimethylamine in diethyl ether at −78° and allowing the solutions to slowly warm to room temperature. The solution was filtered and the phosphorodiamine was distilled.

Hexamethylphosphoramide was from Aldrich. *Anal.* Calcd. for PO[N(CH₃)₂]₃: C, 40.02; H, 10.12; N, 23.45. Found: C, 40.11; H, 10.01; N, 23.31.

N,N,N′,N′-Tetramethyl(chloromethyl)phosphorodiamide. *Anal.* Calcd. for ClCH₂PO[N(CH₃)₂]₂: C, 32.53; H, 7.64; N, 15.17. Found: C, 32.50; H, 7.59; N, 14.51.

N,N′-Dimethyl(chloromethyl)phosphoramide Chloride. *Anal.* Calcd. for ClCH₂PO(Cl)[N(CH₃)₂]: C, 20.45; H, 4.58; N, 7.96. Found: C, 20.51; H, 4.62; N, 7.78.

Pentamethylphosphorodiamidate. *Anal.* Calcd. for CH₃OPO[N(CH₃)₂]₂: C, 36.14; H, 9.09; N, 16.85. Found: C, 35.99; H, 9.24; N, 16.78.

Tetrachloroethylene (Eastman Spectrograde), C₂Cl₄, was dried with 4A molecular sieves and stored in a desiccator prior to use.

Phenol (Eastman) was distilled through a 2.5-m. column, then sublimed under vacuum. The crystals were stored in a vacuum desiccator prior to use.

Radiochlorine Labeling. Chlorine-36 was introduced into the phosphonic chlorides by mixing labeled HCl (Oak Ridge National Laboratory No. Cl-36 (P)) with purified tetraethylammonium chloride and heating to dryness on a steam bath for 10 hr. The phosphonic chloride was labeled by equilibration with the labeled salt and then recovered by distillation.

Exchange Procedure. Solutions of tetraethylammonium chloride and labeled phosphonic chloride were prepared in dry 1,2-dichloroethane, then cooled to the temperature of interest (±0.1°) for 0.5 hr. The solutions were quickly mixed and replaced in the bath. Quenching was accomplished by pouring the 1,2-dichloroethane solution into dry ether at −78°. The precipitated tetraethylammonium chloride was immediately filtered and dried.

The halide salt was dissolved in a minimal amount of water and made 1 *N* in nitric acid. By titration,[12] an aliquot of standard size was determined and precipitated with a 10% excess of 0.03 *N* mercurous nitrate. The precipitate was mounted for counting using standard techniques.

The chlorine-36 activity was determined using either an end-window Geiger–Müller detector or an end-window gas-flow proportional detector. Corrections were made for coincidence losses and variations in counting geometry for all samples.

Homogeneous and heterogeneous quench studies allowed correction for exchange during precipitation and isolation of the mounted sample.

Phenol Frequency Shift Studies. Phenol frequency shift studies were conducted.[13] A Beckman IR-7 with scale expansion and a Perkin-Elmer Model 521 infrared spectrometer, calibrated for the region of interest, were employed. All solutions were prepared in tetrachloroethylene.

Results

Radiochloride Exchange Studies. From the observed specific activity of the precipitated sample and the time of reaction, it was possible to obtain the half-time of exchange, $t_{1/2}$, and to calculate a number of possible rate constants using standard techniques.[14]

Employing an IBM 7094 computer, each specific activity value was adjusted to "zero time" and corrected for possible exchange during quench. $t_{1/2}$ was obtained from a two-dimensional least-squares fit of the data. A comparison of calculated rate constants indicated a second-order expression of the form

$$R = k_2[\text{RPOCl}_2][\text{Et}_4\text{NCl}]\theta \tag{5}$$

where values of θ, the degree of dissociation for Et₄NCl, have been previously reported.[11]

Approximately twelve exchange samples were employed in the calculation of each k_2 shown in Table I. The error limits reported represent the 96% confidence level as determined by standard statistical methods.

Complete exchange within the time of separation was observed for arsenic trichloride, phosphorus trichloride, and methyl sulfinyl chloride with labeled chloride ion in 1,2-dichloroethane at −30°.

Phenol Frequency Shift. Complexed phenol infrared spectra were obtained for various concentrations of the phosphorodiamine and the phosphorochloride with phenol (1.88 × 10⁻² *M*) in tetrachloroethane. After obtaining $\Delta\nu_{\text{OH}}$ and correcting for concentra-

$$\Delta\nu_{\text{OH}} \text{ (cm.}^{-1}) = \nu_{\text{free phenol}} - \nu_{\text{complexed phenol}} \tag{6}$$

tion effects, it was possible to obtain the enthalpy of acid–base interaction given in Table II[13]

$$-\Delta H_{\text{kcal./mole}} = 0.016\Delta\nu_{\text{OH}} + 0.63 \tag{7}$$

For each of the donors studied, the infrared spectrum showed a slight decrease in the phosphoryl stretching frequency upon hydrogen bonding to phenol, indicating only phosphoryl oxygen coordination.

In comparing the effects of various substituent groups in RPOCl₂ on the rate constant for the exchange re-

(10) I. B. Douglas and B. S. Fahah, *J. Org. Chem.*, **23**, 330 (1958).
(11) D. L. Lydy, V. A. Mode, and J. G. Kay, *J. Phys. Chem.*, **69**, 87 (1965).
(12) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. II, 2nd Ed., Interscience Publishers, New York, N. Y., 1947, pp. 331, 332.

(13) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).
(14) A. C. Wahl and N. A. Bonner, Ed., "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 7–11.

Table I. Second-Order Rate Constant for Chloride-36-RPOCl₂ Exchange in 1,2-Dichloroethane at −30.0°

R	k_2, l. mole⁻¹ sec.⁻¹	k_2 (av.), l. mole⁻¹ sec.⁻¹
C₆H₅	1.04 ± 0.03 1.07 ± 0.03 1.09 ± 0.03 1.11 ± 0.03 1.03 ± 0.03	1.07
CH₃	0.734 ± 0.022 0.823 ± 0.024 0.978 ± 0.030 0.808 ± 0.024	0.84
Cl	0.392 ± 0.012 0.429 ± 0.013 0.368 ± 0.010 0.390 ± 0.012 0.422 ± 0.013 0.429 ± 0.013	0.41
CH₃O	0.349 ± 0.010 0.362 ± 0.010 0.370 ± 0.011	0.36
C₆H₅O	0.00261 ± 0.00026 0.00300 ± 0.00030 0.00307 ± 0.00031	0.0029
PSCl₃	0.0157 ± 0.0005 0.0175 ± 0.0005 0.0155 ± 0.0005 0.0208 ± 0.0006 0.0189 ± 0.0006	0.018

Table II. Phenol Frequency Shift and Enthalpy of Acid–Base Interaction

R	RPOCl₂ — $\Delta\nu_{OH}$,ᵃ cm.⁻¹	RPOCl₂ — $-\Delta H$, kcal. mole⁻¹	RPO[N(CH₃)₂]₂ — $\Delta\nu_{OH}$,ᵃ cm.⁻¹	RPO[N(CH₃)₂]₂ — $-\Delta H$, kcal. mole⁻¹
(CH₃)₂N	...	...	442	7.7
C₆H₅	177	3.4	433	7.6
CH₃	165	3.3	...	...
Cl	114ᵇ	2.5ᵇ	...	...
CH₃O	155	3.1	408	7.2
ClCH₂	...	...	406ᶜ	7.1ᶜ
C₆H₅O	146	3.0	226	4.2

ᵃ $\nu_{free\ phenol}$ = 3611 cm.⁻¹ ᵇ From ref. 13. ᶜ For ClCH₂PO(Cl)[N(CH₃)₂], $\Delta\nu_{OH}$ = 231 cm.⁻¹, $-\Delta H$ = 4.3 kcal./mole.

action, it is necessary to consider the differences arising from changing the number of chloro groups on phosphorus. In these compounds, the number of degenerate pathways available for the reaction increases when R is Cl. Geometrical and optical isomers must be considered in addition to the usual rotational isomers.[15,16]

The statistical formulation of the rate constant includes rotational symmetry factors for the activated complex, the phosphorus reactant, and chloride, σ^*, σ_A, and σ_B, respectively. Also included is the number of degenerate isomeric forms, α, for the transition complex. Thus, the rate constant may be written

$$k_2 = \alpha\left(\frac{\sigma_A\sigma_B}{\sigma^*}\right)\frac{kT}{h}\exp\left(\frac{-\Delta E^\circ}{RT}\right)$$

We define k_2' as

$$k_2' = \frac{1}{\alpha}\left(\frac{\sigma^*}{\sigma_A\sigma_B}\right)k_2 = \frac{kT}{h}\exp\left(\frac{-\Delta E^\circ}{RT}\right) \quad (8)$$

(15) R. A. Marcus, *J. Chem. Phys.*, **43**, 1598 (1965).
(16) Equation 17' of ref. 15 should be consulted.

and compare k_2' values for various R groups. Values of k_2', α, and σ_A are given in Table III.

Table III. Values of k_2'

	k_2	α	σ_A	k_2'
C₆H₅POCl₂	1.07	2	1	0.53
CH₃POCl₂	0.84	2	1	0.42
CH₃OPOCl₂	0.36	2	1	0.18
POCl₃	0.41	1	3	0.14
C₆H₅OPOCl₂	0.0029	2	1	0.0015
PSCl₃	0.018	1	3	0.006

Discussion

Since an ionic mechanism has been eliminated for POCl₃, it is of interest to ascertain the order of the reaction for a series of substituted phosphorus compounds. Both electron-releasing groups (e.g., CH₃) and groups capable of conjugation (e.g., C₆H₅) would stabilize positive charge on the phosphorus facilitating an ionic mechanism proceeding by release of chloride ion (eq. 1). However, this has not been observed to occur. All of the reactions studied followed simple second-order kinetics (first-order in chloride and first-order in RPOCl₂) in a solvent whose solvating tendencies are similar to those of POCl₃ (e.g., the dielectric constants at 22° for POCl₃ and 1,2-dichloroethane are 13.3 and 10.5, respectively).[17]

Extrapolating the results of Green and Hudson[3] to this system, the exchange reaction is assumed to occur via the mechanism shown in eq. 4, the entering and leaving chlorines occupying the apical positions in the trigonal bipyramidal transition state. This is a reasonable extrapolation of the earlier results and is further supported by molecular orbital calculations and infrared studies which show[18,19] that in a trigonal bipyramidal intermediate a chlorine in the equatorial position will be more tightly bonded than one in the apical position.

The observed rate constants are all very similar with the exception of those for C₆H₅OPOCl₂ and PSCl₃. Since these studies were carried out in a poorly solvating solvent, it may be more appropriate to attempt an interpretation of these small differences based on electronic effects than to try to interpret the larger differences in rate constants often found in polar solvents. Solvation effects may dominate the trends in the polar solvents. In the interpretation of the rate data, one can view the transition state as a Lewis acid–base adduct of chloride ion and the phosphorus compound. One might expect that the stronger the acid–base interaction, the lower the activation enthalpy and the faster the reaction in the absence of unusual entropy terms. One of the first factors to be considered in an attempted rationalization of the rate constants on this basis is the formal positive charge on the phosphorus in the four-coordinate compounds. If the increase in positive charge were to correlate with the rate constant, it would be proposed that the acidity of these materials and the relative rate constants were

(17) C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," 45th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, p. E 30.
(18) P. C. Van der Voorn and R. S. Drago, to be published.
(19) P. C. Van der Voorn, K. F. Purcell, and R. S. Drago, *J. Chem. Phys.*, in press.

related to these ground-state properties; *i.e.*, the increased positive charge on phosphorus leads to a stronger interaction with chloride ion and a lower activation enthalpy. Since the donor strength of the phosphoryl oxygen in this related series of compounds will reflect the variation in the electron density around the phosphorus atom, this property has been examined by measuring the phenol frequency shift upon adduct formation (see Table II).

The donor strengths for compounds of general formula $RPO[N(CH_3)_2]_2$ decreased in the order $(CH_3)_2N \sim C_6H_5 > OCH_3 > OC_6H_5$. The order of donor strengths for the compounds of general formula $RPOCl_2$ is $C_6H_5 > CH_3 > OCH_3 > OC_6H_5 > Cl$. This produces a composite set of substituent effects: $(CH_3)_2N \sim C_6H_5 > CH_3 > OCH_3 > OC_6H_5 > Cl$. It is believed that the decrease in electron density on phosphorus is in the same order as the decrease in basicity. Since a methyl carbon is less electronegative (tetetete $= 2.48$)[20] than a phenyl carbon (trtrtrπ $= 2.75$) or an sp^3 nitrogen ($sp^2pp = 6.70$), the observed ordering suggests a π-bonding interaction between the phenyl group or nitrogen and the phosphorus. The relative |electronegativity of oxygen (te^{2}te^{2}tete $= 5.93$) and chlorine ($s^2p^2p^2p = 2.95$) also suggests more extensive π bonding with the methoxy than with the chloro group.

The inductive and conjugative order of the substituent groups inferred from the donor strengths is found to correlate with reported values of the nuclear quadrupole resonance frequencies of the chlorine.[21] Values of 25.4, 26.6, 27.3, 27.7, and 29.0 Mc./sec. are reported for $C_6H_5POCl_2$, CH_3POCl_2, CH_3OPOCl_2, $C_6H_5OPOCl_2$, and $POCl_3$, respectively. The magnitude of the coupling constant is related to chlorine "s" character, π bonding, and ionicity. As the electron-withdrawing character of the substituents increases (*via* π or σ mechanisms), the ionic character in the phosphorus–chlorine bond is expected to decrease and the quadrupole coupling constant to increase. Chlorine π-bonding would be expected to increase as the electron-withdrawing character of the substituent increases and thus would lead to a decrease in the coupling constant. It is impossible to estimate from qualitative considerations the changes in chlorine "s" character with change in substituent. The donor strengths are more easily interpreted and serve to clarify the interpretation of the n.q.r. frequencies. Since the observed changes in coupling constant are found to correlate with the order of donor strengths, the coupling constant increase is attributed predominantly to a decrease in the ionicity of the phosphorus–chlorine bond.

Since there have been many incorrect interpretations of nuclear magnetic resonance data in terms of electron density on an atom, it is informative to note the lack of such a correlation in this related series of compounds. This is illustrated by comparing the inductive order with the following order of P^{31} chemical shifts[22]: $POCl_3$ (-1.9) $< [(CH_3)_2N]_3PO$ (-23) $< C_6H_5POCl_2$ (-34.5) $< CH_3POCl_2$ (-44.5) (δ values in parentheses, H_3PO_4 as an external standard). As was

observed for a series of widely differing phosphorus compounds π-bonding effects and local paramagnetic contributions serve to distort the electronic and magnetic environment of the phosphorus-31 nucleus to such an extent that a correlation of the chemical shift with electron density on phosphorus is not possible at present.

It is clearly seen that the order for increasing rate of chlorine exchange, $OC_6H_5 < Cl < OCH_3 < CH_3 < C_6H_5$, does not correlate with the order for increasing positive charge on the phosphorus, $C_6H_5 < CH_3 < OCH_3 < OC_6H_5 < Cl$.

The following explanation can be offered to account for the observed order for k_2'. Roughly approximating the bonding in five-coordinate phosphorus as an sp^2 hybrid to the equatorial groups and a three-center bond to the apical groups,[23] phosphorus will become more electronegative toward groups in the plane upon formation of the transition state. It is probably more correct to state that there will be more "s" character in the orbitals used to bond the groups in the equatorial position of the transition state than in the orbitals used for the bonding of these groups in the ground state. Indirect support for this increase in electronegativity with increasing "s" character may be obtained from valence orbital electronegativities[20] calculated for phosphorus(III). A value of 2.79 is reported for te^{2}tetete *vs.* 2.98 for trtrtrπ^2. As a result of this increase in electronegativity upon formation of the transition state, electron withdrawal by the R group in the equatorial position will directly affect the energy required for the formation of the transition state. As R becomes more electronegative, the energy requirement should increase. The difference in the exchange rates for CH_3POCl_2 and $POCl_3$ (see Table I) can be attributed mainly to this effect. However, as was observed for the donor strengths, a conjugative effect is also present for compounds containing the substituents C_6H_5, OCH_3, and OC_6H_5. Since the phosphorus–R distance is shorter in the transition state and phosphorus electronegativity has increased, π bonding should be facilitated in the transition state. Consequently, the energy required to attain the transition state in molecules where the substituent can π bond would be lowered relative to that where π bonding is absent. For this reason, $C_6H_5POCl_2$ is observed to have a faster rate of chloride exchange than CH_3POCl_2. The compound CH_3OPOCl_2 is also found to have a much faster rate of chloride exchange than would be predicted using the above arguments based on electronegativity. This may also be attributed to more extensive π bonding in the transition state than in the ground state. The extensive delocalization of the oxygen lone pairs onto the phenyl ring in $C_6H_5OPOCl_2$, which gave rise to a decreased donor strength for $C_6H_5OPO[N(CH_3)_2]_2$, would give rise to less π bonding in the transition state and account for a slower rate of exchange compared to CH_3OPOCl_2. The order of magnitude of this decrease is surprising when one looks at the order of donor strengths. Other effects may be operative.

The same type of π-bonding argument would also account for the very slow rate of chloride exchange observed for $PSCl_3$. Both the phosphoryl oxygen and

(20) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).
(21) E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2459 (1961).
(22) N. Muller, P. C. Lauterbur, and J. Goldenson, *ibid.*, **78**, 3557 (1956).

(23) R. E. Rundle, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **23**, 195 (1962).

the thiophosphoryl sulfur would be in the equatorial plane of the transition state. Since there is much less phosphorus π bonding to sulfur than to oxygen, it is reasonable to expect a much smaller contribution to stabilization of the transition state through π bonding in $PSCl_3$. Since oxygen is more electronegative than sulfur, $POCl_3$ would be expected to exchange more slowly than $PSCl_3$ on the basis of the inductive argument presented above correlating the formal charge on phosphorus with the difficulty in obtaining the transition state.

It should be mentioned that in the previous discussion, we have been relating an enthalpy of activation to an observed rate of exchange. It is assumed that the principal factor affecting the exchange order is the enthalpy for the formation of the transition state. We have obtained a crude value of approximately 14 kcal./mole for the enthalpy of activation for $POCl_3$. We cannot distinguish unambiguously between the enthalpies of activation of the compounds studied because of experimental error introduced by the rapid exchange occurring at temperatures significantly higher than those reported herein.

A Calorimetric Procedure for Determining Free Energies, Enthalpies, and Entropies for the Formation of Acid–Base Adducts

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In this article, a calorimetric method is presented which allows simultaneous measurement of both the equilibrium constant and enthalpy of adduct formation. Thermodynamic data obtained by this procedure for the adduct of $(CH_3)_3SnCl$ with $CH_3C(O)N(CH_3)_2$ in the solvent CCl_4 are reported. The equilibrium constant is found to agree within experimental error with the value obtained from an infrared study of this system.

Introduction

In a previous article,[2] we have reported an equation for the rigorous evaluation of an equilibrium constant from spectrophotometric data. Equation 1 was derived for a 1:1 complex $(A + B \rightleftharpoons C)$ under conditions where the complex and free acid or base spectral curves overlapped and the molar absorptivity of the complex could not be measured directly. In eq. 1,

$$K^{-1} = \frac{A^0 - A^T}{\epsilon_B - \epsilon_C} - ([A]_0 + [B]_0) + \frac{[A]_0[B]_0(\epsilon_B - \epsilon_C)}{A^0 - A^T} \quad (1)$$

ϵ_B denotes the molar absorptivity of the free base or acid, $[A]_0$ and $[B]_0$ are the initial concentrations of the acid and base, respectively, A^0 is the absorption of a solution of concentration $[A]_0$ or $[B]_0$, ϵ_C is the molar absorptivity of the complex, A^T is the total absorbance, and K^{-1} is the reciprocal of the formation equilibrium

constant. Simultaneous equations for several sets of experimental data are solved to produce values for the two unknowns K^{-1} and ϵ_C.

If instead of measuring spectrophotometric absorbance the heat evolved on combination of an acid and a base is measured, this quantity can be used in place of A^T to calculate an equilibrium constant. The analog of ϵ_C in the enthalpy experiment is $\Delta H°$, the molar enthalpy of formation of the adduct. Consequently, both K and $\Delta H°$ can be evaluated simultaneously by this technique. The necessary equations are derived and the best experimental conditions for obtaining the data are discussed.

Experimental Section

Materials. Eastman White Label N,N-dimethylacetamide was stored over Linde 4A molecular sieves for 2 days, refluxed at reduced pressure over calcium hydride for 2 hr., and fractionally distilled through a 30-in. Vigreux column. The middle fraction was collected, b.p. 42–42.5° (20 mm.).

Trimethyltin chloride, obtained from Metal and Thermit Chemicals, was sublimed at 25° under reduced pressure, m.p. 37.5°.

Fisher Spectranalyzed carbon tetrachloride was dried over Linde 4A sieves and was used in both the infrared and calorimetric work.

Spectra. Infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a CIC variable temperature chamber (Model 104). The temperature of the solutions was measured to $\pm 1°$ with a thermometer positioned adjacent to the infrared cell. Preliminary experiments using a copper-

(1) Abstracted in part from the Ph.D. thesis of T. F. Bolles, University of Illinois, Urbana, Ill.

(2) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.,* **81,** 6138 (1959).