Properties and Reactions of Trimethyl Phosphite, Trimethyl Phosphate, Triethyl Phosphate, and Trimethyl Phosphorothionate by Ion Cyclotron Resonance Spectroscopy

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Received July 3, 1978

Abstract: The gas-phase ion-molecule reactions occurring in trimethyl phosphite, trimethyl phosphate, triethyl phosphate, and trimethyl phosphorothionate have been investigated by ion cyclotron resonance spectroscopy. Protonated parent ions, tetracoordinated phosphonium ions, and cluster ions are the reaction products observed. The proton affinities of these compounds have been determined to be 222.9, 214.2, 218.7, and 216.6 kcal/mol, respectively (relative to $PA(NH_3) = 207.0$ kcal/mol). Homolytic bond dissociation energies of the protonated species are calculated using adiabatic ionization potentials determined by photoelectron spectroscopy. The trends in these quantities are discussed. A reasonable value for the correlated homolytic bond dissociation energy of trimethyl phosphite indicates that the first ionization potential of this molecule should be assigned to the phosphorus lone pair. The application of chemical ionization mass spectrometry to the analysis of phosphorus esters is briefly discussed.

Although the solution chemistry of organophosphorus compounds is a well-studied topic,[1] relatively few studies of the gas-phase ion chemistry of phosphorus compounds have been reported. The ion-molecule reactions in phosphine and the methyl phosphines have been investigated.[2-6] Proton-transfer reactions and condensation reactions with loss of simple molecules and radicals are the processes which occur at pressures below 0.05 Torr. Above this pressure the formation of cluster ions is also observed.[5] Ion-molecule reactions of PF_3,[7,8] OPF_3,[8,9] and SPF_3[9] have also been reported. Wanczek and co-workers have reported studies of the gas-phase ion chemistry of a range of phosphorus compounds.[10]

The gas-phase proton affinities of several phosphorus compounds have been determined by ICR techniques and are listed in Table I.[6,7,11] The proton affinity of a base, B, is defined as the standard enthalpy change for reaction 1, where all species and quantities refer to the gas phase. The homolytic bond dissociation energy, $D(B^+-H)$, is defined as the standard enthalpy change for reaction 2. It is related to the proton affinity of B by the adiabatic ionization potentials of B and H (eq 3). Strictly defined, the homolytic bond dissociation energy is calculated using the first adiabatic ionization potential of B in eq 3. However, for the purpose of comparisons among homologous compounds, the correlated homolytic bond dissociation energy must be considered.[12] This quantity is calculated from eq 3, using the adiabatic ionization potential of the orbital of B which corresponds to the bonding orbital in BH^+. For the phosphorus compounds studied to date the first ionization potential corresponds to ionization from this orbital. Adiabatic ionization potentials and homolytic bond dissociation energies for these compounds are given in Table I.

$$BH^+ \rightarrow B + H^+ \quad PA(B) = \Delta H^\circ \tag{1}$$

$$BH^+ \rightarrow B^+ + H \quad D(B^+-H) = \Delta H^\circ \tag{2}$$

$$D(B^+-H) = PA(B) + IP(B) - IP(H) \tag{3}$$

An understanding of the relationships between the chemical properties of phosphorus esters and their biological activity is essential in order to predict their behavior in living organisms.[13-16] For example, effective pesticides must be able to penetrate the ion barrier of insect nervous systems.[17] Therefore, the basicity of potential pesticides must be low enough such that they are un-ionized under physiological conditions.[18] A knowledge of their physical properties is also important for the development of analytical techniques for phosphorus esters. In particular, the design of chemical ionization mass spectrometric techniques[19] for these compounds requires a knowledge of their gas-phase ion chemistry.

This paper presents the results of an ion cyclotron resonance (ICR) investigation of the gas-phase ion-molecule reactions and proton affinities of four simple phosphorus esters: trimethyl phosphite, trimethyl phosphate, triethyl phosphate, and trimethyl phosphorothionate.

Experimental Section

The general features of ICR instrumentation and its operation in trapped ion experiments have been described previously.[20] All experiments were performed at room temperature. Pressure measurements were made using a Schulz-Phelps gauge located adjacent to the ICR cell. This gauge is calibrated against an MKS Instruments Baratron Model 90H1-E capacitance manometer in the region 10^{-5}-10^{-3} Torr.

Photoelectron spectra were obtained using a photoelectron spectrometer of standard design built in the Caltech shops.[21] Argon was used to calibrate all spectra. The energy scale is accurate to ±0.02 eV as determined by examining a range of compounds with known ionization potentials.

All chemicals were reagent grade materials from commercial sources and were used as supplied except for degassing at liquid nitrogen temperatures.

Results

Trimethyl Phosphite. Mass Spectrum. The ICR mass spectrum of trimethyl phosphite agrees with the reported spectrum.[22] The ions present in the mass spectrum at 20 eV are $P(OCH_3)_2^+$ (*m/e* 93, 26%), $P(OCH_3)_3^+$ (*m/e* 124, 21%), $OP(OCH_3)_2^+$ (*m/e* 109, 20%), $HP(OCH_3)_2^+$ (*m/e* 94, 15%), $HPOCH_3^+$ (*m/e* 63, 10%), and $HPO(OCH_3)^+$ (*m/e* 79, 8%).

Ion Chemistry. The variation of the relative ion abundances with time is given in Figure 1. The ion $P(OCH_3)_2^+$ (*m/e* 93), which is formed by electron impact, also results from reactions of $HPOCH_3^+$ (*m/e* 63) and $OP(OCH_3)_2^+$ (*m/e* 109) with the neutral (reactions 4 and 7).[23]

The principal reaction of $P(OCH_3)_2^+$ is the clustering reaction 9 to form $P_2(OCH_3)_5^+$ (*m/e* 217), which is the most abundant ion at long times. $P(OCH_3)_2^+$ also undergoes methyl cation transfer, yielding $P(CH_3)(OCH_3)_3^+$ (*m/e* 139) (reaction 10), and proton transfer to give $HP(OCH_3)_3^+$ (*m/e* 125) (reaction 11). The protonated parent ion, $HP(OCH_3)_3^+$, is also

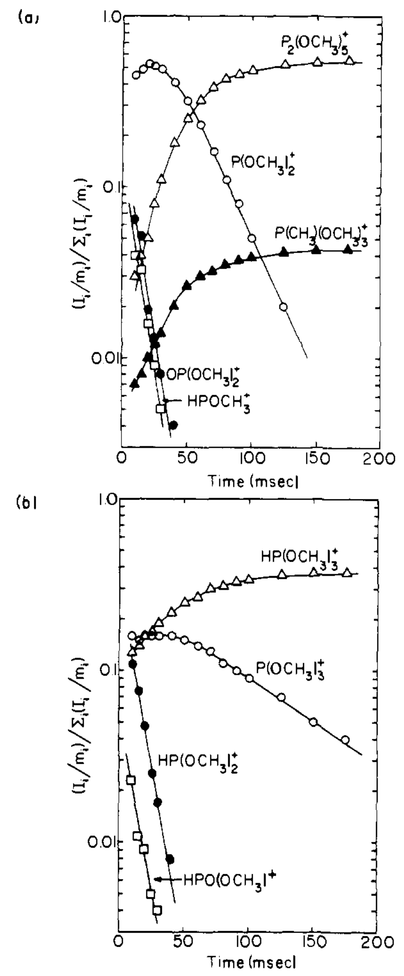


Figure 1. Temporal variation of ion concentrations for several species in trimethyl phosphite at 5.6 × 10^{-6} Torr pressure and 20 eV electron energy.

$$\mathrm{HPOCH_3^+ + P(OCH_3)_3 \xrightarrow{80\%} P(OCH_3)_2^+ + HP(OCH_3)_2} \tag{4}$$

$$\mathrm{HPOCH_3^+ + P(OCH_3)_3 \xrightarrow{20\%} HP(OCH_3)_3^+ + POCH_3} \tag{5}$$

$$\mathrm{HPO(OCH_3)^+ + P(OCH_3)_3 \longrightarrow HP(OCH_3)_3^+ + OPOCH_3} \tag{6}$$

$$\mathrm{OP(OCH_3)_2^+ + P(OCH_3)_3 \xrightarrow{100\%} P(OCH_3)_2^+ + OP(OCH_3)_3} \tag{7}$$

$$\mathrm{OP(OCH_3)_2^+ + P(OCH_3)_3 \xrightarrow{trace} P(OCH_3)_4^+ + OPOCH_3} \tag{8}$$

$$\mathrm{P(OCH_3)_2^+ + P(OCH_3)_3 \xrightarrow{90\%} P_2(OCH_3)_5^+} \tag{9}$$

$$\mathrm{P(OCH_3)_2^+ + P(OCH_3)_3 \xrightarrow{7\%} P(CH_3)(OCH_3)_3^+ + OPOCH_3} \tag{10}$$

$$\mathrm{P(OCH_3)_2^+ + P(OCH_3)_3 \xrightarrow{3\%} HP(OCH_3)_3^+ + P(OCH_2)(OCH_3)} \tag{11}$$

$$\mathrm{HP(OCH_3)_2^+ + P(OCH_3)_3 \xrightarrow{100\%} HP(OCH_3)_3^+ + P(OCH_3)_2} \tag{12}$$

$$\mathrm{HP(OCH_3)_2^+ + P(OCH_3)_3 \xrightarrow{trace} P_2(OCH_3)_4^+ + HOCH_3} \tag{13}$$

$$\mathrm{P(OCH_3)_3^+ + P(OCH_3)_3 \longrightarrow HP(OCH_3)_3^+ + P(OCH_2)(OCH_3)_2} \tag{14}$$

Table I. Proton Affinities, Adiabatic Ionization Potentials, and Homolytic Bond Dissociation Energies of Phosphorus Esters and Related Phosphorus Compounds

molecule	PA[a,b]	IP[a]	$D(B^+-H)$[a]
$P(OCH_3)_3$	222.9 ± 0.3	196 (8.50)[c]	106
$SP(OCH_3)_3$	216.6 ± 0.3	199 (8.65)[d]	102
$OP(OCH_3)_3$	214.2 ± 0.3	230 (9.99)[e]	131
$OP(OC_2H_5)_3$	218.7 ± 2	226 (9.79)[e]	131
PH_3	192.1[f]	230 (9.96)[f]	108
CH_3PH_2	206.5[f]	210 (9.12)[e]	103
$(CH_3)_2PH$	218.7[f]	195 (8.47)[e]	101
$P(CH_3)_3$	228.2[f]	187 (8.11)[e]	102
PF_3	160 ± 5[g]	269 (11.66)[h]	116
OPF_3	179[i]	294 (12.77)[h]	159

[a] kcal/mol. Values in parentheses in eV. [b] Proton affinities relative to PA(NH_3) = 207.0 kcal/mol (see ref 11). [c] Estimated from the photoelectron spectrum published in ref 42. [d] Private communication from A. H. Cowley. [e] Estimated from the photoelectron spectrum obtained in this laboratory. [f] Reference 11. [g] Reference 7. [h] Bassett, P. J.; Lloyd, D. R. *J. Chem. Soc., Dalton Trans.* **1972**, 248. [i] Dixon, D. A.; Beacuhamp, J. L., unpublished results.

formed by proton transfer from $HPOCH_3^+$ (*m/e* 63), $HPO(OCH_3)^+$ (*m/e* 79), $HP(OCH_3)_2^+$ (*m/e* 109), and $P(OCH_3)_3^+$ (*m/e* 124) (reactions 5, 6, 12, and 14). Proton transfer from the parent ion, $P(OCH_3)_3^+$, initially does not take place. It may be formed in a relatively unreactive excited state which then is collisionally deactivated. This phenomenon has been observed previously for the parent ions of $(CH_3)_3As$[24] and $(CH_3)_3N$.[25] Small quantities of the ions $P(OCH_3)_4^+$ (*m/e* 155) and $P_2(OCH_3)_4^+$ (*m/e* 186) are produced in minor reactions of $OP(OCH_3)_2^+$ and $HP(OCH_3)_2^+$, respectively (reactions 8 and 13).

Rate constants for the reactions of the primary ions are listed in Table II. These values were calculated from the limiting slopes of semilogarithmic plots of ion abundance vs. time.

Proton Affinity. In mixtures of $P(OCH_3)_3$ with pyridine and with cyclohexylamine the ratio of the protonated parent ions reached a constant value. Double-resonance experiments confirmed that proton transfer between the bases was occurring. Equilibrium constants measured in these experiments are summarized in Table III, along with free energies and enthalpies of proton transfer. Entropy effects were assumed to be small and limited to symmetry number corrections.[11,26] These data yield PA($P(OCH_3)_3$) = 222.9 ± 0.3 kcal/mol. All proton affinities are relative to PA(NH_3) = 207.0 kcal/mol. As has been discussed elsewhere, the proton affinity of NH_3 remains somewhat controversial.[21] The value used here represents a best estimate of the true value, which has an uncertainty of ±2 kcal/mol.

Trimethyl Phosphate. Mass Spectrum. The ICR mass spectrum of trimethyl phosphate at 70 eV agrees with the reported spectrum.[27] The principal ions in the 70-eV mass spectrum are $HPO(OCH_3)_2^+$ (*m/e* 11, 46%), $HPO(OCH_3)^+$ (*m/e* 79, 14%), $H_2PO(OCH_3)^+$ (*m/e* 80, 14%), $OP(OCH_3)_2^+$ (*m/e* 109, 11%), $HOPO(OCH_3)^+$ (*m/e* 95, 10%), and $OP(OCH_3)_3^+$ (*m/e* 140, 6%).

Ion Chemistry. The time evolution of the ion abundances in trimethyl phosphate is shown in Figure 2. The protonated parent is the dominant secondary ion. Double-resonance experiments demonstrated that this ion is formed in the reaction

$$\mathrm{MH^+ + OP(OCH_3)_3 \rightarrow HOP(OCH_3)_3^+ + M} \tag{15}$$

where MH^+ represents $OP(OCH_3)_3^+$ (*m/e* 140), $HPO(OCH_3)_2^+$ (*m/e* 110), $HOPO(OCH_3)^+$ (*m/e* 95), $H_2PO(OCH_3)^+$ (*m/e* 80), and $HPO(OCH_3)^+$ (*m/e* 79). The protonated parent clusters to form a proton-bound dimer:

$$\mathrm{HOP(OCH_3)_3^+ + OP(OCH_3)_3 \rightarrow H(OP(OCH_3)_3)_2^+} \tag{16}$$

Table II. Rate Constants for the Ion-Molecule Reactions in Trimethyl Phosphite, Trimethyl Phosphate, Triethyl Phosphate, and Trimethyl Phosphorothionate[a]

reaction	k_i[b]	Σk_i[b]
$HPOCH_3^+ + P(OCH_3)_3 \rightarrow P(OCH_3)_2^+ + HP(OCH_3)_2$	3.8	4.8
$\rightarrow HP(OCH_3)_3^+ + POCH_3$	1.0	
$HPO(OCH_3)^+ + P(OCH_3)_3 \rightarrow HP(OCH_3)_3^+ + OPOCH_3$	6.5	
$OP(OCH_3)_2^+ + P(OCH_3)_3 \rightarrow P(OCH_3)_2^+ + OP(OCH_3)_3$	5.8	5.8
$\rightarrow P(OCH_3)_4^+ + OPOCH_3$	<0.1	
$P(OCH_3)_2^+ + P(OCH_3)_3 \rightarrow P_2(OCH_3)_5^+$	1.4	1.6
$\rightarrow P(CH_3)(OCH_3)_3^+ + OPOCH_3$	0.1	
$\rightarrow HP(OCH_3)_3^+ + P(OCH_2)(OCH_3)$	0.05	
$HP(OCH_3)_2^+ + P(OCH_3)_3 \rightarrow HP(OCH_3)_3^+ + P(OCH_3)_2$	4.8	4.8
$\rightarrow P_2(OCH_3)_4^+ + HOCH_3$	<0.1	
$P(OCH_3)_3^+ + P(OCH_3)_3 \rightarrow HP(OCH_3)_3^+ + P(OCH_2)(OCH_3)_2$	0.5	
$P(OCH_3)_2^+ + SP(OCH_3)_3 \rightarrow P(SCH_3)(OCH_3)_3^+ + OPOCH_3$	1.1	2.7
$\rightarrow P_2SO(OCH_3)_3^+ + CH_3OCH_3$	0.3	
$\rightarrow SP_2(OCH_3)_5^+$	1.3	
$HPS(OCH_3)_2^+ + SP(OCH_3)_3 \rightarrow HSP(OCH_3)_3^+ + SP(OCH_3)_2$	7.0	
$SP(OCH_3)_3^+ + SP(OCH_3)_3 \rightarrow S_2P_2(OCH_3)_6^+$	1.7	
$HPO(OCH_3)^+ + OP(OCH_3)_3 \rightarrow HOP(OCH_3)_3^+ + OPOCH_3$	4.9	
$H_2PO(OCH_3)^+ + OP(OCH_3)_3 \rightarrow HOP(OCH_3)_3^+ + HPO(OCH_3)$	6.1	
$HOPO(OCH_3)^+ + OP(OCH_3)_3 \rightarrow HOP(OCH_3)_3^+ + OPO(OCH_3)$	3.6	
$OP(OCH_3)_2^+ + OP(OCH_3)_3 \rightarrow P(OCH_3)_4^+ + OPO(OCH_3)$	1.9	3.8
$\rightarrow P_2O_2(OCH_3)_5^+$	1.9	
$HPO(OCH_3)_2^+ + OP(OCH_3)_3 \rightarrow HOP(OCH_3)_3^+ + OP(OCH_3)_2$	2.8	
$OP(OCH_3)_3^+ + OP(OCH_3)_3 \rightarrow HOP(OCH_3)_3^+ + OP(OCH_2)(OCH_3)_2$	2.0	
$HOP(OCH_3)_3^+ + OP(OCH_3)_3 \rightarrow H(OP(OCH_3)_3)_2^+$	0.7	
$P(OH_4)^+ + OP(OC_2H_5)_3 \rightarrow HOP(OC_2H_5)_3^+ + OP(OH)_3$	17.0	
$(HO)_3POC_2H_5^+ + OP(OC_2H_5)_3 \rightarrow HOP(OC_2H_5)_3^+ + OP(OH)_2OC_2H_5$	15.0	
$(HO)_2P(OC_2H_5)_2^+ + OP(OC_2H_5)_3 \rightarrow HOP(OC_2H_5)_3^+ OP(OH)(OC_2H_5)_2$	12.0	
$HOP(OC_2H_5)_3^+ + OP(OC_2H_5)_3 \rightarrow H(OP(OC_2H_5)_3)_2^+$	6.0	

[a] All data from trapped-ion studies at 20 (trimethyl phosphate), 70 (trimethyl and triethyl phosphate), and 14 eV (trimethyl phosphorothionate). [b] In units of 10^{-10} cm^3 molecule^{-1} s^{-1}. Each rate constant is an average of three determinations. Accuracy in rate constants estimated to be ±50% due to uncertainties in pressure measurement.

Table III. Proton Affinities of Phosphorus Esters Derived from Equilibrium Constants for Proton-Transfer Reactions

$HXP(OR)_3^+ + B \rightleftharpoons BH^+ + XP(OR)_3$	K[a]	ΔG[b]	ΔH[b]	PA(B)[c,d]	PA(XP(OR)$_3$)[d]
$HP(OCH_3)_3^+ + C_5H_5N \rightleftharpoons C_5H_5NH^+ + P(OCH_3)_3$	0.55	0.4	0.4	222.8	223.2
$HP(OCH_3)_3^+ + c\text{-}C_6H_{11}NH_2 \rightleftharpoons c\text{-}C_6H_{11}NH_3^+ + P(OCH_3)_3$	0.90	0.1	−0.5	223.2	222.7
$HOP(OCH_3)_3^+ + C_6H_5NH_2 \rightleftharpoons C_6H_5NH_3^+ + OP(OCH_3)_3$	0.09	1.4	0.8	213.5	214.3
$HOP(OCH_3)_3^+ + (C_6H_5)_2CCH_2 \rightleftharpoons (C_6H_5)_2CCH_3^+ + OP(OCH_3)_3$	0.78	0.1	0.1	213.9	214.0
$HOP(OC_2H_5)_3^+ + 1,3,5\text{-}(CH_3O)_3C_6H_3 \rightarrow 1,3,5\text{-}(CH_3O)_3C_6H_4^+ + OP(OC_2H_5)_3$				227.5	<222.6
$C_2H_5NH_3^+ + OP(OC_2H_5)_3 \rightarrow HOP(OC_2H_5)_3^+ + C_2H_5NH_2$				218.7	>218.1
$HOP(OC_2H_5)_3^+ + 3\text{-}(CH_3CO)C_5H_4N \rightleftharpoons 3\text{-}(CH_3CO)C_5H_4NH^+ + OP(OC_2H_5)_3^+$				219.1	~219.1[e]
$HOP(OC_2H_5)_3^+ + C_4H_4N_2 \rightleftharpoons C_4H_4N_2H^+ + OP(OC_2H_5)_3$				218.5	~218.9[e]
$HSP(OCH_3)_3^+ + 4\text{-}CH_3OC_6H_4CHO \rightleftharpoons 4\text{-}CH_3OC_6H_4CHOH^+ + SP(OCH_3)_3$	0.15	1.1	1.1	215.5	216.6

[a] Average of at least three independent determinations. [b] In kcal/mol. [c] From a compilation of R. W. Taft. These values differ slightly from those reported in Taft, R. W. In "Proton-Transfer Reactions", Caldin, E., Gold, V., Eds.; Wiley: New York, 1975; p 31. [d] Proton affinity in kcal/mol. All data relative to PA(NH_3) = 207.0 kcal/mol. [e] Equilibrium not established (see text).

The remaining primary ion, $OP(OCH_3)_2^+$ (*m/e* 109), transfers a methyl cation to the neutral to form $P(OCH_3)_4^+$ (*m/e* 155) and clusters:

$$OP(OCH_3)_2^+ + OP(OCH_3)_3 \xrightarrow{50\%} P(OCH_3)_4^+ + OPO(OCH_3) \qquad (17)$$

$$OP(OCH_3)_2^+ + OP(OCH_3)_3 \xrightarrow{50\%} P_2O_2(OCH_3)_5^+ \qquad (18)$$

Rate constants for the reactions in trimethyl phosphate are listed in Table II.

Proton Affinity. Proton-transfer equilibria were observed in mixtures of $OP(OCH_3)_3$ with aniline and with 1,1-diphenylethene. Data from these experiments are presented in Table III. The proton affinity of trimethyl phosphate is found to be 214.2 ± 0.3 kcal/mol.

Triethyl Phosphate. Mass Spectrum. The ICR mass spectrum agrees with the reported spectrum.[28] The major ions at 70 eV are $P(OH)_4^+$ (*m/e* 99, 30%), $(HO)_2P(OC_2H_5)_2^+$ (*m/e* 155, 29%), $(HO)_3POC_2H_5^+$ (*m/e* 127, 19%), $OP(OH)_2^+$ (*m/e* 81, 13%), and $OP(OH)(OC_2H_5)^+$ (*m/e* 109, 9%).

Ion Chemistry. The ion chemistry is rather straightforward with the only process observed being the proton-transfer reaction 19, where MH^+ equals $(HO)_2P(OC_2H_5)_2^+$ (*m/e* 155), $(HO)_3POC_2H_5^+$ (*m/e* 127), $OP(OH)(OC_2H_5)^+$ (*m/e* 109), $P(OH)_4^+$ (*m/e* 99), and $OP(OH)_2^+$ (*m/e* 81). The protonated parent rapidly clusters with the neutral, yielding the proton-bound dimer $H(OP(OC_2H_5)_3)_2^+$ (*m/e* 365) (reaction 20). The

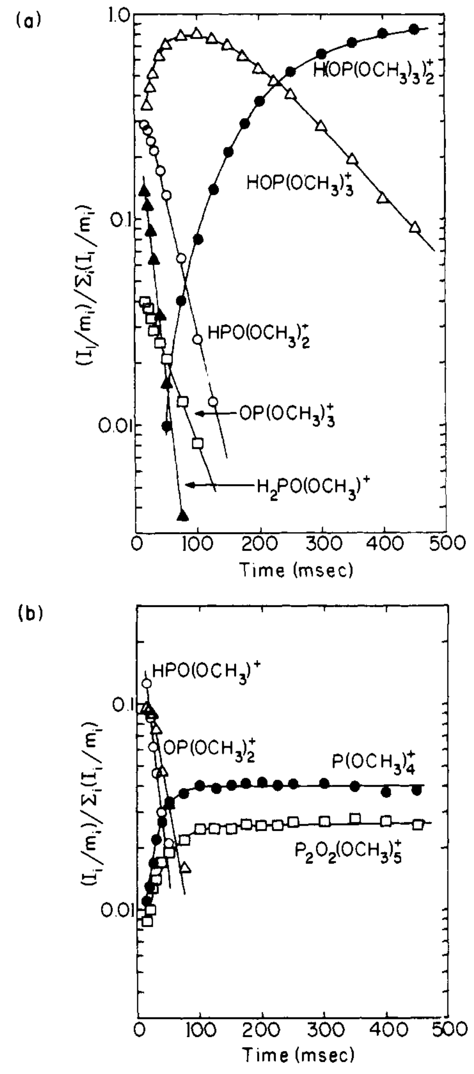


Figure 2. Temporal variation of ion concentrations in trimethyl phosphate at 3.2 × 10^{-6} Torr pressure and 70 eV electron energy: (a) major species; (b) minor species.

rate constants for the reactions of the three most abundant primary ions and the protonated parent are listed in Table II.

$$MH^+ + OP(OC_2H_5)_3 \rightarrow HOP(OC_2H_5)_3{}^+ + M \quad (19)$$

$$HOP(OC_2H_5)_3{}^+ + OP(OC_2H_5)_3 \rightarrow H(OP(OC_2H_5)_3)_2{}^+ \quad (20)$$

Proton Affinity. Because of the rapid rate of clustering of the protonated parent both with the triethyl phosphate neutral and with other Lewis bases, proton-transfer equilibria between triethyl phosphate and added bases could not be established. The observation that proton transfer occurs in one direction in mixtures of triethyl phosphate and certain bases permits the assessment of upper and lower limits for the proton affinity of triethyl phosphate. In mixtures of triethyl phosphate with 3-acetylpyridine and with pyridazine, proton transfer in both directions is detected in double-resonance experiments. This indicates that the free energy of protonation of triethyl phosphate is within about 2 kcal/mol of that of these compounds. The results of these experiments are summarized in Table III. The proton affinity of triethyl phosphate is estimated to be 219 ± 2 kcal/mol.

Trimethyl Phosphorothionate. Mass Spectrum. The mass spectrum of trimethyl phosphorothionate has not been previously reported. The ions observed in the 70-eV ICR mass spectrum include $CH_3{}^+$ (*m/e* 15, 3.6%), PO^+ and CH_3S^+ (*m/e* 47, 5.1%), PS^+ and CH_4OP^+ (*m/e* 63, 8.1%), $CH_4O_2P^+$ (*m/e* 79, 3.9%), $C_2H_6O_2P^+$ (*m/e* 93, 30.0%), $C_2H_6O_2PS^+$ (*m/e* 125, 3.6%), $C_2H_7O_2PS^+$ (*m/e* 126, 14.4%), $C_3H_9O_3PS^+$ (*m/e* 156, 20.4%), and $C_3H_{10}O_3PS^+$ (*m/e* 157, 2.4%). The mass spectrum closely resembles that of $SP(SCH_3)(OCH_3)_2$.[27] A major difference between the spectra is the decreased abundance of $SP(OCH_3)_2{}^+$ (*m/e* 125) in the spectrum of $SP(OCH_3)_3$. This is due to the greater strength of the P-OR bond relative to the P-SR bond in the radical cation.

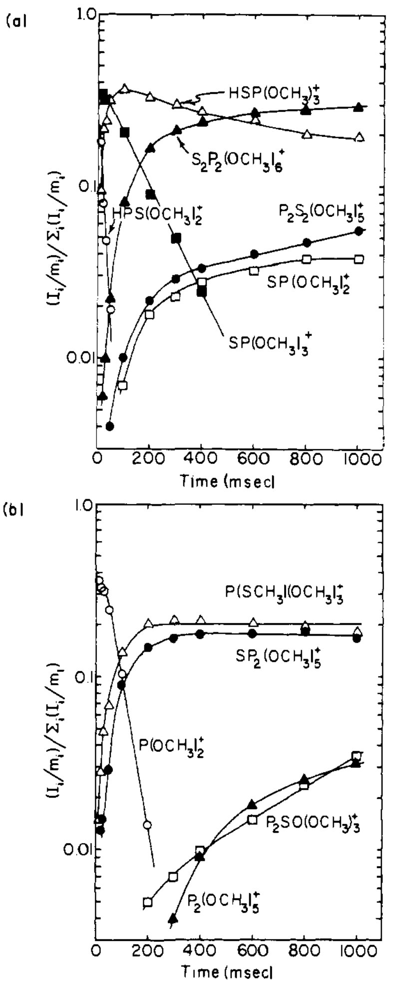


Figure 3. Temporal variation of ion concentrations of trimethyl phosphorothionate at 1.3 × 10^{-6} Torr pressure and 19 eV electron energy: (a) the reaction sequences initiated by $SP(OCH_3)_3{}^+$ and $HPS(OCH_3)_2{}^+$; (b) the reaction sequence initiated by $P(OCH_3)_2{}^+$.

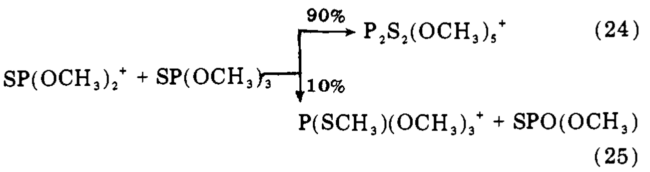
Ion Chemistry. Trapped ion experiments were performed at electron energies of 14 and 19 eV. The major primary ions present at these electron energies are $P(OCH_3)_2{}^+$ (*m/e* 93), $HSP(OCH_3)_2{}^+$ (*m/e* 126), and $SP(OCH_3)_3{}^+$ (*m/e* 156). The parent ion, $SP(OCH_3)_3{}^+$ (*m/e* 156), clusters with the parent neutral (reaction 21). The other two primary ions initiate complex reaction sequences, illustrated by the trapped ion data in Figure 3.

$$SP(OCH_3)_3{}^+ + SP(OCH_3)_3 \rightarrow S_2P_2(OCH_3)_6{}^+ \quad (21)$$

Rapid proton transfer from $HPS(OCH_3)_2{}^+$ (*m/e* 126) to the neutral yields $HSP(OCH_3)_3{}^+$ (reaction 22). The protonated parent loses methanol to give $SP(OCH_3)_2{}^+$ (*m/e* 125) (reaction 23). Loss of S from $HSP(OCH_3)_3{}^+$ would also result in an ion of *m/e* 125. However, this process is thermodynamically less favorable. In reaction 24 $SP(OCH_3)_2{}^+$ (*m/e* 125) forms the cluster ion $P_2S_2(OCH_3)_5{}^+$ (*m/e* 281). A small fraction of $SP(OCH_3)_2{}^+$ transfers $CH_3{}^+$ to the neutral to give $P(SCH_3)(OCH_3)_3{}^+$ (*m/e* 171) (reaction 25).

$$HPS(OCH_3)_2^+ + SP(OCH_3)_3 \rightarrow HSP(OCH_3)_3^+ + SP(OCH_3)_2 \quad (22)$$

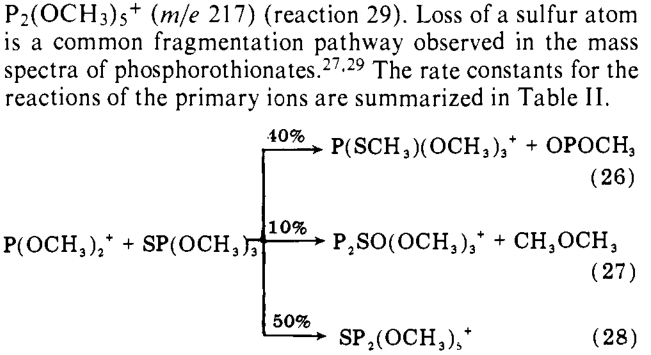
$$HSP(OCH_3)_3^+ \rightarrow SP(OCH_3)_2^+ + HOCH_3 \quad (23)$$



$$SP(OCH_3)_2^+ + SP(OCH_3)_3 \xrightarrow{90\%} P_2S_2(OCH_3)_5^+ \quad (24)$$

$$\xrightarrow{10\%} P(SCH_3)(OCH_3)_3^+ + SPO(OCH_3) \quad (25)$$

The fragment ion $P(OCH_3)_2^+$ (*m/e* 93) also transfers CH_3^+ (reaction 26). The minor product ion $P_2SO(OCH_3)_3^+$ (*m/e* 203) is formed in the condensation reaction 27. This mass could correspond to $HP_2O(OCH_3)_4^+$, which would result from a condensation with loss of CH_2S, rather than CH_3OCH_3. The ion $P(OCH_3)_2^+$ also clusters with the neutral (reaction 28). A portion of the clusters expels a sulfur atom to give $P_2(OCH_3)_5^+$ (*m/e* 217) (reaction 29). Loss of a sulfur atom is a common fragmentation pathway observed in the mass spectra of phosphorothionates.[27,29] The rate constants for the reactions of the primary ions are summarized in Table II.



$$P(OCH_3)_2^+ + SP(OCH_3)_3 \xrightarrow{40\%} P(SCH_3)(OCH_3)_3^+ + OPOCH_3 \quad (26)$$

$$\xrightarrow{10\%} P_2SO(OCH_3)_3^+ + CH_3OCH_3 \quad (27)$$

$$\xrightarrow{50\%} SP_2(OCH_3)_5^+ \quad (28)$$

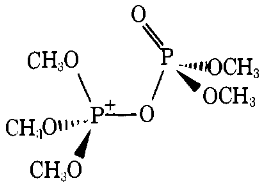
$$SP_2(OCH_3)_5^+ \rightarrow P_2(OCH_3)_5^+ + S \quad (29)$$

Proton Affinity. In mixtures of $(CH_3O)_3PS$ and *p*-methoxybenzaldehyde equilibrium between the protonated parent ions of the two species was achieved. Processes, such as reaction 23, which involve the protonated parent ion were sufficiently slow to permit equilibrium to be obtained. Data from these experiments are presented in Table III. The proton affinity of trimethyl phosphorothionate is 216.6 ± 0.3 kcal/mol.

Discussion

Ion Chemistry. Although the number of ion-molecule reactions of these phosphorus esters is large, they fall with few exceptions into one of two classes: reactions in which a tetracoordinated phosphonium ion is formed and clustering reactions. The phosphonium ions $P(OCH_3)_4^+$, $P(CH_3)(OCH_3)_3^+$, and $P(SCH_3)(OCH_3)_3^+$ are formed in reactions 8, 10, 17, 25, and 26. The protonated parent ions of each of these esters may also be classified as tetracoordinated phosphonium ions. Solution studies of protonated phosphorus compounds in strongly ionizing media have shown that phosphates[30] and thiophosphates[31] are protonated on the phosphoryl oxygen and sulfur and that phosphites[30] are protonated on phosphorus. There is no expectation that the site of protonation differs in the gas phase. The gas-phase proton affinities of phosphorus bases are higher than those of similar oxygen bases.[6,11] Thus, it is reasonable that phosphites should be protonated on phosphorus.

The cluster ions are of two types, proton-bound dimers and ions with the formula $P_2X_a(OCH_3)_b$ (X = O or S; a = 0–2; b = 3, 5, or 6). The bimolecular rate constants for the clustering reactions remain within ±20% of their average values over pressures which vary by at least a factor of 2 in the pressure range 10^{-7}–10^{-5} Torr employed in these experiments. The clustering reactions are, therefore, largely bimolecular at these pressures. Evidence for bimolecular kinetics has also been found for clustering reactions in fluoromethylsilanes.[32] Formation of the proton-bound dimers occurs in the phosphates. Reasonable structures for the other cluster ions can be suggested by considering that the ion results from donation of lone-pair electrons from the neutral to the phosphorus atom of the ion. For example, structure I can be proposed for the product ion $P_2O_2(OCH_3)_5^+$ (*m/e* 249) formed in reaction 18.



I

Proton Affinities, Adiabatic Ionization Potentials, and Homolytic Bond Dissociation Energies. The proton affinities, adiabatic ionization potentials, and homolytic bond dissociation energies of the phosphorus esters and related compounds are listed in Table I. A number of trends in these quantities are noteworthy. The proton-affinity order $PA(SP(OCH_3)_3) > PA(OP(OCH_3)_3)$ reflects the decreased electronegativity[33] and increased polarizability[34] of sulfur compared to oxygen. The same order applies to other related sulfur and oxygen compounds, e.g., $PA(H_2S) > PA(H_2O)$.[11] The proton affinities of tervalent compounds in Table I decrease with increasing electron-withdrawing ability of the substituents in the series $P(CH_3)_3$, $P(OCH_3)_3$, PF_3. More extensive considerations of the base strengths of cyclic and acyclic phosphites have recently appeared elsewhere.[35]

The homolytic bond dissociation energies of $OP(OCH_3)_3$, $OP(OC_2H_5)_3$, and OPF_3 are large in comparison with those of most common oxygen bases (e.g., $D((CH_3)_2CO^+\text{-}H) = 109$ kcal/mol[36]). Substitution of CH_3O for CH_3 in R_2CO to give the carbonyl analogue of $OP(OCH_3)_3$ results in a marked increase in homolytic bond dissociation energy to $D((CH_3O)_2CO^+\text{-}H) = 133$ kcal/mol.[37] The substituents CH_3O and F are probably responsible for the large bond energies in the phosphoryl compounds. These substituents must stabilize the conjugate acid relative to the molecular ion. The mechanism of the stabilization may involve both inductive and resonance effects. Clarification of the role of these effects requires data for systems in which the effects are separable. Insights would also be provided by ab initio theoretical studies of model systems.

The proton affinity of triethyl phosphate exceeds that of trimethyl phosphate by 4.5 kcal/mol. This methyl substituent effect appears to be large, considering that the additional substitution occurs three bonds distant from the site of protonation. The difference in the proton affinities of tripropyl- and tributylamine is only 1.4 kcal/mol.[38] In the protonated phosphates considerable positive charge is located on the alkoxy oxygens and phosphorus, which are one and two bonds distant from the alkyl groups. Thus, charge dispersal enhances the substituent effect of the alkyl group.

The difference in the heats of protonation of trimethyl and triethyl phosphate in HSO_3F is quite small, only 0.2 kcal/mol.[39] The inductive effect of the larger alkyl groups is almost completely neutralized by opposing effects in the enthalpies of solvation. The difference in the heats of solvation of $OP(OCH_3)_3$ and $OP(OC_2H_5)_3$ is 1.6 kcal/mol.[39] Using the thermodynamic cycle previously described,[40] a difference in the heats of solvation of the conjugate acids ($\Delta H_s((CH_3O)_3POH^+) - \Delta H_s((C_2H_5O)_3POH^+)$) of −2.6 kcal/mol is obtained. This value is similar to the difference of −1.9 kcal/mol between the heats of solvation of $(CH_3)_3NH^+$ and $(C_2H_5)_3NH^+$.[40]

Assignment of the Photoelectron Spectrum of $P(OCH_3)_3$. Correlations of the homolytic bond dissociation energies of homologous compounds can aid in the assignment of their photoelectron spectra.[12] The first ionization potential of trimethyl phosphite has been somewhat controversial.[35,41,42] Any of the higher ionization potentials of trimethyl phosphite lead to a correlated homolytic bond dissociation energy which is unreasonably high in comparison with other values in Table I. This discrepancy could be resolved by assuming that the phosphite is protonated on oxygen. However, for reasons given above, this possibility seems unlikely. The more acceptable alternative is to assign the first ionization potential to the phosphorus lone pair.[43]

Chemical Ionization Mass Spectrometry. An optimum system for chemical ionization mass spectrometric analysis of a class of compounds is one in which the desired compounds are selectively ionized and give spectra with prominent molecular or quasi-molecular ions. Chemical ionization of the phosphorus esters dioxathan and phosphamidon using the reagent gas isobutane yielded a quasi-molecular ion only for the latter compound.[44] The relatively high proton affinities of the phosphorus esters in the present work suggest that these compounds would be amenable to ionization by selective protonation. Selective protonation is accomplished by using a reagent gas of high proton affinity. This technique has two advantages: (1) contaminants in the sample which have lower proton affinities than the reagent gas are not represented in the chemical ionization mass spectrum and (2) protonation of sample molecules is "softer" (less exothermic) than protonation by ions in more traditional reagent gases (CH_4, C_4H_{10}) with the result that fragmentation is reduced. Reagent gases consisting of mixtures of hydrocarbons and amines have been used to produce chemical ionization mass spectra of alkyldiphenylphosphine oxides[45] and tri(2-butoxyethyl) phosphate[46] which contain abundant $[M + H]^+$ and other quasi-molecular ions.

Acknowledgments. This research was supported in part by the U.S. Army Research Office under Grant No. DAAG29-76-G-0274. One of us (R.V.H.) would like to thank the National Science Foundation for a Graduate Fellowship (1973–1976).

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