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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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1 and 2 of the previous paper, of the mixed phosphoranes. To simulate these spectra, the intrinsic chemical shifts for each species, ω_j (presented in Table II of the previous paper), the rate constants, k_{jl}, and the transverse relaxation time(s), T_2, are needed. T_2, calculated from the width of the narrowest peak associated with each species, proved small and constant, so that a single value of T_2 was adequate for all of the calculations. The crucial problem for us was the determination of the values of the k_{jl}'s. If we begin by confining ourselves to the interconversions of the phosphoranes and phosphonium cations that comprise 95% of the species detected in series 2 (i.e., P(1), P(2), P(3), P(4), and P(5)), the problem is reduced to the determination of 8 rate constants. Even this limited problem appeared intractable; so we sought an approximation that could later be tested.

Fast and Slow Exchanges. A further insight into the problem is gained by characterizing the NMR signals as resulting from "fast" or "slow" exchanges. As expected for "slow" exchange,[4-6] the signal for P(1) is broadened at higher temperatures; by contrast, the signals for the mixed phosphoranes P(3) and P(5) appear sharper at higher temperatures; they also appear further downfield.[10] The signals for P(3) and P(5) then behave as signals for "fast" exchange; the downfield shift indicates that the phosphoranes are more highly dissociated at higher temperatures.

Mathematical Formulation. The general solution for a multi-site exchange problem leads to a matrix equation[11,12]

$$\mathbf{A}\cdot\mathbf{G} = iM_t\gamma H_1\mathbf{P} \tag{1}$$

where

$$A_{jj} = -(\alpha_j + \sum_l k_{jl})$$
$$A_{jl} = k_{lj} \text{ for } l \text{ odd} \tag{2}$$
$$A_{jl} = k_{lj}{}^* \text{ for } l \text{ even}$$
$$j \neq l;\ k_{lj}{}^* = k_{lj}[\mathrm{PhO^-}] \text{ or } k_{lj}[\mathrm{ArO^-}]$$

Thus the pseudo-first-order rate constants for the reverse reactions, rather than the second-order rate constants, appear in the matrix. Since the concentrations of phenoxide and p-nitrophenoxide ions cannot be measured directly, the ratios of concentrations of phosphoranes to phosphonium salts, which can be measured, are used instead. Thus, for example, the off-diagonal element $k_{21}{}^*$ is given by $7.5[\mathrm{P(1)}]/[\mathrm{P(2)}]\ \mathrm{s^{-1}}$, where $7.5\ \mathrm{s^{-1}}$ is k_{12}. **P** and **G** are column matrices with elements p_j and g_j. In these equations,

$$\alpha_j = \left[\frac{1}{T_{2,j}} - i(\omega_j - \omega_r)\right]$$

M_t is the total magnetization, p_j's are the populations of the species P(j), and g_j's are the complex magnetic moments of the jth species. H_1 is the external magnetic field, γ is the gyromagnetic ratio for the phosphorus nucleus, ω_j's are the intrinsic frequencies for the P(j), and ω_r is the variable frequency of measurement. The solution of these equations for the complex magnetic moment G requires the inversion of the matrix, **A**. This formidable problem was elegantly solved by both Binsch[13] and Gordon.[14] In their procedure, **A** is written as the sum of two matrices **K** and **B**, where **B** is the diagonal matrix

$$B_{jj} = -i\omega_{,r} \text{ and } B_{jl} = 0, \text{ for } j \neq l \tag{3}$$

K is defined by difference. The only modification of this approach that we introduced arose because, for our purposes, the values of T_2 for all of the phosphoranes were the same, so that we could redefine the elements,

$$B_{jj} = -i\omega_r - 1/T_2 \tag{4}$$

The matrix manipulations to solve eq 1 can be performed once for each set of rate constants. A relatively simple further calculation of the real component of **G** for ω_r allows a simulation of the spectra for exchange. The computer program that incorporates our minor modification into the equations of Binsch and of Gordon is available as supplementary material for this paper, appearing in the microfilm edition of this volume of the journal.

Two-Site Exchanges. We begin with the reasonable assumption (later verified) that the ionization of p-nitrophenoxide ion from any given mixed phosphorane is rapid compared with that of phenoxide from that same phosphorane. This permits, as a first approximation, the separation of the multi-site exchange process into a series of two-site processes where the p-nitrophenoxide ion, but only the p-nitrophenoxide ion, undergoes ionization. The familiar equations for two-site[4-6] exchange processes allows computation of the shape of a spectrum for any given value of the time constant τ. Conversely, by comparing the observed spectra with those calculated for various τ's, the appropriate value of τ can be assigned to each spectrum.

In particular, for the fast exchange processes described here, the *position* of the NMR signal allows a determination of the relative concentrations of the species present. This information, together with the *shape* of the NMR signal allows the determination of the rate constant for exchange. Unfortunately, the procedures to obtain all of the rate and equilibrium constants cannot be generalized, and the constants must be approached more or less on an individual basis.

The Equilibrium Constants, K_{32} and K_{54}. The equilibrium constant, K_{32}, can be obtained from the position of the peak for the phosphorane, P(3), in equilibrium with the phosphonium salt, P(2). The position of the peak for fast exchange is given by the equation

$$\omega = \omega_2\frac{[\mathrm{P(2)}]}{[\mathrm{P(2)}] + [\mathrm{P(3)}]} + \omega_3\frac{[\mathrm{P(3)}]}{[\mathrm{P(2)}] + [\mathrm{P(3)}]} \tag{5}$$

If the sum of the concentrations of P(2) and P(3) is known from integration of the spectrum and from the total concentration of phosphorus compounds in the solution, then the concentrations of both P(2) and P(3) can be calculated.

In order, however, to calculate the equilibrium constant, K_{32}, the concentration of p-nitrophenoxide ion is also needed, since

$$K_{32} = \frac{[\mathrm{P(2)}][\mathrm{ArO^-}]}{[\mathrm{P(3)}]} \tag{6}$$

Fortunately, in solutions with no excess phosphonium salt or p-nitrophenoxide ion, the only cation present in measurable concentration is P(2). This conclusion can be established qualitatively from inspection of the spectra (Figures 1 and 2 of the previous paper) where only the signal from P(3) is appreciably shifted from its intrinsic frequency. Quantitatively,

$$\frac{K_{32}}{K_{54}} = \frac{[\mathrm{P(2)}][\mathrm{P(5)}]}{[\mathrm{P(3)}][\mathrm{P(4)}]} \tag{7}$$

Since P(2) and P(3) are in rapid equilibrium, the ratio of P(2)] to [P(3)] can be determined from the position of the signal from the two, in accordance with eq. 5; the ratio of [P(5)] to [P(4)] can similarly be determined, although the small displacement of the signal for the equilibrium mixture from the intrinsic chemical shift for P(5) somewhat diminishes the accuracy of the determination. Some typical data are presented in Table I; with these data, the ratio of K_{32}/K_{54} is found to be ~100. Then, in solutions where the concentration of P(2) is not large, that of P(4) is negligible; the concentrations of P(6) and

Table I. Two-Site Exchange Parameters

solution	P_2/P_3	P_4/P_5	K_{32}/K_{54}	K_{32}, M	K_{54}, M	k_{32}, s^{-1}	k_{54}, s^{-1}
2b	0.045	4.7×10^{-4}	96	1.4×10^{-4}	1.5×10^{-6}	2.4×10^4	
2c	0.070	5.5×10^{-4}	130	1.6×10^{-4}	1.2×10^{-6}	2.4×10^4	
2d	0.524	7.1×10^{-3}	74				1.0×10^3
2e	1.165	1.3×10^{-2}	90				1.0×10^3
1a	0.066	5.8×10^{-4}	114			2.4×10^4	
1	(R = 0.55)[a]	3.1×10^{-3}					1.0×10^3

[a] Solution prepared as in series 1 with $R = 0.55$.

P(8) are even smaller than that of P(4). Thus, when no excess of phosphonium ions is added, P(2) is the only cation present in appreciable concentration; electroneutrality requires that $[\mathrm{ArO}^-] = [\mathrm{P(2)}]$, so that

$$K_{32} = \frac{[\mathrm{P(2)}]^2}{[\mathrm{P(3)}]} \text{ and } K_{54} = 0.01K_{32} \tag{8}$$

The rates for the dissociations related to K_{32} and K_{54} can be determined from the shapes of the exchange signals for P(3) and P(5). For the two-site exchange

$$\tau_{32} = \frac{1}{k_{32}(1 + [\mathrm{P(3)}]/[\mathrm{P(2)}])} \tag{9}$$

and a similar equation holds for τ_{54}. Typical data are presented in Table I. With these rate and equilibrium constants in hand, one can of course calculate the association constants k_{23} and k_{45} for the addition of *p*-nitrophenoxide ion to the cations P(2) and P(4); they are 10^8 and 10^9 M^{-1} s^{-1}, respectively. These rate constants are close to the diffusion limit. Furthermore, since the ratio of K_{54}/K_{32} is 0.01 (Table I), and since K_{98} is extremely small (vide infra), we conclude that *p*-nitrophenoxy substituents destabilize phosphonium cations so that P(6) and P(8) are more reactive than P(2) and P(4). Under these circumstances, one may reasonably assume that the rate constants, k_{67} and k_{89}, for the association of *p*-nitrophenoxide ion with the cations P(6) and P(8) are equal to or greater than 10^9 M^{-1} s^{-1}. Similar arguments apply in even greater force to the association of phenoxide ions with the various phosphonium cations in acetonitrile as solvent; all of these rates must approach the diffusion limit.

Two more constants that can be estimated from the multi-two-site approximation to the partial systems are the equilibrium constant, K_{34}, and rate constant, k_{34}, for the dissociation of phenoxide ion from P(3). The assumption that we could treat the system as a series of two-site exchanges requires that the constant k_{34} be small compared with k_{32} and k_{54}; calculation (as shown below) confirms this assumption.

The value of the disproportionation constant L_1, defined in the previous paper, is given by

$$L_1 = K_{32}K_{34}/K_{12}K_{54} = 0.23 \tag{10}$$

With the values of K_{12}, K_{32}, and K_{54} in hand, one may calculate K_{34} as 1×10^{-12} M. Since we have justified assigning the diffusion limited rate constant of 10^{10} M^{-1} s^{-1} to k_{43} for the association of phenoxide ion with methyldiphenoxy-*p*-nitrophenoxyphosphonium ion, P(4), then k_{34}, for the dissociation of phenoxide ion from P(3), is 0.01 s^{-1}. The value is only a millionth of k_{32}, the rate constant for the dissociation of *p*-nitrophenoxide ion from the same phosphorane.

Multi-site Exchange for the Partial System. The data so far obtained have yielded approximations to the 8 rate constants and all of the populations in various solutions that interconnect P(1), P(2), P(3), P(4), and P(5). To test the validity of the two-site approximation, the multi-site exchange for this partial system was calculated, using the modified Binsch-Gordon equations and the computer program previously cited. A series of spectra calculated for two-site exchange and for multi-site exchange are compared with the experimentally determined spectra in Figure 1. Obviously, both the approximation and the true calculation reproduce the experimental spectra quite well, but inspection reveals that the width and relative height of the signal from P(1) are reproduced more precisely in the multi-site simulation. These simulations were repeated with rate constants differing from those chosen by 20%, and the fit was significantly worse; presumably the values chosen are in error by less than this amount. The data are summarized in Table II.

Table II. Parameters for the Multi-Site and Multi-Two-Site Simulation of Spectra of Solutions of Series II

	2b	2c	2d	2e
		Relative Populations		
P(1)	0.253	0.245	0.197	0.156
P(2)	0.022	0.035	0.211	0.373
P(3)	0.492	0.488	0.403	0.320
P(4)	0.00011	0.00013	0.00133	0.00194
P(5)	0.238	0.232	0.187	0.149
		Rate Constants, s^{-1}		
k_{12}	0.0,[a] 3.0[b]	0.0,[a] 3.0[b]	0.0,[a] 7.5[b]	0.0, [a]7.5[b]
k_{32}	2.4×10^4	2.4×10^4	2.4×10^4	2.4×10^4
k_{34}	0.0,[a] 0.028[b,c]	0.0,[a] 0.028[b,c]	0.0,[a] 0.028[b,c]	0.0,[a] 0.028[b,c]
k_{54}	1.0×10^3	1.0×10^3	1.0×10^3	1.0×10^3

[a] Rate constant for multi-two-site simulation. [b] Rate constant for multi-site simulation. [c] Maximum value.

A comment is necessary concerning the value of k_{34}. From the measured values of L_1, K_{32}, and K_{12}, and from the estimate of k_{21} as 10^{10} M^{-1} s^{-1}, we calculate the value of k_{34} of 0.01 s^{-1}. Nevertheless, in our comparison of the multi-two-site formulation with the multi-site formulation of the problem, we chose to use the maximum possible value for k_{34} of 0.028 s^{-1}. This value was calculated from the statistical value of L_1 and the value of 1.8×10^{10} M^{-1} s^{-1} for k_{21}. The latter constant can be obtained from the ratio of k_{12}/K_{12}, i.e., 7.5 s^{-1}/(4×10^{-10} M).

Equilibrium Constants: the Phenol Problem. In a previous section of this paper, the equilibrium constant K_{32} was calculated on the assumption that the concentration of *p*-nitrophenoxide ion equaled that of P(2), but in acetonitrile solution phenols react with their anions to produce hetero- and homoconjugative complexes[15,16] (hydrogen-bonded dimers). To the extent that our solutions were not quite dry, and hydrolysis had taken place, a complication must then have arisen in the determination of the concentration of ArO^-. From the best spectra, i.e., those that showed the least hydrolysis, we calculated[10] that a small amount of *p*-nitrophenolate ion would be held as the homoconjugate, but that this would require only a small correction to K_{32}; its value is closer to 1.0×10^{-4} than to 1.5×10^{-4} M. Incidentally, the small and variable amounts of *p*-nitrophenol produced by hydrolysis vitiated attempts to quantify the concentration of *p*-nitrophenolate ion spectrophotometrically.

Equilibrium Constants: the Problem of Hexacoordinated Anions. Prior investigations of the chemistry of phosphoranes have revealed the intervention of hexacoordinated anions in the hydrolysis of phosphoranes;[17] most significantly for the present discussion, methyltetraphenoxyphosphorane[8] has been shown to react with phenoxide ion to yield the anion, $CH_3P(OC_6H_5)_5^-$ with a formation constant of >1000 M^{-1}. A question must then arise as to whether such hexacoordinated phosphorus anions are present in appreciable concentrations in the solutions here under study. If a major fraction of the anions needed to maintain electroneutrality had been contributed by hexacoordinated phosphorus anions, rather than by *p*-nitrophenoxide ion, then the value of K_{32} (and of all the other equilibrium constants that were derived from K_{32}) would have been seriously in error. Fortunately, such is not the fact.

Hexacoordinated phosphorus anions are characterized by ^{31}P NMR spectra with chemical shifts around −150 ppm. Control experiments were therefore carried out under conditions designed to maximize the formation of these hexacoordinated anions, and a search for them was conducted. Even in the presence of a full molar equivalent of *p*-nitrophenoxide ion, only a little of the hexacoordinated anion is formed; the error introduced by neglecting this complication is therefore small.

Extrapolation to the Total System: Equilibrium Constants. The data presented in Tables I and II allow a reasonable extrapolation for all of the remaining rate and equilibrium constants. The extrapolation was made on the assumption that the effects of *p*-nitrophenoxy substituents would be additive. In the previous paper, we assumed an increment, u, to the stabilization energy for phosphoranes for each *p*-nitrophenoxy group. This energy translates to a multiplicative factor, η, in the dissociation constants, with one factor of η for each *p*-nitrophenoxy group in a phosphonium salt. The difference in bond energies between phenoxy and *p*-nitrophenoxy groups in a phosphorane translates into a factor ζ favoring the ionization of *p*-nitrophenoxide over phenoxide.

If we define as the κ the dissociation constant for a hypothetical phosphorane from which only one phenoxy group can dissociate, then, in the terms given above, $K_{12} = 4\kappa$, $K_{34} = 3\eta\kappa$, $K_{56} = 2\eta^2\kappa$, $K_{78} = \eta^3\kappa$, $K_{32} = \zeta\kappa$, $K_{54} = 2\eta\zeta\kappa$, $K_{76} = 3\eta^2\zeta\kappa$, and $K_{98} = 4\eta^3\zeta\kappa$. Since $K_{32}/K_{54} = 100$, $1/\eta = 200$, and the values of K_{76} and K_{98} can be obtained by extrapolation. Furthermore, since K_{12} and L_1, and L_2 and L_3 are known, the values of K_{34}, K_{56}, and K_{78} are completely determined.

Extrapolation to the Total System: Rate Constants. Since all of the rate constants for the association of phenolate or *p*-nitrophenolate ions with the phosphonium salts are known or at the diffusion limit, and since all the equilibrium constants for dissociation of the phosphoranes are known, one may then calculate the rate constants for the dissociation of the phosphoranes. These data are gathered in Table III.

Finally, using our modification of the Binsch-Gordon equations and the computer program already cited, we simulated the spectra for the entire system. An example is presented in Figure 2. No attempt has been made to see whether simultaneous changes in several constants might be compensatory, and lead to as good agreement with experiment as that here shown. In these and the previous computer simulations of the spectra (Figure 1), double precision was needed; the range of rate constants introduced into the program was so enormous that, without double precision, the calculated results were meaningless. The excellent agreement between the experimental and the simulated spectra of Figure 2 is somewhat deceptive. As a result of the fast exchange between P(8) and P(9), and between P(6) and P(7), the signals are at their narrowest extreme, so that the agreement only confirms the relative magnitudes of the extrapolated constants, K_{76} and K_{98}. An additional check on the validity of the assignments was therefore needed. Such a check was provided by an independent measurement of the dissociation of methyltetra-*p*-nitrophenoxyphosphorane, P(9).

Table III. Rate and Equilibrium Constants for the Dissociation of Mixed Aryloxyphosphoranes to Phosphonium Cations and Aryl Oxide Anions in Acetonitrile at ~25 °C.

Dissociations Involving *p*-Nitrophenoxide Anion		
$K_{32} = 1 \times 10^{-4}$ M[a]	$k_{32} = 2.4 \times 10^4$ s^{-1} [a]	$k_{23} = 2.4 \times 10^8$ M^{-1} s^{-1} [a]
$K_{54} = 1 \times 10^{-6}$ M[a]	$k_{54} = 1.0 \times 10^3$ s^{-1} [a]	$k_{45} = 1.0 \times 10^9$ M^{-1} s^{-1} [a]
$K_{76} = 7.5 \times 10^{-9}$ M	$k_{76} = 7.5$ s^{-1}	$k_{67} = 1.0 \times 10^9$ M^{-1} s^{-1}
$K_{98} = 5.0 \times 10^{-11}$ M	$k_{98} = 0.05$ s^{-1}	$k_{89} = 1.0 \times 10^9$ M^{-1} s^{-1}
Dissociations Involving Phenoxide Anion		
$K_{12} = 4 \times 10^{-10}$ M[a]	$k_{12} = 7.5$ s^{-1} [a]	$k_{21} = 10^{10}$ M^{-1} s^{-1} [a]
$K_{34} = 1.0 \times 10^{-12}$ M[a]	$k_{34} = 0.01$ s^{-1} [a]	$k_{43} = 10^{10}$ M^{-1} s^{-1} [a]
$K_{56} = 1.5 \times 10^{-15}$ M	$k_{56} = 1.5 \times 10^{-5}$ s^{-1}	$k_{65} = 10^{10}$ M^{-1} s^{-1}
$K_{78} = 2.6 \times 10^{-18}$ M	$k_{78} = 2.6 \times 10^{-8}$ s^{-1}	$k_{87} = 10^{10}$ M^{-1} s^{-1}

[a] Measured constants; constants are extrapolated (see text) unless otherwise noted.

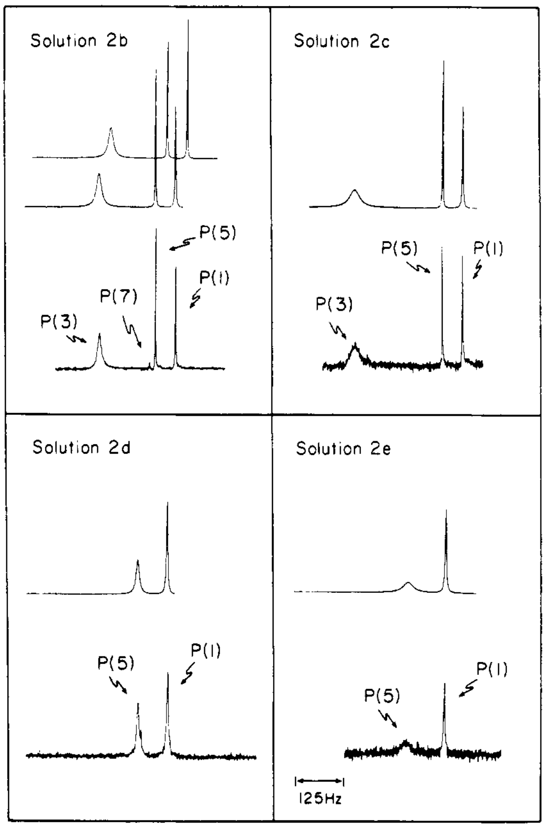

Figure 1. Simulated and experimental $^{31}P(^1H)$ NMR spectra for solutions described in the legend of Figure 2 of the previous paper,[1] in acetonitrile at ~29 °C, T_2 = 0.2 s. The experimental spectrum, for each solution, is the lower or lowest one, and the spectrum for the multi-site simulation is directly above it. The third spectrum shown for solution 2b is that obtained for multi-two-site simulation; it has been displaced to higher fields for clarity of presentation. The positions of the peaks are the same for the multi-two-site as for the multi-site simulation, but the intensities are somewhat different; similar, although generally smaller differences are noted for the other spectra.

Confirmation of the Extrapolated Dissociation Constant for P(9). One of the major findings of this investigation is that a *p*-nitrophenoxy substituent retards the dissociation of oxyanions from phosphoranes by a factor of ~200. In our ex-

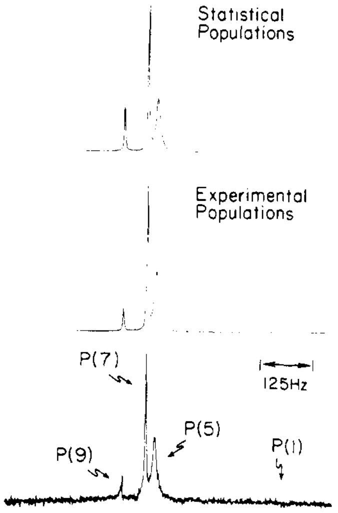

Figure 2. Simulated and experimental $^{31}P(^{1}H)$ NMR spectra of a solution of mixed aryloxyphosphoranes in acetonitrile at $\approx$29 °C. For this solution, $R = 0.55$ and the total molarity of the phosphorane plus phosphonium salt was 0.95 M; T_2 was set equal to 0.5 s. The spectra are arranged as follows: upper, simulated using statistically expected populations; middle, simulated using experimentally determined populations; lower, experimental spectrum.

trapolation for the dissociation constants from P(3) to P(9), we found that the dissociation constant for P(3) is 10^6 greater than that for P(6). Since pure P(9) is available and since *p*-nitrophenoxide ion has a strong visible absorption, measurement of an upper limit for the dissociation of P(9) can be carried out spectrophotometrically.

The resulting value of K_{98} is 6 times that presented in Table III. The number obtained by spectrophotometry represents, however, an upper limit, since at least part of the measured optical density must represent the absorption of methyltetra-*p*-nitrophenoxyphosphorane itself, and at least part must represent absorption from the traces of nitrophenol produced by the hydrolysis of P(9) with adventitious water. Although spectrophotometry does not quantitatively confirm the value of K_{98}, it does confirm the qualitative conclusion that the dissociation of P(9) is minute compared to that of P(3).

Limits of Error. The system here presented is a complicated one—perhaps the most complicated that has been worked out in detail by NMR spectroscopy—and the 10^{14} range of equilibrium constants and 10^{12} range in rate constants is enormous. Despite the apparent precision obtained in matching the spectra to those simulated with the constants in Table III, some uncertainties are apparent. In particular, although we had previously found that the rate constant, k_{12}, for the dissociation of methyltetraphenoxyphosphorane was 7.5 s^{-1} at probe temperature (presumed to be 25 °C), we now fit our new data to a dissociation rate constant of 3 s^{-1} at 29 °C. The uncertainty in k_{34} was discussed in an earlier section of this paper.

The errors that could arise from the homo- and heteroconjugative dimers of the phenols and from hexacoordinated phosphorus anions have previously been discussed and dismissed. One additional possibility for error would arise if the exchanges here examined occurred at least in part by bimolecular processes.[18] Since the data were obtained over a range of concentrations, and seem internally consistent, it seems unlikely that bimolecular processes are important; this matter, however, remains for further investigation.

Conclusion

The qualitative conclusion from our multisite analysis are these. As expected, *p*-nitrophenoxide dissociates much more rapidly than does phenoxide ion in reactions that yield the same phosphonium salt. The statistically corrected ratios range from 10^4 for k_{32}/k_{12} to 5×10^5 for k_{98}/k_{78}. In acetonitrile, the difference in pK's between phenol and *p*-nitrophenol[16] is 6 log units; the rate data correlate with Brønsted β's from 0.67 to nearly 1.0. The equilibrium constants for the dissociation of *p*-nitrophenoxide ion from the phosphoranes differ by a factor, statistically corrected, of 200 for each *p*-nitrophenoxy substituent corresponding to a β of 0.38 and an energy, μ, of $\sim$3 kcal/mol.

The extrapolation of these data to water as solvent, rather than acetonitrile, can at least in part be related by prior research from this laboratory;[19,20] the consequences of these data for the hydrolysis of phosphates will be considered in later publications.

Experimental Section

Methods, compounds, and solvents were the same as those reported in the previous paper.[1]

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Supplementary Material Available: Computer program to simulate ^{31}P NMR spectra for multi-site exchange between phosphonium salts and phosphoranes (3 pages). Ordering information is given on any current masthead page.

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