Phosphorus-31 Spin–Lattice Relaxation. I. Aqueous Orthophosphoric Acid and Some Related Systems

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Abstract: The ^{31}P spin-lattice relaxation time, T_1, of orthophosphoric acid was found to vary at 31°C from 0.14 sec for the molten 100% acid up to 12.5 sec for 0.1 wt % H_3PO_4 in water. The T_1 of the ^1H nucleus in these solutions was also found to increase with decreasing phosphoric acid concentration, so that the ratio $(T_1)_P/(T_1)_H$ remains essentially constant at ca. 2.2. From experiments involving substitution of hydrogen by deuterium, it was concluded that the dipole–dipole relaxation mechanism contributed more than three-quarters to the rate of ^{31}P spin-lattice relaxation of aqueous phosphoric acid, with the remainder probably being due to the spin-rotation mechanism. The concentration dependence of the T_1 measured for the ^{31}P nucleus in pyrophosphoric acid was found to parallel at a higher value the curve measured for orthophosphoric acid and this is mainly attributed to a change in the dipole–dipole relaxation due to substitution of one of the hydrogens surrounding the orthophosphate PO_4 group by a phosphorus to form the pyrophosphate PO_4 group. For dilute solutions of anhydrous phosphoric acid in several different organic solvents, the observed T_1 was not much different than that found for the molten pure anhydrous H_3PO_4, even though the overall relaxation mechanism appears to be primarily dipole–dipole interaction between the protons and the phosphorus of the H_3PO_4 assemblage. Titration of a 0.2 M aqueous solution of phosphoric acid with concentrated tetramethylammonium hydroxide led to an oscillatory variation of the T_1 observed for the ^{31}P nucleus. The maxima in this oscillatory curve appeared at the pH corresponding to the individual species PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, and, in the presence of concentrated perchloric acid, $P(OH)_4^+$. This oscillatory behavior results from the rapid interconversion of one of these ions into another in the binary mixtures which occur during titration.

Since the number and variety of chemical compounds based on phosphorus is very large, it should be expected that the ^{31}P spin-lattice relaxation study of liquid samples ought to have the same general value to phosphorus chemists such as ^{13}C spin-lattice relaxation has afforded[1,2] organic chemists. However, the ^{31}P measurements should be more readily obtained and ought to be applicable to a much wider range of concentrations as compared to ^{13}C data, because of the 100% natural abundance of the ^{31}P nucleus. There are some reports[3-11] of ^{31}P spin-lattice relaxation measurements on liquid samples, but much of this work deals with un-ionizable, small, nearly spherical molecules, generally as neat liquids. The relaxation mechanisms which have been observed to dominate consist of the interaction of the ^{31}P nuclear spin with the molecular rotation (spin-rotation); the dipole–dipole interaction between pairs of ^{31}P nuclei or between ^{31}P and ^1H nuclei; and, perhaps, the relaxation due to the tumbling of structures exhibiting large chemical-shift anisotropy, although the occurrence[6] of the latter mechanism has been ably disputed[12] for the phosphorus compounds in question. In the case of the phosphorus oxyacids, scalar relaxation[13] due to exchange of protons between the oxyacid and the solvent water molecules must also be considered.

In the study reported herein, we have examined the spin-lattice relaxation of orthophosphoric acid and of the products obtained by titrating a dilute solution of it with concentrated tetramethylammonium hydroxide or dissolving it in various concentrations of perchloric acid. These titrants were chosen since the tetramethylammonium ion as well as the perchlorate ion are known to be extremely poor complexing agents. In addition, orthophosphoric acid is compared with pyrophosphoric acid with respect to spin-lattice relaxation. Orthophosphoric acid was chosen for this study because of its key position in both pure and applied phosphorus chemistry. This acid is the parent compound of the extensive series of condensed phosphoric acids, the derivatives of some of which (ATP, ADP, and AMP, and the nucleic acids) dominate much of biochemistry.

Experimental Details

NMR Spectrometer System. A Varian XL-100-15 multinuclear spectrometer was employed with an internal heteronuclear lock (usually on ^1H but sometimes on ^2H) to provide field stabilization. This system has been enlarged to include a Transform Technology, Inc. (TT-100) Fourier-transform unit, the data system of which consists of a Nicolet 1080 computer having 20K of 20-bit word storage, which permits transforms as large as 16K of words to be accumulated and quickly processed. A 100 KHz, 12-bit digitizer provides flexibility in the accumulation of data over a wide variety of sample conditions. Programs or data may be transferred between the computer core and a magnetic disk using replaceable cartridges each of which allows storage of 600K words.

The TTI rf pulse unit supplies peak power output in excess of 1 kW, although in our setup it is usually attenuated to 500 W for use with a modified Varian 4415 probe. This combination provides a 90° pulse for ^{31}P nuclei in 65 μsec. The pulse module also includes the capability for manual adjustment of the signal phase in the transformed spectra. Thus, rapid phase correction is achieved by adjustment of "primary" and "range" phase knobs.

NMR Measurements. Measurements of spin-lattice relaxation times, T_1, were accomplished by use of the inversion-recovery pulse method,[14] employing rf pulses at 180 and 90° separated by a delay time, τ. The more accurate calculation of the spin-lattice relaxation was obtained from a plot of ln $(I_\infty - I_\tau)$ vs. τ where I stands for the intensity of the line. This procedure yields a straight line having a slope of $-1/T_1$. The less accurate "inversion-point" value, $T_1 = \tau_{\text{null}}/\ln 2$, was always found to be reasonably close to the one obtained from the intensity plots. Most of the NMR determinations were carried out at a measured temperature of 31 ± 2°. Temperature control resulted from the room air conditioning as moderated by a plastic box surrounding the magnet, which kept the temperature during any one T_1 determination to within 0.2°.

For the CP "85%" phosphoric acid used in these studies, steps taken to remove whatever paramagnetic impurities were present had little effect on the measured spin-lattice relaxation times. Thus, in a series of measurements carried out on the same day, it was found that degassing the dissolved oxygen from the concentrated (nominally 85%) phosphoric acid by bubbling nitrogen through it for either 5 or 45 min resulted in either case in an increase of T_1 from 0.50 to 0.52 sec, while several freeze-pump-thaw cycles also caused the T_1 to increase to 0.52 sec. For the dilute acids it was also found that the freeze-pump-thaw cycling gave no better results than did nitrogen bubbling. The dissolution of a small amount of solid ethylenediaminetetraacetic acid (EDTA) in the concentrated acid on another day raised the T_1 of a degassed sample from 0.51 to 0.52 sec. All of these changes lay within one standard deviation for replicate measurements determined over a period of more than 2 months. However, in this entire study, all samples were routinely degassed by nitrogen bubbling for 5-10 min.

The ^{31}P chemical shifts, δ, were measured with respect to the $(CD_3)_2CO$ lock standard and are reported with respect to 85% phosphoric acid, with downfield shifts being negative. The ^{31}P line widths were manually measured at half-height from appropriate spectral tracings and were reproducible to 0.02 Hz. The line width obtained[15] for the $P(OH)_4^+$ ion was 0.11 Hz, a value that corresponds to the narrow-line limit of the spectrometer.

The reproducibility of the ^{31}P spin-lattice relaxation time measurements was tested over a period of a year on a 13.9 *M* phosphoric acid solution (nominally 85% H_3PO_4) and a 500-fold dilution of it. By the graphical procedure, the average of 15 measurements of T_1 for the 13.9 *M* acid was 0.506 sec with a standard deviation of 0.014 sec (3%), while, by the inversion-point method, the values were 0.52 and 0.03 sec (6%), respectively. Likewise for the diluted acid, the result from plotting was 12.5 sec with a standard deviation of 0.7 sec (6%), while, from the inversion point, 12.1 sec was found with a standard deviation of 1.0 (8%).

Sample Preparation. The studies on orthophosphoric acid corresponding to concentrations of 13.9 *M* or less were carried out using Baker and Adamson CP phosphoric acid which was designated as 85% H_3PO_4 but by analysis turned out to be 82.4%. The deuterated phosphoric acid, D_3PO_4, was prepared by heating together Mallinckrodt 99.8% deuterium oxide with the proper proportion of Fisher phosphorus pentoxide to give 85% D_3PO_4. pH titration showed this acid to be indeed 14.2 *M*. The crystalline orthophosphoric acid, 100% H_3PO_4, was obtained from Matheson Coleman and Bell and the crystalline pyrophosphoric acid, $H_4P_2O_7$, from Dr. C. Y. Shen of the Monsanto Co. The tetramethylammonium hydroxide, $N(CH_3)_4OH$, was obtained from the Aldrich Chemical Co. and was prepared in ca. 5 *N* concentration with deionized water, after vacuum condensation and removal of the methanol. The perchloric acid was 11.55 *N*. All of the standard deuterium-containing compounds were Mallinckrodt products, specified for NMR use (>99.5% deuterated).

pH titration of 0.1 *M* H_3PO_4 by the 5 *N* $N(CH_3)_4OH$ was carried out to obtain pH values in the range of 1.25 to 12. Higher pH values were achieved by adding nearly anhydrous $N(CH_3)_4OH$ to the acid and calculating the pH on the basis that pH = pOH − 14 and that pOH = −log [OH^-]. For solutions more acidic than 0.1 *M* aqueous phosphoric acid, crystalline H_3PO_4 was added to various dilutions of concentrated (11.55 *N*) $HClO_4$ to obtain a 0.1 *M* H_3PO_4 concentration, with the solution pH being set equal to −log $[H^+]_{total}$.

Results and Discussion

Preliminary Estimation of T_1. By using the standard equations for intra- and intermolecular dipole-dipole relaxation of phosphoric acid, it should be possible to obtain an estimation of the ^{31}P spin-lattice relaxation time to be expected, since it would seem that in both the neat liquid and in aqueous solutions the abundance of hydrogen atoms ought to cause ^1H-^{31}P dipole-dipole interaction to be the dominant relaxation process. Furthermore, some of the approximations (primarily the use of the macroscopic viscosity in eq 4 and 5) employed for estimating dipole-dipole interaction often tend to overemphasize the relaxation and hence inadvertently might be expected to give better results than the approximations warrant.

Every contribution to the overall spin-lattice relaxation time, $(T_1)_{total}$, may be summed by the following equation in which $(1/T_1)_i$ refers to the contribution by each mechanism and/or each atom involved in a particular internuclear mechanism.

$$(1/T_1)_{total} = \sum_i (1/T_1)_i \qquad (1)$$

The dipole-dipole relaxation of nucleus A of spin ½ by nucleus B of spin *I* is given by the following expression[13,16] in which $\alpha = (4/3)I(I + 1)$, except that $\alpha = 1.5$ for B identical with A; *b* is the distance between these nuclei; τ_c is a correlation time for the relaxing motion in the liquid; and γ_A and γ_B are the respective magnetogyric ratios.

$$1/T_1 = (\alpha \hbar^2 \gamma_A{}^2 \gamma_B{}^2 / b^6)\tau_c \qquad (2)$$

By integrating this expression, allowing τ_c to be the time (i.e., $r^2/12D$) a molecule takes to diffuse across the relative distance *r*, the following equation[14] is obtained for the contribution of each A or B nucleus to the intermolecular dipole-dipole relaxation of an A nucleus due to the translatory motion of the molecules making up the fluid.

$$(1/T_1)_\Sigma = N_0 \int_d^\infty (\alpha \hbar^2 \gamma_A{}^2 \gamma_B{}^2 / r^6)(r^2/12D)(4\pi r^2)\mathrm{d}r = (\pi \alpha N_0/6)(\hbar^2 \gamma_A{}^2 \gamma_B{}^2 / d)/D \qquad (3)$$

In eq 3, *D* is the diffusion coefficient and N_0 is the number per unit volume of pertinent molecules which interact to give the chosen contribution to the spin relaxation of the A nucleus. The values of τ_c for rotational motion of a molecule and of *D* for translation may be estimated from the respective modified Debye and Stokes-Einstein relationships[14] which assume a sphere of radius *a* moving in a medium having an effective viscosity of η.

$$\approx 4\pi\eta a^3/3kT \qquad (4)$$

$$D \approx kT/6\pi\eta a \qquad (5)$$

We estimate from the density of the pure materials that $a = 2.22$ Å and $N_0 = 1.15 \times 10^{22}$ for the H_3PO_4 molecule and that $a = 1.55$ Å and $N_0 = 3.34 \times 10^{22}$ for the H_2O molecule. Furthermore, X-ray diffraction studies on orthophosphoric acid[17,18] indicate that one of the three hydrogens is bound quite closely to the phosphorus (b_{PH} = ca. 1.57 Å) in the crystal and that the remaining two are farther out (b_{PH} = 2.07 Å, for ∠POH = 105° and O-H = 1.00 Å). We also estimate that the distance of closest approach, *d*, of the phosphorus to the hydrogen of another phosphoric acid[13] or a neighboring water molecule is about 2.46 Å for ∠POH = 105° with $(P\text{-}O)_{av}$ = 1.56 Å and O···H = 1.53 Å, while the distance of closest approach between two phosphorus atoms is $2a_{H_3PO_4} = 4.43$ Å.

By placing the appropriate values in eq 2 and 4 we estimate that at 31°C the $1/T_1$ intramolecular contribution to the dipole-dipole relaxation of the ^{31}P nucleus of H_3PO_4 due to the proton which is assumed to lie close to the phosphorus, as in the crystal, is 6.80 η while, for each of the more distant protons, it is 1.30 η. Likewise, the contribution calculated from eq 3 and 5 for the effect of other phosphoric acid molecules in the neat liquid is 0.68 η for each H_3PO_4 hydrogen and 0.03 η for the phosphorus. The contribution per hydrogen for the water of an infinitely dilute phosphoric acid solution is 1.32 η. Obviously, these numbers may be appropriately summed to give the value of T_1 in either pure anhydrous liquid phosphoric acid or its dilute solution, with appropriate attention being paid to the degree of ionization in the latter case. The relaxation time of intermediate concentrations may be estimated by appropriate use of the mole fractions of H_2O and H_3PO_4, again accounting for the dissociation of the latter. By this means, we have estimated that T_1 at 31° for 100% phosphoric acid (η = 1.51 P) should be around 0.06 sec, since $1/T_1 \approx 1.51\,[6.80 + 2 \times 1.30 + 3 \times 0.68 + 0.03]$. Likewise, for ca. 0.01 *M* H_3PO_4 (η = 0.008 P) in which one of the hydrogens is about 50% dissociated, we estimate a value of T_1 of 11 sec from $1/T_1 \approx 0.008\,[6.80 + 1.5 \times 1.30 + 2 \times 1.32]$, on the assumption

Table I. ^{31}P and ^{1}H Spin–Lattice Relaxation Times of Aqueous Orthophosphoric Acid at 31°C

H_3PO_4 concn				Measured T_1, sec			
M	wt %	mol fraction	Viscosity, P	^{31}P	^{1}H	$(T_1)_P/(T_1)_H$	$1/\pi(w - 0.1)^a$ for ^{31}P, sec
19.12	100.0	1.00	1.51	0.14			
13.90	82.5	0.45	0.26	0.51	0.21	2.4	0.042
6.95	50.5	0.15	0.045	1.45	0.67	2.2	0.103
3.48	29.2	0.07	0.020	2.7	1.24	2.2	0.19
1.74	15.7	0.03	0.012	4.4	2.1	2.1	0.4
0.869	8.7	0.015	0.0097	6.2			0.5
0.278	2.7	5×10^{-3}	0.0085	8.7	3.9	2.2	0.5
0.139	1.3	2×10^{-3}	0.0082	10.4			0.7
0.0278	0.3	5×10^{-4}	0.0081	12.5			1.6
0.0139	0.1	2×10^{-4}	0.0080	11.0	(4.0)	2.8	0.5
0	0	0	0.0078		4.0		

[a] A reciprocal line-width function equal to T_2 if there is no site exchange or other broadening. *w* is the measured CW line width (in Hz) at half-height, under conditions where there is no evidence for saturation, and 0.1 Hz is substrated from this value to account for the inhomogeneties in the magnetic field.

Table II. ^{31}P Spin–Lattice Relaxation in Various Solutions of Orthophosphoric Acid at 31°

Molar Concn	Solute	Solvent	T_1, sec
14.1	D_3PO_4	D_2O	3.2
	H_3PO_4	H_2O	0.47
0.20	D_3PO_4	D_2O	34.
	H_3PO_4	H_2O	9.6
0.20	D_3PO_4	$(D_3C)_2CO$	7.0
	H_3PO_4	$(D_3C)_2CO$	0.44
	D_3PO_4	$(H_3C)_2CO$	8.2
	H_3PO_4	$(H_3C)_2CO$	0.51
0.36	H_3PO_4	$[(CH_3)_2N]CO$	0.38
0.19	H_3PO_4	$[(CH_3)_2N]CO$	0.77
0.23	H_3PO_4	CH_3OH	1.19
0.12	H_3PO_4	CH_3OH	1.28
0.47	H_3PO_4	$(HOCH_2)_2CH(OH)$	0.34

that one of the two H_3PO_4 hydrogens lying 2.07 Å from the phosphorus is dissociated, or $T_1 \approx 14$ sec from $1/T_1 \approx 0.008\ [0.50 \times 6.80 + 2 \times 1.30 + 2 \times 1.32]$ assuming that the dissociation involves the closely lying H_3PO_4 hydrogen ($b_{PH} = 1.57$ Å).

Values of T_1 for intermediate compositions have also similarly been estimated and agree reasonably well with the experimental numbers reported in Table I. However, these crude estimations do not afford an adequate basis for determining whether or not the ionic dissociation in dilute solution involves the assumed closely lying hydrogen of the H_3PO_4 molecule or one of the two more distant ionizable hydrogens. It should be noted that they also tell nothing about the rates of exchange of the phosphoric acid protons with each other and with those of the water.

Aqueous Orthophosphoric Acid. As can be seen in Table I, the ^{31}P spin-lattice relaxation time of orthophosphoric acid increases gradually with dilution, reaching what appears to be a maximum value at a concentration of ca. 0.03 *M*. The existence of this maximum depends on the value obtained for the lowest dilution studied, 0.014 *M*, a value which resulted from a total of 36 hr of time averaging. The proton spin-relaxation of the single peak corresponding to the rapidly exchanging protons of the phosphoric acid plus the water was also measured on some of the samples and this ^{1}H relaxation was found to vary practically in proportion to the ^{31}P relaxation of the PO_4 group. Note that, while the macroviscosities reported in Table I decreased by about 150-fold when going from 19 *M* H_3PO_4 to ca. 1 *M* H_3PO_4, both the ^{31}P and ^{1}H spin-lattice relaxation times increased about 40-fold.

In order to investigate experimentally the role of dipole-dipole relaxation in aqueous phosphoric acid, solutions were prepared in which all hydrogens were substituted by deuterium atoms. From eq 2 and 3 it is clear that the ratio of the protonated to the deuterated ^{31}P spin-lattice relaxation times attributable solely to the dipole-dipole relaxation mechanism must be equal to $(3/4)\gamma_H^2/2\gamma_D^2$. Thus, on the basis of eq 1, we can separate the dipole-dipole contributions from the sum of the other contributions $(T_1)_x$, on the assumption that the scalar relaxation in the deuterated systems may be ignored. This is done through the following relationship: $[(1/T_1)_H - (1/T_1)_x]/[(1/T_1)_D - (1/T_1)_x] = (3/4)\gamma_H^2/2\gamma_D^2 = 15.91$, where $(1/T_1)_H$ and $(1/T_1)_D$ refer to the observed ^{31}P relaxation in the normal system and in the fully deuterated system, respectively. Thus, we find from the data of Table II that in 14.1 *M* aqueous phosphoric acid ca. 91% of the relaxation rate, $(1/T_1)_{obsd}$, is attributable to the dipole-dipole mechanism and in 0.2 *M* aqueous phosphoric acid this contribution represents ca. 77%. If we neglect relaxation due to chemical-shift anisotropy (as surely seems reasonable and is in accord with Gillen's argument[12]) and hence conclude that $(T_1)_x$ is solely a spin-rotation contribution,[19,12] we estimate that for spin-rotation relaxation alone, T_1 is about 5.3 sec for 14.1 *M* and 42 sec for 0.2 *M* H_3PO_4 in water. Since the spin-rotation relaxation time appears to behave[18] abnormally by increasing with the decrease in macro viscosity involved in H_3PO_4 dilution, we tentatively conclude that the rotational freedom of the PO_4 group is inhibited as the H_2O/H_3PO_4 mole ratio is increased by dilution, while the translational freedom (which accounts for the viscosity) is accentuated.

The function $1/\pi(w - 0.1)$, in which *w* is the unsaturated ^{31}P line width measured at half-height, is presented in the final column of Table I. For this system, if there were not site-exchange broadening [so that $1/\pi(w - 0.1)$ would then equal T_2], numerical equivalence of T_1 and T_2 would demand much more narrow ^{31}P line widths than were observed. Indeed, the function $1/\pi(w - 0.1)$ is consistently about 14 times smaller than the respective value of T_1. Using eq 4 for estimating the correlation time τ_c from the macroscopic viscosity, we find that, even for the highly viscous 100 wt % H_3PO_4 acid, $\omega_0\tau_c = 0.4$ and that $\omega_0\tau_c$ has dropped to 0.07 for the 82.5% acid. Since $\omega_0\tau_c$ seems to be smaller than unity,[20] T_2 ought nearly to equal T_1, at least for the acids of lower viscosity.[21] Thus, it appears that somewhat over 90% of the observed ^{31}P line broadening in orthophosphoric acid is due to fluctuations in the magnetic shielding of each phosphorus atom, fluctuations associated with the exchange of the acid protons on its PO_4 group. Assuming that these alternative protonic arrangements exhibit chemical shifts differing by 1 ppm (a not unreasonable value[22]), the average lifetime, τ_{ex}, for the exchange process

Table III. ^{31}P Spin–Lattice Relaxation Time of Aqueous $H_4P_2O_7$ at 31°C

Concn[a]	T_1, sec	1.21 × $(T_1)_{H_3PO_4}$,[b] sec
1.70	5.6	5.3
0.84	7.6	7.5
0.34	10.5	9.9
0.170	12.6	12.0
0.084	13.0	13.4
0.017	13.5	15.4

[a] Concentration in moles of phosphorus per liter. [b] Calculated from the T_1 of orthophosphoric acid at the same phosphorus concentration, as interpolated from Table II.

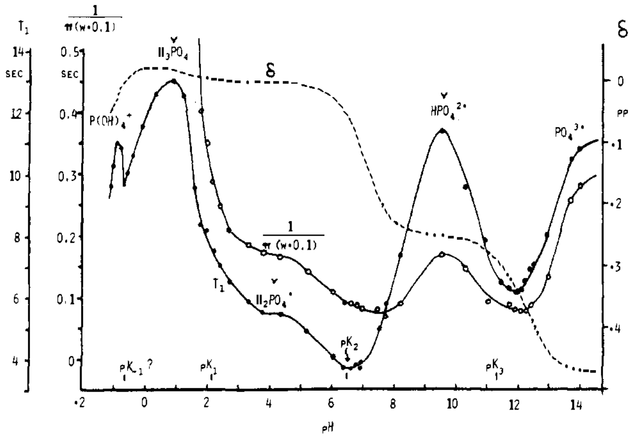

Figure 1. pH titration plot of 0.2 *M* orthophosphoric acid showing the variation of some NMR parameters. The line with solid points denotes the variation of the observed spin-lattice relaxation time, T_1; whereas the line with open circles gives the value of the function $1/\pi(w - 0.1)$ with this quantity and the value of T_1 being measured in seconds. The dotted curve shows the variation of the chemical shift, δ. Note that the solution viscosity throughout most of this pH range is essentially that of water but that at either end ($0 \geq pH \leq 13$) the viscosity rises considerably because of the high concentration of either acid or base.

would be in the neighborhood of 10^{-3} to 10^{-5} sec, according to the expression:[23]

$$\tau_{ex} = [w - (1/\pi T_1) - 0.1]/B(\Delta\nu)^2 \qquad (6)$$

where *B* is a constant which in this case will have a value around 4.5 and $\Delta\nu$ is the chemical-shift difference. It should be noted that the $P(OH)_4^+$ cation resulting from the dissolution of orthophosphoric acid in concentrated perchloric acid[15] exhibits an extremely sharp resonance line ($w = 0.11$ Hz, as measured on our spectrometer), a situation which is in accord with a single (probably highly symmetric) arrangement of the four hydrogen atoms per PO_4 group or an extremely small change in chemical shift between different arrangements.

The standard formula[13] (eq 7) for the scalar relaxation of a nucleus of spin ½ due to exchange of a coupled spin-active nucleus may be used with reasonable values (in the neighborhood of 20 Hz) of the coupling constant, *J*, with $\Delta\omega$, the difference in resonance frequencies of the ^1H and ^{31}P nuclei being equal to 5.95×10^7 Hz. In any creditable case, it is found that $(1/T_1)_{sc}$ is much too small to contribute to any of the spin-lattice relaxation times reported in this paper.

$$(1/T_1)_{sc} = (J^2\tau_{ex}/2)/[1 + (\tau_{ex}\Delta\omega)^2] \qquad (7)$$

The temperature variation of T_1 was measured for aqueous orthophosphoric acid but was not found to be interpretable in the usual simple manner,[13,23] presumably because of the complex nature of the system. Values of T_1 = 0.53 sec at 7°C, 0.50 at 34°, 0.33 at 56°, and 0.43 at 77° were obtained for the ^{31}P resonance in 13.9 *M* H_3PO_4.

Table IV. Comparison to Experiment of Adding Relaxation Rate Contributions, Using Only the Ionic Mole Fraction as the Weighting Factor

Point on pH curve	$(1/T_1)_{obsd}$, sec^{-1}	$(1/T_1)_{estm}$,[a] sec^{-1}
$P(OH)^+$	0.091	
pK_{-1} (?)	0.110	0.084
H_3PO_4	0.077	(0.168)[b]
pK_1	0.131	0.131
H_2PO_4	0.184	(0.261)
pK_2	0.274	0.136
HPO_4^{2-}	0.088	(0.272)
pK_3	0.162	0.090
PO_4^{3-}	0.092	(0.180)

[a] $(1/T_1)_{estm} = \chi_A(1/T_1)_A + \chi_B(1/T_1)_B$, where the subscripts A and B correspond to the contributing ions and χ_A and χ_B are the respective mole fractions of the total phosphorus. When pH = p*K*, $\chi_A = \chi_B = 0.5$. [b] The parenthetical values correspond to a weighting value of unity.

H_3PO_4 in Other Solvents. In addition to the data on aqueous phosphoric acid, Table II also contains T_1 values observed for dilute solutions (ca. 0.2 *M*) of phosphoric acid in various solvents, as well as the effect of differential substitution of deuterium for hydrogen in acetone solution. Since T_1 = 8.2 sec for 0.2 *M* D_3PO_4 in acetone and T_1 = 7.0 sec for 0.2 *M* D_3PO_4 in acetone-d_6, it is clear that the substitution of deuterium for hydrogen atoms in the methyl groups of the acetone molecule has not decreased the relaxation rate. This finding suggests that the nearest-neighbor acetone molecules are preferentially oriented so that the carbonyl groups point toward an un-ionized D_3PO_4, with the methyl groups being directed away. The observed change in T_1 upon substituting deuterium for hydrogen in the H_3PO_4 molecule indicates that in either acetone or acetone-d_6, all of the ^{31}P relaxation rates, $(1/T_1)_{obsd}$, are attributable to the intramolecular dipole–dipole mechanism, with the methyl groups making no appreciable contribution to it.

The spin-rotation correlation time, τ_{sr}, is defined by the equation

$$(1/T_1)_{sr} = (2IkT/3\hbar^2)C_{eff}^2\tau_{sr} \qquad (8)$$

where *I* is the moment of inertia and C_{eff} is the effective spin-rotation coupling constant. Since $(1/T_1)_{sr}$ for the ^{31}P nucleus in 0.2 *M* orthophosphoric acid is calculated to be 0.024 sec^{-1} in water and nil (i.e., a small negative value of -10^{-3} sec^{-1}, due to experimental error) in acetone, it would appear for unchanging *I* and C_{eff} that the spin-rotation correlation time for the orthophosphate PO_4 group and its associated hydrogens is larger in acetone than in water. Thus, on the not unreasonable assumption that the moment of inertia and spin-rotation coupling constant of the phosphoric acid molecule would not be noticeably affected by going from an environment of water molecules to acetone molecules, it seems that the PO_4 tetrahedron of phosphoric acid rotates more persistently in water than in acetone.

In Table II, it is seen that the T_1 value for the ^{31}P nucleus in dilute orthophosphoric acid in methanol is about three times larger than that corresponding to a glycerine solution at the same phosphorus concentration. From eq 4 and 5, we might expect this ratio to be much larger, i.e., approximately 1.2×10^3, which is the ratio of the macroviscosity of glycerine (6.29 P) to that of methanol (0.0051 P). Thus, it seems that the microviscosity of glycerine, with respect to motion of the orthophosphoric acid PO_4 group, is only three times larger than that of methanol. This finding is not surprising since standard chemical lore indicates that the alcoholic hydroxyl group of methanol ought to associate with a phosphoric acid molecule about the same as does a glycerol hydroxyl group and that the high viscosity of glycerine is attributable to hydrogen-bond cross-linking between the trifunctional molecules, a process which ought not to have much effect on hydrogen-bonded, small, solute molecules.

The data of Table II further show that the relaxation rate, $(1/T_1)_{\mathrm{obsd}}$, of the ^{31}P nucleus of H_3PO_4 at the same concentration and temperature and about the same viscosity has the value of 0.11 sec^{-1} in water, 0.78 in methanol, 1.5 in tetramethylurea, and 2.0 in acetone. This ordering is consistent with the changes to be expected in the structuring of the solvent around the phosphoric acid molecule.

Pyrophosphoric Acid. The observed spin-lattice relaxation time of aqueous pyrophosphoric acid is presented in the second column of Table III. As can be seen from the last column of this table, the relaxation time of pyrophosphoric acid averages about 21% larger than that of orthophosphoric acid. Probably this difference between the ortho- and pyrophosphoric acids may be attributable chiefly to the change in dipole-dipole relaxation induced by the substitution of a hydrogen of $OP(OH)_3$ by a phosphorus in order to obtain the $OP(OH)_2[OP(O)(OH)_2]$ molecule. Ignoring the viscosity differences between the two acids at the same phosphorus concentration (since their viscosity-concentration curves are not much different), this percentage change would be given by the following expression derived from eq 2: $100[-1 + 3\gamma_H^2/(1.5\gamma_P^2/\rho^6 + 2\gamma_H^2)]$, where ρ is the ratio of the distance between phosphorus atoms in pyrophosphoric acid to the distance between the phosphorus and the replaced hydrogen of the orthophosphoric acid, with τ_c being assumed to be the same for both acids. For $\rho = 1$, the estimated change is 34%, but it is reduced to 21% for $\rho = 0.9$.

In a study[24] of the ^{31}P spin-lattice relaxation of the various resonances observed in an equilibrated neat mixture of condensed phosphoryl chlorides, it was concluded that the spin-rotation relaxation mechanism[6] predominated. However, in this system of molecules in which the hydroxyl groups of the parent phosphoric acids are all substituted by chlorine atoms, it was found that the relaxation time of the pyro compound ($P_2O_3Cl_4$) was 64% larger than that of the ortho ($POCl_3$). As more data are gathered, it will be interesting to note whether the value of T_1 for pyro structures is consistently larger than that of the corresponding ortho molecule.

pH Titration of H_3PO_4. When 0.2 *M* orthophosphoric acid is titrated with either a strong base or a strong acid (either of which is highly concentrated in order to avoid appreciable dilution of the orthophosphoric acid), it is found that the spin-lattice relaxation varies greatly with pH, as shown in Figure 1. In this figure it should be noted that increasing the pH first causes the T_1 value to decrease rapidly and then to flatten off at the pH corresponding to the $H_2PO_4^-$ ion. The T_1 then decreases again but ascends to a maximum at the HPO_4^{2-} ion, finally dropping precipitously to rise again to a high value at the pH of the PO_4^{3-} ion. Adding the very strong perchloric acid to H_3PO_4 causes the T_1 to drop and then rise rapidly again to give a maximum corresponding to the $P(OH)_4^+$ cation, after which it again drops.

The behavior of this oscillating curve is in accord with the concept that, at pH values intermediate between those corresponding to single ionic species, the observed spin-lattice relaxation of a given orthophosphate group is made up of two contributions due to it being present part of the time as one and part as the other of the contributing ionic species. Thus, at the points corresponding to half-neutralization (pH = pK_i for i = 1, 2, 3), the observed relaxation rate, $1/T_1$, should equal half of the sum of the relaxation rates of the contributing ions (eq 1), if the mole fraction were the only weighting factor applicable to the $(1/T_1)$ summation. The results of such calculations are shown in Table IV in which it should be noted that the observed and calculated values agree quite well for pK_{-1} and pK_1. However, the calculated values for pK_2 and pK_3 indicate that the proper weighing factor for these situations is much closer to unity than to ½. Because of mathematical complexities,[25] it did not seem worthwhile to develop the equations since it would then be necessary to estimate other parameters which are not known for this system.

The dashed curve in Figure 1 represents a redetermination[26] of the variation of the orthophosphate ^{31}P chemical shift as a function of pH. These data were obtained on the same solutions as were used for the line width and T_1 measurements and they extend the published curve into the low pH region corresponding to a 0.2 *M* solution of H_3PO_4 in perchloric acids of varying concentration. Note that the chemical shift varies the most in the regions where the pH = pK_i, as would be expected for a coalesced NMR line representing rapid exchange between two chemical species. It follows from this, of course, that the chemical shift should be essentially constant in the neighborhood of the pH values corresponding to the pure ionic species. An exception to this rule seems to occur for the tetrahydroxyphosphonium ion, $P(OH)_4^+$, for which a maximum in the T_1 value and an "infinitely" narrow line width[15] are found at a composition corresponding to a rapidly changing chemical shift.

In addition to the T_1 values, a plot is also given in Figure 1 of $1/\pi(w - 0.1)$, where w is the ^{31}P NMR line width at half-height as measured in hertz. Note that in the basic region this reciprocal line-width function varies concomitantly with the spin-lattice relaxation time. Because of the small values involved (0.05-0.45 sec) for this reciprocal line-broadening function as compared to the spin-lattice relaxation time (3.5-13.0 sec), it is clear that rapid hydrogen exchange between the pair of ions corresponding to any of the intermediate pH values is contributing to the line broadening, a process which is demonstrated by the fact that only a single NMR peak is observed for partially neutralized ionic mixtures. Since the difference between the chemical shifts for the different orthophosphate ions may be obtained from the dashed curve of Figure 1, we can carry out a reasonable estimation of the lifetime for the hydrogen exchange between the ions, using eq 6. For each of the compositions exhibiting a pH equal to pK_i, with $i = -1, 1, 2$, or 3, the exchange lifetime is thus estimated to be about 2×10^{-3} sec.

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An Electron Diffraction Investigation of the Molecular Structures of Gaseous Trimethylphosphine Oxide, Trimethylphosphine Sulfide, Trimethylarsine Oxide, and Trimethylarsine Sulfide

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Abstract: The molecular structures of $(CH_3)_3PO$, $(CH_3)_3PS$, $(CH_3)_3AsO$, and $(CH_3)_3AsS$ have been determined by gaseous electron diffraction at nozzle-tip temperatures of 150–160, 160, 190, and 170–175°C, respectively. The values of the principal distances (r_a) and angles with estimated uncertainties of 2σ are: $r_{P-O} = 1.476\ (0.002)$ Å, $r_{P-C} = 1.809\ (0.002)$ Å, $\angle OPC = 114.4\ (0.7)°$ for $(CH_3)_3PO$; $r_{P-S} = 1.940\ (0.002)$ Å, $r_{P-C} = 1.818\ (0.002)$ Å, $\angle SPC = 114.1\ (0.2)°$ for $(CH_3)_3PS$; $r_{As-O} = 1.631\ (0.003)$ Å, $r_{As-C} = 1.937\ (0.002)$ Å, $\angle OAsC = 112.6\ (1.3)°$ for $(CH_3)_3AsO$; $r_{As-S} = 2.059\ (0.003)$ Å, $r_{As-C} = 1.940\ (0.003)$ Å, $\angle SAsC = 113.4\ (0.4)°$ for $(CH_3)_3AsS$. The sulfur bond lengths lie close to values expected for classical double bonding, but the P–O and As–O distances are especially short corresponding to even higher bond orders. It is shown that the polarities and force constants of the M–Y bonds in these MX_3Y-type molecules confirm a bond type having σ and π components with oppositely directed transfer of charge. Rotational freedom of the methyl group appears to increase in the order $(CH_3)_3PO < (CH_3)_3PS \simeq (CH_3)_3AsO < (CH_3)_3AsS$.

Elements from central groups of the periodic table, such as silicon or phosphorus, form bonds to more electronegative elements which are characteristically short and strong. The distances between atoms of a given type are found to vary, with differences reflecting both the number and electronegativities of other atoms bonded to the same central atom. Thus, the P–O bond in $POCl_3$ is longer than in POF_3[1] and the P–F bonds in the latter are shorter than in PF_3.[2]

The nature of the bonding involving central-group atoms has been much discussed.[1,3-6] Phosphorus compounds of the types PX_3 and PX_3Y have attracted interest particularly because there exists the possibility of charge transfer within the P–Y linkages, and recently several SCF-MO calculations have been made for PX_3 and PX_3Y molecules with X = H, CH_3, F, Cl, and Y = O or BH_3.[7-13] Although a considerable amount of the structural information necessary either for theoretical or semiempirical descriptions of the bonding in MX_3Y-type molecules is available, there is very little on the type $(CH_3)_3MY$ with M = P or As and Y = O or S. In these molecules the M–Y bonds presumably experience minimal, and in any case very similar, interaction with adjacent bonds; intercomparison of structural details thus offers special opportunity for better understanding the M–Y bonding. Knowledge of these $(CH_3)_3MY$ structures could conceivably also be of help in understanding the metal-ligand interactions in complexes[14-16] formed between the molecules and metals.

The present report describes results of electron-diffraction investigations of the structures of the four $(CH_3)_3MY$ molecules mentioned. Of the phosphorus compounds, trimethylphosphine oxide has been studied earlier by electron diffraction,[17] but refinement of the structure was not done and no error limits were reported for the parameter values. There is also a brief report on the structure of trimethylphosphine sulfide in the crystal.[16] No structural information seems to be available for the arsenic compounds.

Experimental Section

The oxides and sulfides were obtained from trimethylphosphine and trimethylarsine by published methods.[18] The compounds were freshly resublimed before use and the hygroscopic oxides handled out of contact with atmospheric moisture. The behavior of the vapor pressure curve for trimethylphosphine oxide[19] suggests asso-