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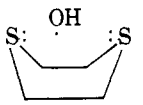

iii

as a precursor of the corresponding *intra*molecular radical cation,[9,10] (b) the lack of *intra*molecular radical cation formation in the case of 2-methyl-1,3-dithiacyclopentane, and (c) the observed dependences of the extinction coefficients seem, however, intuitively more reasonable in terms of the proposed through-space interactions. Further, a direct relationship between the magnitude of the orbital splitting induced by through-bond coupling of ≤ 0.5 eV (e.g., 0.43 eV in 1,3-dithiacyclohexane)[32] and our optical transition energies is not apparent. We cannot, of course, exclude some contribution by through-bond coupling, but we find no compelling grounds for an interpretation of our data on this basis, i.e., to question the formation of a new sulfur–sulfur three-electron-bond in *all* of the radical cation complexes.

Disproportionation among Aryloxyphosphoranes

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Abstract: Methyltetraphenoxyphosphorane and methyltetra-*p*-nitrophenoxyphosphorane, on mixing, rapidly disproportionate to an equilibrium mixture of all of the intermediate phosphoranes and all the phosphonium salts that result from the loss of phenoxide or *p*-nitrophenoxide ion from the phosphoranes. The disproportionation equilibria can be measured by ^{31}P NMR spectroscopy and deviate remarkably little from the statistical distribution, although equilibrium constants for individual dissociations vary over a 10^{14}-fold range. Some understanding of these phenomena is advanced.

Introduction

The acid-catalyzed hydrolysis of phosphates presumably proceeds sequentially through protonated esters and hydroxyphosphoranes. For aryl triesters, the mechanism can be represented[1-3] schematically by the equations

$$(ArO)_3PO + H^+ \rightleftharpoons (ArO)_3P^+OH \quad (1)$$

$$(ArO)_3P^+OH + H_2O \rightleftharpoons (ArO)_3P(OH)_2 + H^+ \quad (2)$$

$$(ArO)_3P(OH)_2 \rightleftharpoons (ArO)_2P^+(OH)_2 + ArO^- \rightarrow (ArO)_2P(=O)OH + ArOH \quad (3)$$

In some instances, pseudorotation[4,5] of the phosphorane intermediates intervenes as part of the hydrolytic process, or as a side reaction. In the present paper, the aryloxyphosphonium salts are offered as models for the protonated esters; the kinetics of their hydrolyses will presumably help in understanding those of the esters.

Mixtures of methyltetraphenoxyphosphorane and methyltetra-*p*-nitrophenoxyphosphorane in dry acetonitrile as solvent disproportionate at room temperature by way of the corresponding aryloxyphosphonium salts. The concentration of at least one of these salts is appreciable, and some of the reactions are fast on the NMR time scale, so that analysis of the equilibria is substantially more complicated than those for the slower equilibrations typical of many of the disproportionations previously analyzed.[6] By taking advantage of the rates and equilibrium constants previously determined for the dissociation of methyltetraphenoxyphosphorane in acetonitrile,[7,8] and a detailed analysis of the ^{31}P NMR spectra, all 16 of the rate constants and all of 8 of the equilibrium constants for this system can be found; they are presented in the accompanying paper.[9] We suggest that this is the most complex system that has so far been analyzed by NMR spectroscopy.

The definitions utilized in these papers are summarized in Scheme I, and the disproportionation constants are given by equations 4-6. The five phosphoranes in the system are designated by the symbols P(1), P(3), P(5), P(7), and P(9), and the four phosphonium salts are designated as P(2), P(4), P(6), and P(8), as shown in Scheme I.

$$L_1 = \frac{[P(1)][P(5)]}{[P(3)]^2} = \frac{K_{34}K_{32}}{K_{12}K_{54}} \quad (4)$$

$$L_2 = \frac{[P(3)][P(7)]}{[P(5)]^2} = \frac{K_{54}K_{56}}{K_{34}K_{76}} \quad (5)$$

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Scheme I[a]

phosphoranes		phosphonium cations	equilibrium constants
$CH_3P(OPh)_4$	P(1)		
	$k_{21}[PhO^-]$ ⇌ k_{12}		$K_{12} = \frac{[P(2)][PhO^-]}{[P(1)]}$
	P(2)	$CH_3P^+(OPh)_3$	
	k_{32} ⇌ $k_{23}[ArO^-]$		$K_{32} = \frac{[P(2)][ArO^-]}{[P(3)]}$
$CH_3P(OPh)_3OAr$	P(3)		
	$k_{43}[PhO^-]$ ⇌ k_{34}		$K_{34} = \frac{[P(4)][PhO^-]}{[P(3)]}$
	P(4)	$CH_3P^+(OPh)_2(OAr)$	
	k_{54} ⇌ $k_{45}[ArO^-]$		$K_{54} = \frac{[P(4)][ArO^-]}{[P(5)]}$
$CH_3P(OPh)_2(OAr)_2$	P(5)		
	$k_{65}[PhO^-]$ ⇌ k_{56}		$K_{56} = \frac{[P(6)][PhO^-]}{[P(5)]}$
	P(6)	$CH_3P^+(OPh)(OAr)_2$	
	k_{76} ⇌ $k_{67}[ArO^-]$		$K_{76} = \frac{[P(6)][ArO^-]}{[P(7)]}$
$CH_3P(OPh)(OAr)_3$	P(7)		
	$k_{87}[PhO^-]$ ⇌ k_{78}		$K_{78} = \frac{[P(8)][PhO^-]}{[P(7)]}$
	P(8)	$CH_3P^+(OAr)_3$	
	k_{98} ⇌ $k_{89}[ArO^-]$		$K_{98} = \frac{[P(8)][ArO^-]}{[P(9)]}$
$CH_3P(OAr)_4$	P(9)		

[a] ArOH symbolizes *p*-nitrophenol.

Table I. Disproportionation Constants for Phosphoranes

constant	exptl value	statistical value
L_1	0.23	0.375
L_2	0.20	0.444
L_3	0.26	0.375

$$L_3 = \frac{[P(5)][P(9)]}{[P(7)]^2} = \frac{K_{76}K_{78}}{K_{98}K_{56}} \quad (6)$$

Results

The final result of this part of the investigation can be summarized simply. The disproportionation constants among the phosphoranes, found experimentally, are remarkably close to those calculated statistically. The substantial effects of substituting *p*-nitrophenoxy for phenoxy substituents nearly cancel in the disproportionation constants; the data are shown in Table I.

Composition of the Solutions. The determination of the constants depends on identifying and integrating the proton-decoupled ^{31}P NMR signals from solutions of the phosphoranes. These solutions were prepared in two different ways. (A) Methyltetraphenoxyphosphorane, P(1), and methyltetra-*p*-nitrophenoxyphosphorane, P(9), were mixed in various proportions. The mole fraction of *p*-nitrophenoxy groups, R, is given by

$$R = \frac{[CH_3P(OAr)_4]_0}{[CH_3P(OPh)_4]_0 + [CH_3P(OAr)_4]_0} \quad (7)$$

where the subscripted quantities refer to concentrations initially added. Although in principle the composition of the solution could be varied from $R = 0.000$ (pure P(1)) to $R = 1$ (pure P(9)), in fact the limited solubility of methyltetra-*p*-nitrophenoxyphosphorane restricts the solutions to those with $R < 0.72$. (B) Methyltriphenoxyphosphonium triflate, P(2), and tetrabutylammonium *p*-nitrophenoxide were mixed in various proportions. The composition of these solutions is given here in terms of the parameter R', where

$$R' = \frac{\sum_{i=1}^{4} i[P(2i+1)]}{\sum_{i=1}^{4} [P(2i+1)]} \quad (8)$$

NMR Spectra of the Phosphoranes and Phosphonium Salts. To analyze the rates and equilibria under discussion, the intrinsic chemical shifts for the ^{31}P NMR spectra of the various phosphoranes and salts, P(1)-P(9), are needed. Like most other phosphoranes, the aryloxyphosphoranes all absorb in the general region of 50 ppm upfield from 85% phosphoric acid, whereas the aryloxyphosphonium salts absorb at ~40 ppm downfield from 85% phosphoric acid. Signals at intermediate positions will arise when, but only when, substantial amounts of both salt and phosphorane are present in solutions, and equilibration is rapid on the NMR time scale. This means that the rate constant for exchange must be large compared with $2\pi\Delta\nu$, or ~20 000 s^{-1}.

The ^{31}P NMR signals from methyltetraphenoxyphosphorane, P(1), and from methyltetra-*p*-nitrophenoxyphosphorane, P(9), can be measured directly, since neither is appreciably dissociated in acetonitrile solution.[8,9] The ^{31}P NMR signals from the other phosphoranes appear in spectra of mixtures; typical examples are shown in Figures 1 and 2, where the solutions were prepared by methods A and B, respectively; the compositions of the solutions are shown in the legends.

Inspection of Figures 1 and 2, and of the accompanying tables of compositions, shows that the concentrations of the phosphoranes vary in a reasonable way. Thus in solution 1a, with $R = 0.26$, the average composition of the solution is that of P(3), which contains three phenoxy and one *p*-nitrophenoxy group. Four signals from phosphoranes appear in Figure 1a, although that from P(7) is only barely visible. Then with solution 1b, where $R = 0.47$, the average composition is near that

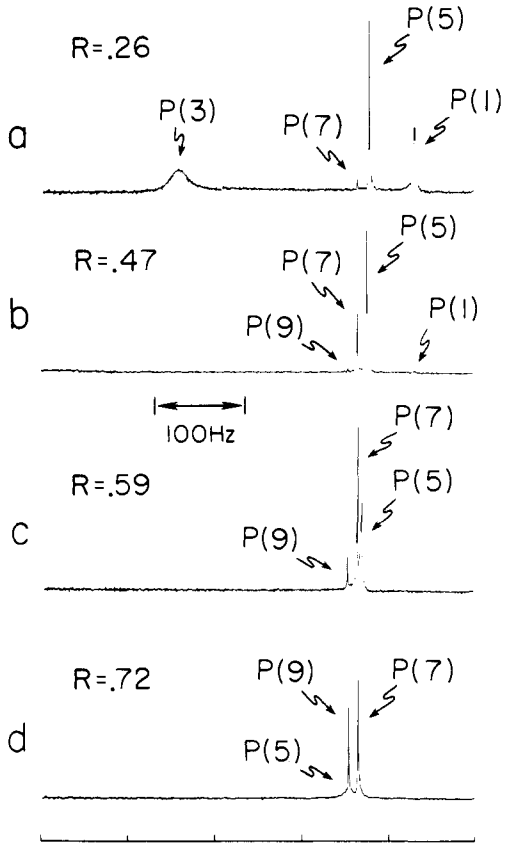

Figure 1. $^{31}P(^1H)$ NMR spectra of solutions of series 1. Different proportions of P(1) and P(9) were added together with acetonitrile as the solvent. *R* represents the fraction of added P(9) to the total amount of phosphorane in each solution. Chemical shifts are given in hertz downfield from the signal for P(1) at a field strength of 40.5 MHz.

solution	*R*	M[a]
1a	0.26	0.095
1b	0.47	0.084
1c	0.59	0.059
1d	0.72	0.076

[a] M is the molarity of the total population of phosphoranes.

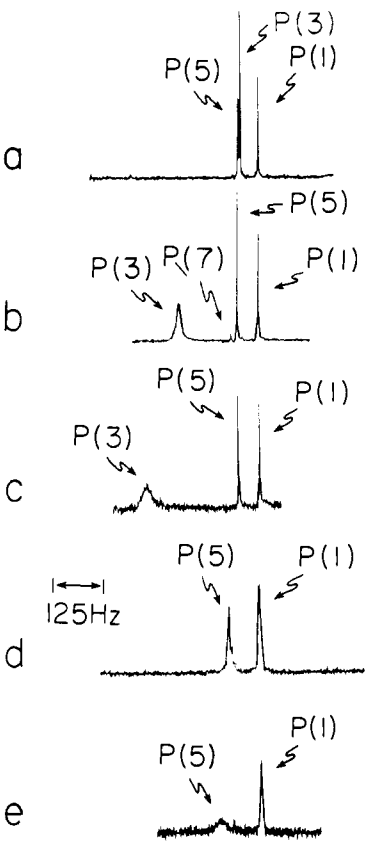

Figure 2. $^{31}P(^1H)$ NMR spectra of solutions of series 2. Different relative proportions of methyltriphenoxyphosphonium triflate were added to tetrabutylammonium *p*-nitrophenoxide with acetonitrile as the solvent. Chemical shifts are given in hertz downfield from the signal for P(1) at a field strength of 40.5 MHz.

solution	composition[a]		
	$N(Bu)_4OPhNO_2$	$CH_3P(PhO)_3OTf$	$[P^{4+}]/[ArO^-]$[b]
2a	0.099	0.055	0.56
2b	0.133	0.133	1.0
2c	0.065	0.065	1.0
2d	0.134	0.171	1.28
2e	0.074	0.118	1.60

[a] Concentrations (M) are those of the starting materials used in the preparation of the samples. [b] Ratio of starting materials.

of P(5), which contains two phenoxy and two *p*-nitrophenoxy groups. Here the signal from P(5) dominates the spectrum, with that from P(7) clearly visible and those from P(1) and P(9) barely observed. The phosphorane P(3) is in rapid equilibrium with the corresponding phosphonium salt, according to eq 9, and so does not give rise to a sharp signal. Although the signal from P(3) does not appear in Figure 1b, it can be seen in spectra with broader spectral width, and occurs further downfield and broader than in 1a. Similar qualitative analysis can be applied to the other spectra.

The peaks for P(3), P(5) and P(7) can also be identified as follows. Since the *p*-nitrophenyl group is more electronegative than the phenyl group, the peaks from the phosphoranes with the most *p*-nitrophenoxy groups would be expected to occur farthest downfield,[10] provided, of course, that the observed peaks arise from the indicated phosphorane alone, and do not result from exchange[11] between phosphoranes and their associated phosphonium salts. Moreover, in the presence of excess *p*-nitrophenoxide ion, the dissociation of methyltriphenoxy-*p*-nitrophenoxyphosphorane, P(3), is largely suppressed, so that (in sharp contrast to the situation that obtains from the solution shown in Figure 1), the position of the signal from P(3) is almost unaffected by exchange.

$$CH_3P(OPh)_3(OAr) \rightleftharpoons CH_3P^+(OPh)_3 + ArO^- \quad (9)$$

That the exchange shown in eq 9 is fast on the NMR time scale can also be shown by varying the temperature of the NMR measurements[12] (Figure 3). Increasing the temperature sharpens the signal from P(3) in solutions such as that shown in Figure 1a; higher temperature also moves the signal further downfield, i.e., toward the signal from phosphonium salts, because of increased dissociation. At the lowest temperature, the signal from P(2) is sharp, at the slow exchange limit. Then, as the temperature is raised, this signal broadens as its rate of exchange with P(3) increases. On the other hand, the signal from P(1) remains sharp throughout the temperature range at the slow exchange limit.

The signals from methyltriphenoxyphosphonium triflate, P(2), and from methyltri-*p*-nitrophenoxyphosphonium chloride, P(8), can be measured directly. The two salts have signals that differ by only 30 Hz; since both signals are separated by >3800 Hz from those from the phosphoranes, the error introduced by linear interpolation for the signals of P(4) and P(6) between those of P(2) and P(8) cannot be important to the purposes of this paper. The intrinsic chemical shifts for the compounds P(1)-P(9), relative to that for methyltetraphenoxyphosphorane, are shown in Table II.

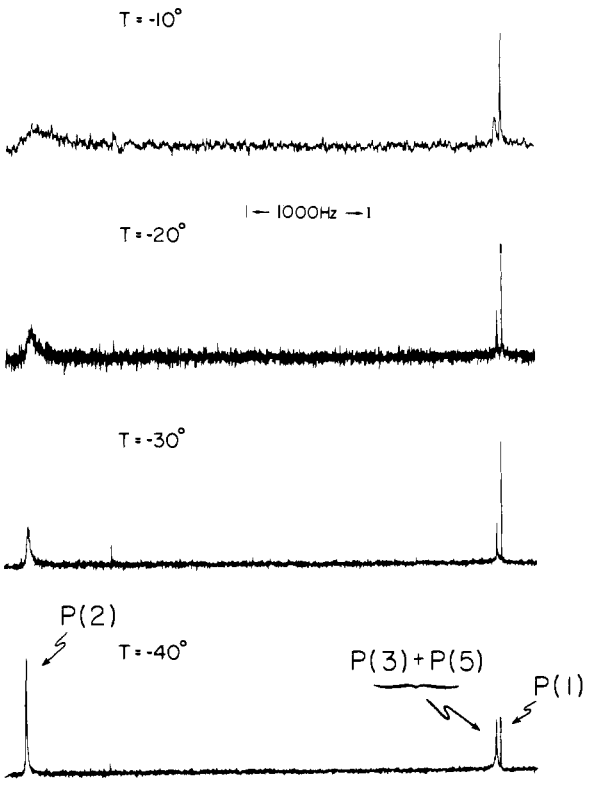

Figure 3. Variable-temperature $^{31}P(^1H)$ NMR spectra of a solution (acetonitrile) of phosphonium salts and phosphoranes. The solution was prepared by the addition of 2 equiv of methyltriphenoxyphosphonium triflate to 1 equiv of tetrabutylammonium *p*-nitrophenoxide.

Table II. $^{31}P(^1H)$ (acetonitrile) Chemical Shifts for Mixed Aryloxyphosphoranes and Phosphonium Salts[a]

phosphorane or phosphonium cation	chemical shift, Hz[b]
P(1), $CH_3P(OPh)_4$	0.0
P(3), $CH_3P(OPh)_3(OPhNO_2)$	35.0
P(5), $CH_3P(OPh)_2(OPhNO_2)_2$	50.0
P(7), $CH_3P(OPh)(OPhNO_2)_3$	65.7
P(9), $CH_3P(OPhNO_2)_4$	77.1
P(2), $CH_2P^+(OPh)_3$	3820
P(4), $CH_3P^+(OPh)_2(OPhNO_2)$	3830[c]
P(6), $CH_3P^+(OPh)(OPhNO_2)_2$	3840[c]
P(8), $CH_3P^+(OPhNO_2)_3$	3850

[a] Chemical shifts are given in hertz downfield from that for P(1), methyltetraphenoxyphosphorane. [b] Field strength equivalent to 40.5 MHz. [c] Interpolated.

Integration under the NMR Peaks. The concentration of the phosphoranes present in various solutions, such as those for the spectra shown in Figures 1 and 2, can in principle be obtained from the areas under the various peaks in those spectra.[13] Integrations of the spectra are valid, subject to the following limitations: First, if a phosphorane is in rapid equilibrium, on the NMR time scale, with a phosphonium salt, then the integral represents the sum of the concentrations of salt and phosphorane. Second, errors might arise from saturation of the signals, and third, areas might be distorted by a nuclear Overhauser effect. The problems are discussed in turn below.

Concentration of P(3). In some spectra, e.g., that shown in Figure 2a, the area under the peak for P(3) is accurately proportional to its concentration. When, however, the peak is moved substantially downfield toward the region of absorption of the phosphonium salts, the peak arises from both the phosphorane and phosphonium salt, P(2). Since the proportion of salt is given by the fraction of displacement of the signal from the position for the intrinsic shift of the phosphorane[11] to that for the corresponding cation, the concentrations of P(2) and P(3) can readily be calculated. Although in some solutions the signal from P(5) is shifted toward the region of signals of the cations, the changes are too small to make an appreciable difference in the concentrations obtained by integration.

Saturation, Overhauser Effect. Within our experimental error, all of the phosphoranes show identical values of 13.5 s for the longitudinal relaxation times. The measurements were carried out by 180°-*t*-90° pulse experiments[14,15] and are explained in detail elsewhere.[12] Since the T_1's for all the phosphoranes are the same, and since data were obtained with both long and short delay times, no errors were introduced by saturation effects. The nuclear Overhauser effect was measured by a modified pulse-decoupler sequence.[13,16] All the NOE's were measured simultaneously, and all were 0.6.

Data. The disproportionation constants are shown in Table I; typical data used in the calculations are shown in Table III. The concentrations of phosphoranes calculated[17] from the statistical values of the disproportionation constants are shown alongside of the concentrations determined experimentally. The differences are remarkably small.

Discussion

Phosphoranes usually assume trigonal-bipyramidal geometry, with two axial and three equatorial substituents.[4,5] In general, electron-withdrawing groups and π acceptors preferential occupy apical sites, whereas bulky groups and ligands capable of p-d back-bonding preferentially occupy equatorial sites. Previous experimental determinations of these preferences have exploited a kinetic approach, where relative apicophilicities[18-23] are determined from the energy of activation required for pseudorotation.[4,5] The approach under discussion here is a thermodynamic one. The relative enthalpy of the phosphorane is presumably dependent on the number and types of its ligand–phosphorus bonds. Furthermore, from the equilibrium constants for dissociation of the phosphoranes (cited in the accompanying paper),[9] we know that *p*-nitrophenoxy groups diminish the dissociation of other ligands, presumably by destabilizing the phosphonium ions that would result from dissociation. Since two aryloxy groups can occupy the two preferred (equatorial or axial) sites, extra energies are added for aryloxy or phenoxy groups, respectively, in excess of two. We define e_x as bond energy for each *p*-nitrophenoxy substituent, e_ϕ as bond energy for each phenoxy substituent, u as stabilization energy of a phosphorane by each *p*-nitrophenoxy group, a_x as extra energy for each *p*-nitrophenoxy group more than two, a_ϕ as extra energy for each phenoxy group more than two. Substituting the above energies into eq 4-8 gives the enthalpic change associated with each disproportionation constant:

$$\Delta H(L_1) = 0.0 \quad \Delta H(L_2) = a_x + a_\phi \quad \Delta H(L_3) = 0.0 \quad (10)$$

It should be noted that the enthalpies for disproportionation are independent of the relative bond energies e_x and e_ϕ.

The values of the disproportionation constants calculated on the assumptions above, are then

$$L_1 = 0.375 \quad L_2 = 0.44e^{-(a_x+a_\phi)/RT} \quad L_3 = 0.375 \quad (11)$$

Provided that the sum of $a_x + a_\phi$ is not large, the enthalpic changes associated with the disproportionation constants are small, and the values of the disproportionation constants reduce to the statistical factors. This argument explains why the values of L_1, L_2, and L_3 are not sensitive to the nature of the substituents provided only that the difference between the thermodynamic apicophilicities of the substituents is not large. If eq

Table III. Relative Concentrations of Phosphoranes[a]

R	M	[P(1)]	[P(3)]	[P(5)]	[P(7)]	[P(9)]
0.25	0.133	0.26 (0.32)	0.500 (0.42)	0.24 (0.21)	(0.05)	(0.00)
0.25	0.065	0.25 (0.32)	0.51 (0.42)	0.24 (0.21)	(0.05)	(0.00)
0.28	0.092	0.26 (0.27)	0.50 (0.42)	0.24 (0.24)	(0.06)	(0.01)
0.47	0.185	(0.08)	0.30 (0.28)	0.53 (0.37)	0.17 (0.22)	(0.05)
0.51	0.081	(0.06)	0.21 (0.24)	0.50 (0.37)	0.25 (0.26)	0.04 (0.07)
0.55	0.095	(0.04)	0.16 (0.20)	0.46 (0.37)	0.32 (0.30)	0.05 (0.09)
0.59	0.060	(0.03)	0.09 (0.16)	0.48 (0.35)	0.36 (0.34)	0.07 (0.12)

[a] Figures in parentheses are statistical values.

11 correctly defines L_2, then $(a_x + a_\phi) = 0.5$ kcal/mol. This value must then be an upper limit for the difference in thermodynamic apicophilicities between a *p*-nitrophenoxy and a phenoxy substituent.

The finding that the difference in apicophilicity between nitrophenoxy and phenoxy substituents is small is not entirely surprising. A range in apicophilicities is provided by Trippet's measurement of the free energies of activation,[22] ΔG^*, for appropriate pseudorotations (ligand, ΔG^* in kcal mol^{-1}): Ph, 22.0; CH=CMe$_2$, 19.9; *i*-Pr, 17.8; Me, 16.9; NMe$_2$, 16.2; N(CH$_2$)$_4$, 16.2; OPh, ~9. Although these ligands represent a far greater difference in structural and electronic type than does that between *p*-nitrophenoxy and phenoxy groups, the range in ΔG^* is relatively small.

The theory presented above predicts that L_2 will be small when the difference in apicophilicity of the ligands a_x and a_ϕ is large. Since fluoride is known to be the most apicophilic ligand, compounds that contain two fluorides and three other less apicophilic ligands should be stable to disproportionation. In fact, preparations and ^{31}P and ^{19}F spectra are reported for the compounds $CH_3PF_2(OPh)_2$ and $P(OPh)_3F_2$, with no mention of disproportionation.[24] Although substantial disproportionation has been reported for PF_2Cl_3,[25] $Et_2NPF_2Br_2$,[26] and RPF_2X_2 (R = alkyl; X = Cl, Br),[27] the disproportionations are driven by the crystallization or ionization of one of the components. For example, PF_2Cl_3 slowly disproportionates over a period of from 3 to 4 days at room temperature to yield the ionic solid, $3[PCl_4^+]2F^-PF_6^-$. Furthermore, when the other isomers, PCl_2F_3 and PCl_4F, were prepared, they were found to disproportionate rapidly to ionic solids.

Experimental Section

Materials. Methyltriphenoxyphosphonium triflate, P(2), and methyltetraphenoxyphosphorane, P(1), were prepared and purified by the procedure of Phillips and Szele[7] as modified by Lerman;[8] ^{31}P{^{1}H} NMR spectra in acetonitrile, δ 41.1 and −53.1 ppm, respectively. Tetrabutylammonium *p*-nitrophenoxide was prepared and purified as described by Davis et al.[28] The salt was dried at 100 °C in vacuo over P_2O_5; mp 146–147 °C (lit. mp 149 °C).

Methyltetra-*p*-nitrophenoxyphosphorane, P(9), was prepared in a double Schlenk recrystallizer equipped with magnetic stirrers and protected from atmospheric moisture by an argon overflow.[29] The chemistry roughly paralleled that used for similar preparations by Ramirez et al.[30] Methyltetrachlorophosphorane[31] (1.95 g, 10.4 mmol) and dry *p*-nitrophenol (5.8 g, 42 mmol) were suspended in 20 mL of dry 1,2-dichloroethane. When the mixture was stirred, hydrogen chloride was evolved for 3 h. The bulk of the gas and of the solvent were removed under vacuum, whereupon the resulting oil crystallized. This material is a *p*-nitrophenol adduct of methyltri-*p*-nitrophenoxyphosphonium chloride. It was identified by its ^{31}P{^{1}H} NMR spectrum in acetonitrile, δ +41.5 ppm, by its ^{1}H NMR spectrum,[12] and by its hydrolysis to yield di-*p*-nitrophenyl methylphosphonate. Although the analyses that we obtained suggested that the compound was contaiminated by a few percent of a chloride impurity, an X-ray analysis of the crystals, solvated with benzene, fully established its composition and structure.[32]

The *p*-nitrophenol adduct of the salt was converted into the desired phosphorane by stirring it with 15 mL of dry tetrahydrofuran and 1.5 mL (1.38 g, 12.99 mmol) of 2,6-lutidine that had been distilled from clacium hydride. After 5 min of stirring, the lutidinium salts were separated by filtering the solution into the second arm of the crystallizer.

The resulting solution was cooled for 1 h in an ice bath, and the mother liquor removed by filtration back into the first arm of the crystallizer. The product (4.45 g, 7.4 mmol) was transferred and stored under argon in a Schlenk-type storage tube. Analytically pure methyltetra-*p*-nitrophenoxyphosphorane could be obtained from the crude product by recrystallizing it from acetonitrile: colorless prisms; mp 187–188 °C; ^{31}P{^{1}H}NMR in acetonitrile, δ −51.3 ppm. Anal. Calcd for $C_{25}H_{15}O_{12}N_4P$: C, 50.17; H, 3.20; P, 5.17; N, 9.35; Cl, 0.00. Found: C, 50.01; H, 3.12; P, 5.13; N, 9.30; Cl, 0.13.

Acetonitrile was purchased from Burdick-Jackson; it is specified as containing only 0.006% water and was found in our laboratories to be as pure and dry as any acetonitrile we could prepare. Acetonitrile-d_3 (99% D, Stohler Isotope Chemicals) was stirred at room temperature with calcium hydride for 4 h, then refluxed for 2 h, and distilled onto 4-Å molecular sieves. Tetrahydrofuran (Fisher) was dried by distilling it from sodium benzophenone ketyl onto molecular sieves (4 Å, Linde). Methylene chloride and 1,2-dichlorethane (Fisher) were dried by distillation from P_2O_5 and stored over the 4-Å molecular sieves.

Methods. General. The work here described required precautions against moisture.[29] Solids were prepared and purified in Schlenk-style glassware (Ace Glass). Solvents were transferred by the use of serum caps and cannulation with hollow needles under argon pressure. All the manipulations utilized a double manifold pressure-vacuum line.

Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Infrared spectra were obtained with a Perkin-Elmer 137 spectrophotometer. Ultraviolet-visible spectra were taken on a Cary 15 spectrophotometer. Melting points, taken in sealed capillaries, are corrected.

NMR Spectroscopy. ^{31}P NMR spectroscopy was performed with a Varian XL-100 spectrophotometer operating at 40.5 MHz in the Fourier transform mode and equipped for variable-temperature measurements. Chemical shifts are reported in parts per million relative to an external standard of 85% aqueous phosphoric acid. Locking utilized an internal deuterium signal, and unless otherwise specified, the spectra are ^{1}H noise decoupled. ^{31}P spectra were run in carefully dried 12-mm tubes. In the preparation of solutions with methyltetra-*p*-nitrophenoxyphosphorane, it was sometimes necessary to warm the tubes to 40 °C with vigorous vortexing to achieve solution. With the procedures described under general methods, solutions 0.05 M in tetraphenoxyphosphorane revealed no detectable hydrolysis. Occasionally 0.02 M triphenyl phosphate was added as an internal reference.

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Ionization of Aryloxyphosphoranes in Acetonitrile: Rates and Equilibria

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Abstract: Methyltetraphenoxyphosphorane and methyltetra-*p*-nitrophenoxyphosphorane disproportionate on mixing to yield all five of the possible phosphoranes, $CH_3P(OPh)_n(OAr)_{4-n}$, and all four of the intermediate phosphonium cations, $CH_3P^+(OPh)_n(OAr)_{3-n}$. All 16 of the rate constants and all 8 of the dissociation constants for this system have been obtained by multi-site line-shape analysis of proton-decoupled ^{31}P NMR spectra of solutions in acetonitrile. The determinations depend upon the prior measurements of the rate and equilibrium constants for the dissociation of methyltetraphenoxyphosphorane, together with reasonable assumptions and extrapolations. The equilibrium constants span a range of 10^{14}, and the rate constants a range of 10^{12}; most of the association reactions are diffusion limited.

Introduction

In the previous paper,[1] we presented the disproportionation constants that interrelate the five phosphoranes that are in equilibrium when methyltetraphenoxyphosphorane and methyltetra-*p*-nitrophenoxyphosphorane are mixed. In this paper, we report all of the 16 rate constants for the dissociation of these phosphoranes to phosphonium salts, and for the association of the phosphonium salts with phenoxide ion or *p*-nitrophenoxide to yield phosphoranes, together with the corresponding equilibrium constants for the dissociations.

The rate and equilibrium constants involved in the disproportionation system are shown in Scheme I of the previous paper. The system is complicated relative to any other of which we are aware. Some of the equilibrations involved are fast on the NMR time scale, but, while some of the NMR signals are at the fast exchange limit, some are at the slow exchange limit, and some are in the intermediate range. The equilibrations had to be treated as a multi-site exchange system, with all the mathematical complexity that that statement implies. Previous systems for disproportionation have frequently involved slower exchanges[2] or, if they were fast, have been treated as a series of two-site exchanges,[3] although the need for greater sophistication has specifically been noted.[3] Furthermore, in many instances, prior studies[2] have not dealt with intermediates (such as the phosphonium salts) that, here at least, are essential to the mechanism of exchange. Although the analysis of the present system was approached by successive approximations, starting from a treatment of the system as a series of two-site exchanges,[4-6] the rate constants were finally confirmed by a full, multi-site analysis of the equilibriation among all the five phosphoranes and all of the four corresponding phosphonium salts.

The rate[7,8] and equilibrium constants[8] for the dissociation of methyltetraphenoxyphosphorane, P(1), in acetonitrile at 25 °C had previously been determined by a combination of conductivity measurements and of a study of the temperature dependence of the appropriate NMR spectra. In particular, the rate constant[8] for the association of phenoxide ion with methyltriphenylphosphonium cation proved to be $\sim 10^{10}$ M^{-1} s^{-1}, i.e., at the diffusion limit. (The combination of oppositely charged ions is frequently diffusion controlled, even in water as solvent.[9])

Rates of Dissociation for a Partial System

The rates of dissociation of the phosphoranes can be extracted from ^{31}P NMR spectra, such as those shown as Figures

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