Effects of Molecular Structure on Basicity. Gas-Phase Proton Affinities of Cyclic Phosphites

Ronald V. Hodges,[1a] F. A. Houle,[1a] J. L. Beauchamp,*[1a] R. A. Montag,[1b] and J. G. Verkade*[1b]

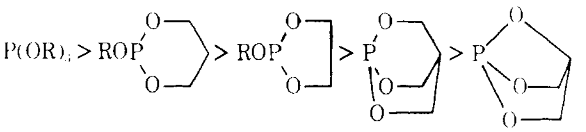
Contribution No. 5701 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, and the Department of Chemistry, Gilman Hall, Iowa State University, Ames, Iowa 50010. *Received July 11, 1978*

Abstract: The proton affinities of several monocyclic and bicyclic phosphite esters are determined by ion cyclotron resonance spectroscopy. The order of proton affinities is identical with the solution basicity order reported earlier. Thus, increasing steric constraint decreases the proton affinity of the phosphorus lone pair in phosphites. Moreover, the phosphorus lone pair in monocyclic six-membered-ring phosphites is more basic in the axial than in the equatorial position. Adiabatic ionization potentials are obtained from photoelectron spectra of the phosphites. Increases in ionization potential are found to parallel decreases in proton affinity. This relationship between the ionization potential and proton affinity suggests that the first ionization potential of the phosphites corresponds to ionization from the phosphorus lone pair orbital. These trends are rationalized in terms of changes in the interactions of the oxygen lone pair orbitals with the phosphorus lone pair and π-bonding orbitals.

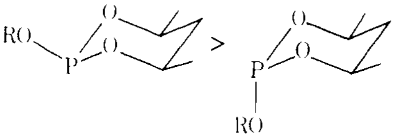
Considerable evidence has been accumulated which indicates that increasing steric constraint reduces the Lewis basicity of trialkyl phosphites.[2] Thus, investigations of the displacement equilibrium

$$H_3BL + L' \rightleftharpoons H_3BL' + L \qquad (1)$$

(where L and L′ are phosphite esters),[3] NMR $^1J_{PH}$ values of protonated phosphites,[4,5] and IR frequencies of adducts of phosphites with borane[3,6] and phenol[7] suggest the basicity order[2]



Similar experiments suggest that the basicity of monocyclic six-membered-ring phosphites is conformation dependent[8,9] in that the phosphorus lone pair is more basic in the axial than the equatorial position.[2,4]



These experiments yield only basicity orders and are subject to solvent effects. Gas-phase proton affinities provide a quantitative measure of base strength in the absence of solvent effects. The proton affinity of a base B is defined as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+:

$$BH^+ \rightarrow B + H^+ \qquad \Delta H = PA(B) \qquad (2)$$

For two bases B_1 and B_2, a knowledge of the preferred direction of the proton-transfer reaction

$$B_1H^+ + B_2 \rightleftharpoons B_2H^+ + B_1 \qquad (3)$$

establishes the sign of the free-energy change for the reaction, ΔG. Gas-phase proton-transfer reactions can be observed by ion cyclotron resonance (ICR) techniques.[10] If the proton affinities differ by no more than 3 kcal/mol, equilibrium between B_1H^+ and B_2H^+ can often be established in an ICR trapped ion experiment.[11,12] The free-energy change for reaction 3 is calculated from the measured equilibrium constant according to $\Delta G = -RT \ln K$. If it is assumed that entropy effects are small and are limited to changes in rotational symmetry numbers, then the relative proton affinity $\Delta H = PA(B_1) - PA(B_2)$ is readily calculated.[11-13] If the absolute proton affinity of one of the bases is known, then measurement of their relative proton affinity establishes the proton affinity of the other base.

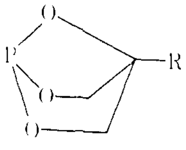
For the purpose of thermodynamic analysis, the removal of a proton from BH^+ can be divided into two steps: homolytic cleavage of the B-H$^+$ bond and charge transfer between B^+ and H (reaction 4). The proton affinity is then given by the sum of the enthalpies of these two processes (eq 5). For a series of

$$BH^+ \rightarrow B^+ + H \rightarrow B + H^+ \qquad (4)$$

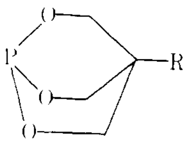
$$PA(B) = D(B^+\text{-}H) + IP(H) - IP(B) \qquad (5)$$

homologous compounds, the proton affinity is often found to be a linear function of the adiabatic ionization potential of the orbital which becomes the bonding orbital in BH^+.[14-16]

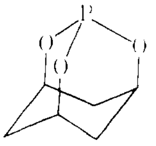
This paper reports determinations of the proton affinities of the constrained phosphites **1-9** by ICR techniques. The adiabatic ionization potentials of these phosphites, measured by photoelectron spectroscopy, are used to calculate homolytic bond dissociation energies, $D(B^+\text{-}H)$.



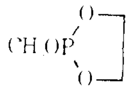
1, R = H
2, R = CH



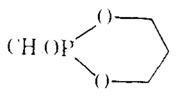
3, R = H
4, R = CH



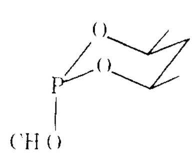
5



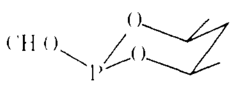
6



7



8



9

Experimental Section

The general features of ICR instrumentation and its operation in trapped ion experiments have been previously described.[10,17] 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 for each gas

0002-7863/80/1502-0932$01.00/0

Table I. Proton Transfer Equilibrium Constants, Free Energies, and Enthalpies

phosphite $H^+ + B \rightleftharpoons BH^+ +$ phosphite	K^a	ΔG^b	ΔH^b	PA(B)$^{b-d}$	PA(phosphite)^{b,c}
$\mathbf{1}H^+ + c\text{-}C_3H_5CN \rightleftharpoons c\text{-}C_3H_5CNH^+ + \mathbf{1}$	10.6	−1.4	−1.4	197.9^e	196.5
$\mathbf{1}H^+ + n\text{-}C_5H_7CN \rightleftharpoons n\text{-}C_3H_7CNH^+ + \mathbf{1}$	0.51	0.4	0.4	196.1^e	196.5
$\mathbf{2}H^+ + \overline{CH_2CH_2CH_2CH_2O} \rightleftharpoons \overline{CH_2CH_2CH_2CH_2O}H^+ + \mathbf{2}$	4.7	−0.9	−0.6	201.1^e	200.6
$\mathbf{2}H^+ + CH_3COOCH_3 \rightleftharpoons (CH_3COOCH_3)H^+ + \mathbf{2}$	0.75	0.2	0.2	200.1^e	200.3
$\mathbf{3}H^+ + CH_3COCH_2COCH_3 \rightleftharpoons (CH_3COCH_2COCH_3)H^+ + \mathbf{3}$				209.3	209.7^f
$\mathbf{3}H^+ + (CH_3)_6C_6 \rightleftharpoons ((CH_3)_6C_6)H^+ + \mathbf{3}$				209.7	210.2^f
$CF_2HCH_2NH_3^+ + \mathbf{4} \rightarrow \mathbf{4}H^+ + CF_2HCH_2NH_2$				210.6	>210.0
$\mathbf{4}H^+ + (t\text{-}C_4H_9)_2S \rightarrow (t\text{-}C_4H_9)_2SH^+ + \mathbf{4}$				215.1	<215.5
$\mathbf{4}H^+ + HCON(CH_3)_2 \rightleftharpoons (HCON(CH_3)_2H^+ + \mathbf{4}$	9	−1.3	−1.3	213.7	212.4
$\mathbf{5}H^+ + 2\text{-}ClC_5H_4N \rightleftharpoons 2\text{-}ClC_5H_4NH^+ + \mathbf{5}$	1.1	−0.1	−0.1	216.5	216.4
$\mathbf{5}H^+ + (t\text{-}C_4H_9)_2S \rightleftharpoons (t\text{-}C_4H_9)_2SH^+ + \mathbf{5}$	0.9	0.1	0.5	215.1	>215.6
$\mathbf{6}H^+ + 2\text{-}ClC_5H_4N \rightleftharpoons 2\text{-}ClC_5H_4NH^+ + \mathbf{6}$	27	−2.0	−2.0	216.5	214.5
$\mathbf{6}H^+ + (t\text{-}C_4H_9)_2S \rightleftharpoons (t\text{-}C_4H_9)_2SH^+ + \mathbf{6}$	0.80	0.1	0.5	215.1	215.6
$n\text{-}C_3H_7NH_3^+ + \mathbf{7} \rightarrow \mathbf{7}H^+ + n\text{-}C_3H_7NH_2$				220.2	219.6
$\mathbf{7}H^+ + C_5H_5N \rightleftharpoons C_5H_5NH^+ + \mathbf{7}$	8.8	−1.3	−1.3	222.8	221.5
$\mathbf{8}H^+ + 3\text{-}CH_3C_5H_4N \rightleftharpoons 3\text{-}CH_3C_5H_4NH^+ + \mathbf{8}$	0.08	1.5	1.5	225.5	227.0
$\mathbf{8}H^+ + (C_2H_5)_2NH \rightleftharpoons (C_2H_5)_2NH_2^+ + \mathbf{8}$	13	−1.5	−1.9	227.4	225.5
$\mathbf{8}H^+ + 2\text{-}CH_3C_5H_4N \rightleftharpoons 2\text{-}CH_3C_5H_4NH^+ + \mathbf{8}$	11	−1.4	−1.4	226.3	224.9
$\mathbf{9}H^+ + 4\text{-}CH_3C_5H_4N \rightleftharpoons 4\text{-}CH_3C_5H_4NH^+ + \mathbf{9}$	0.36	0.6	0.6	226.8	227.4
$\mathbf{9}H^+ + \overline{CH_2(CH_2)_4N}H \rightleftharpoons \overline{CH_2(CH_2)_4N}H_2^+ + \mathbf{9}$	0.69	0.2	−0.2	227.8	227.6

[a] Average of at least three independent determinations. [b] kcal/mol. [c] Proton affinity relative to PA(NH_3) = 207.0 kcal/mol. The actual proton affinity of NH_3 remains controversial and is discussed in detail: Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.*, **1979**, *101*, 4067. The value 207 ± 2 kcal/mol is chosen as a "preferred value" which is sufficiently accurate for the purposes of the present study. [d] Except as noted, proton affinities are from a compilation by R. W. Taft. A number of values are slightly modified from those given: Taft, R. W. In "Proton-Transfer Reactions", Caldin, E., Gold, V., Eds.; Wiley: New York, 1975. [e] Reference 11. [f] Proton transfer observed in both directions but equilibrium was established slowly. PA(phosphite) is an estimate based on the preferred direction of proton transfer as evidenced in ion-abundance measurements.

for a given emission current (5 μA) and magnetic field (6 kG) against an MKS Instruments Baratron Model 90H1-E capacitance manometer in the region 10^{-5}–10^{-3} Torr. Pressures in the trapped ion experiments were in the range 10^{-7}–10^{-5} Torr. Pressure calibrations were not performed for **3** (or its methyl derivative **4**), piperidine, or diethylamine, but were assumed to be equal to those for **2**, aniline, and **8**, respectively. An uncertainty of ±0.3 kcal/mol in the proton affinity is estimated owing to uncertainties in pressure measurement. In some cases establishment of equilibrium conditions was hindered by low proton transfer reaction rates or competing reactions. In these cases the reported uncertainty is appropriately increased.

Photoelectron spectra were obtained using a photoelectron spectrometer of standard design built in the Caltech shops. The instrument comprises a helium discharge lamp, 127° electrostatic analyzer, and Channeltron electron multiplier. Spectra were accumulated in a Tracor-Northern NS-570A multichannel scaler with 4K memory. Argon was used to calibrate all spectra, and the energy scale is accurate to ±0.02 eV as ascertained by checking compounds with known ionization potentials.

The cyclic phosphites were prepared by literature methods.[4,18-21] The mass spectra of all of the phosphites contained an abundant molecular ion. Other chemicals were reagent grade materials from commercial sources and were used as supplied.

Results

$\overline{P(OCH_2)_2CO}H$ (1). In mixtures of **1** and $c\text{-}C_3H_5CN$ or $n\text{-}C_3H_7CN$, the ratio of protonated parent ion abundances reached a constant value. Double-resonance experiments established that proton transfer was occurring in both directions, thus demonstrating that proton-transfer equilibria had been achieved. The equilibrium constants, free energies, and enthalpies for proton transfer are presented in Table I. These data yield PA(**1**) = 196.5 ± 0.3 kcal/mol.

$\overline{P(OCH_2)_2CO}CH_3$ (2). Proton-transfer equilibria were observed in mixtures of **2** with tetrahydrofuran and with CH_3COOCH_3. The free energies and enthalpies of proton transfer calculated from the measured equilibrium constants are listed in Table I. These data yield PA(**2**) = 200.4 ± 0.3 kcal/mol.

$P(OCH_2)_3CH$ (3). In mixtures of **3** with acetylacetone and hexamethylbenzene, slow, reversible proton transfer reactions were observed. In both cases the reaction favored the protonated phosphite, as evidenced from the temporal variation of ion abundances. From these results a proton affinity for $P(OCH_2)_3CH$ of 209.7 ± 1.0 kcal/mol is estimated.

$P(OCH_2)_3CCH_3$ (4). In a mixture of **4** and $CF_2HCH_2NH_2$, proton transfer from the protonated amine to the phosphite occurs, but the reverse is not observed. This implies that the free energy of protonation of the phosphite is greater than that for the amine and, thus, PA(**4**) > 210.0 kcal/mol. Similarly, the observation of proton transfer from the protonated phosphite to $(t\text{-}C_4H_9)_2S$ establishes an upper limit for PA(**4**) of 215.5 kcal/mol. In a mixture of **4** and $HCON(CH_3)_2$ proton transfer in both directions was detected. Measurement of the equilibrium constant in this system was difficult because a competing reaction, which was not identified, removes the protonated species. An approximate equilibrium constant, free energy, and enthalpy of proton transfer are listed in Table I along with the results of the other experiments with **4**. From these data a proton affinity for $P(OCH_2)_3CCH_3$ equal to 212.4 ± 0.6 kcal/mol is calculated.

$P(OCH)_3(CH_2)_3$ (5). Double-resonance experiments established that proton transfer occurs in both directions in a mixture of **5** and 2-chloropyridine. An unidentified reaction of a protonated species competes with proton transfer in this system also. An approximate equilibrium constant and the resulting free energy and enthalpy of proton transfer are given in Table I. Proton-transfer equilibria were observed in mixtures of **5** and $(t\text{-}C_4H_9)_2S$. Data from these mixtures are presented in Table I. Using the latter data, PA(**5**) = 215.6 ± 0.3 kcal/mol is calculated.

$CH_3O\overline{POCH_2CH_2O}$ (6). Proton transfer in both directions in mixtures of **6** with 2-chloropyridine and $(t\text{-}C_4H_9)_2S$ is observed. Data from these experiments are given in Table I. A reaction which competes with proton transfer occurs in the mixtures of 2-chloropyridine and **6**. The equilibrium constant determined for the mixtures with $(t\text{-}C_4H_9)_2S$ is judged to be more reliable. From this equilibrium constant PA(**6**) = 215.6 ± 0.3 kcal/mol is obtained.

$CH_3O\overline{POCH_2CH_2CH_2O}$ (7). In mixtures of $n\text{-}C_3H_7NH_2$

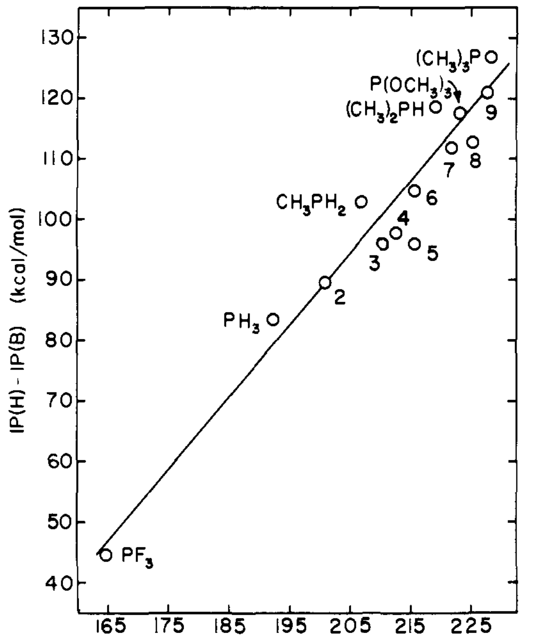


Figure 1. The quantity IP(H) − IP(B) plotted vs. PA(B) for tervalent phosphorus compounds (values from Table II).

and 7, proton transfer from the protonated amine to the phosphite occurs. This implies that PA(7) > 219.6 kcal/mol. Proton-transfer equilibria in mixtures of 7 with pyridine were observed. These experiments are summarized in Table I. The proton affinity of 7 is determined to be 221.5 ± 0.7 kcal/mol.

$CH_3O\overline{POCH(CH_3)CH_2CH(CH_3)O}$ (8). Proton transfer in both directions was observed in mixtures of **8** with 3-methylpyridine, diethylamine, and 2-methylpyridine. In the mixtures with the first two compounds a competing reaction removed the protonated species, rendering accurate determination of the equilibrium constant difficult. This problem was much less severe in the mixtures with 2-methylpyridine. Using data from the latter experiments, a proton affinity for **8** of 224.9 ± 0.5 kcal/mol is calculated. The results of these experiments are summarized in Table I.

$CH_3O\overline{POCH(CH_3)CH_2CH(CH_3)O}$ (9). Proton-transfer equilibria were observed in mixtures of **9** with 4-methylpyridine and piperidine. The proton-transfer equilibrium constants, free energies, and enthalpies are presented in Table I. From these data a proton affinity for **9** of 227.5 ± 0.3 kcal/mol is calculated.

Photoelectron Spectra. Adiabatic ionization potentials for the phosphites were estimated from their photoelectron spectra and are given in Table II. The first ionization bands were generally smooth and bell shaped. The adiabatic ionization potentials were picked by extrapolating the leading (approximately straight) edge of the bands to the base line of the spectra. While this did not always correspond to the onset of the band, it was considered to be the most consistent method of choosing adiabatic values for the purposes of the present work. "Tailing" in some of the spectra was such that an initial onset could not be readily identified. Reported values for adiabatic ionization potentials are regarded as accurate to within ±0.1 eV. This contributes an uncertainty of ±2 kcal/mol to calculated homolytic bond dissociation energies. The difference between the vertical and adiabatic ionization potentials of the phosphites is approximately constant in the series and equals ~0.6 eV. A similar difference has been noted for the series of methylphosphines.[11]

Table II. Proton Affinities, Adiabatic Ionization Potentials, and $D(B^+-H)$ Homolytic Bond Dissociation Energies of Tervalent Phosphorus Compounds

compd	PA[a]	IP[a]	$D(B^+-H)$[a]
1	196.5		
2	200.4	224 (9.72)[b]	111
3	209.7	217 (9.42)	113
4	212.4	216 (9.35)[b]	115
5	215.6	217 (9.42)[b]	120
6	215.6	209 (9.06)	111
7	221.5	202 (8.74)	110
$P(OCH_3)_3$	222.9	196 (8.50)[c]	106
8	224.9	200 (8.69)	112
9	227.5	192 (8.34)	107
PF_3	165 ± 5[d]	269 (11.66)[e]	121
PH_3	192.1	230 (9.96)[f]	108
CH_3PH_2	206.5	210 (9.12)[f]	103
$(CH_3)_2PH$	218.7	195 (8.47)[f]	101
$(CH_3)_3P$	228.2	187 (8.11)	102

[a] kcal/mol. Values in parentheses in eV. Except as noted, reported ionization potentials were determined in the present study. [b] Reference 24. [c] Reference 22. [d] Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1978,** *17*, 1585. The value $PA(NH_3) = 207.0$ kcal/mol also results in an increase in $PA(PF_3)$ from the value reported in this article. [e] Bassett, P. J.; Lloyd, D. R. *J. Chem. Soc., Dalton Trans.* **1972,** 248. [f] Reference 11.

Discussion

The proton affinities, adiabatic ionization potentials, and $D(B^+-H)$ homolytic bond dissociation energies for the phosphites and other tervalent phosphorus compounds are presented in Table II. The gas-phase proton affinity order of the phosphites is the same as the basicity order in solution.[2-7] Thus, this order is a result of differences in the intrinsic properties of the isolated molecules. The significant difference in the proton affinities of **8** and **9** (2.6 kcal/mol) represents the first purely conformational effect on basicity observed in the gas phase.

The proton affinity data reflect changes in the ionization potentials and homolytic bond dissociation energies according to eq 5. The homolytic bond dissociation energies of the phosphites exhibit some variation, but do not follow a consistent trend. The decrease in proton affinity with increasing constraint parallels an increase in ionization potential. Figure 1 illustrates the correlation between the ionization potential and the proton affinity for the tervalent phosphorus compounds studied to date. From this plot the proton affinities of other tervalent phosphorus compounds can be estimated, if their ionization potentials are known. The equation

$$PA(B) = 0.853[459 - IP(B)] \qquad (6)$$

is useful for this purpose, where all quantities are expressed in kcal/mol. The closeness of the coefficient relating PA(B) to IP(B) to unity indicates that homolytic bond energies are approximately constant for the series of compounds considered.

In a study of the proton affinities and photoelectron spectra of nitriles, a correlation between the proton affinity and the adiabatic ionization potential of the nitrogen lone pair orbital was observed.[14] No correlation was found with the first ionization potential, which corresponds to ionization from the C≡N π orbitals. This suggests that the ionization potential of the orbital which becomes the bonding orbital in $B-H^+$ is the one which is expected to correlate with the proton affinity. The existence of a correlation between the proton affinity and first ionization potential of the phosphites is evidence that this ionization occurs from the phosphorus lone pair orbital. Additional evidence for the correctness of this assignment stems from a study of the PES spectra of $ZP(OR)_3$ compounds (Z = lone pair or chalconide) in which it was concluded[22] that the first ionization potential in the spectrum of $P(OMe)_3$ is due to the phosphorus lone pair and not to the oxygen lone pairs as originally believed by these authors.[23] A PES study of **3** and its chalconide derivatives leads to the same conclusion.[24] Shifts in lone pair orbital energies of phosphites upon complexation to metal centers provides additional support for the new assignment.[25]

The relationship between the proton affinity and ionization potential revealed in the present study indicates that the proton-affinity order is determined by differences in the abilities of the phosphites to assume a positive charge. This conclusion supports previous rationalizations of the basicity order, in which the trend is ascribed to differences in the interaction of the oxygen lone pairs with phosphorus.[2,4,26] The repulsive interaction of the phosphorus and oxygen lone pairs destabilizes the phosphorus lone pair in the neutral phosphite,[2,27] while π bonding between oxygen and phosphorus in the protonated phosphite and the molecular ion delocalizes the positive charge.[2,24,28] Both of these interactions serve to decrease the ionization potential and increase the proton affinity. The changes in geometry which accompany increasing constraint of the phosphite alter the spatial orientation and hybridization of the oxygen lone pair orbitals such that their interactions with the phosphorus lone pair and π-bonding orbitals are weakened.[2] The decrease in the basicity of an equatorial vs. an axial phosphorus lone pair in **8** and **9** may also be ascribed to a weakening of these interactions.[2,24,27] The extent to which phosphorus d orbitals are important in the π-bonding effects may well be small, however.

The 5 kcal/mol increase in proton affinity upon methyl substitution in **1** is large in comparison with the effect of methyl substitution remote from the site of protonation in other compounds. For example, substitution of CH_3 for H in RCH_2CHO and RCH_2CN raises the proton affinity by about 3 kcal/mol.[11] Although not accurately determined, the increase of 2.7 kcal/mol resulting from methyl substitution in **3** appears "normal" if not slightly on the high side. The existence of three pathways for through-bond interactions between the methyl group and the phosphorus atom in the bicyclic molecule may augment the methyl effect relative to that in acyclic compounds.

Acknowledgments. This research was supported in part by the U.S. Army Research Office under Grant DAAG29-76-G-0274 (J.L.B.) and by the National Science Foundation under Grant CHE-75-21340 (J.G.V.). One of us (R.V.H.) would like to thank NSF for a Graduate Fellowship (1973-1976) and one of us (F.A.H.) would like to thank IBM for a fellowship (1977-1978).

References and Notes

(1) (a) California Institute of Technology; (b) Iowa State University.
(2) Verkade, J. G. *Phosphorus Sulfur* **1976,** *2*, 251.
(3) White, D. W.; Verkade, J. G. *Phosphorus* **1973,** *3*, 9.
(4) Vande Griend, J. J.; Verkade, J. G.; Pennings, J. F. M.; Buck, H. M. *J. Am. Chem. Soc.* **1977,** *99*, 2459.
(5) Vande Griend, L. J.; Verkade, J. G. *Phosphorus* **1973,** *3*, 13.
(6) Heitsch, C. W.; Verkade, J. G. *Inorg. Chem.* **1962,** *1*, 863.
(7) Vande Griend, L. J.; White, D. W.; Verkade, J. G. *Phosphorus* **1973,** *3*, 5.
(8) White, D. W.; Verkade, J. G. *Phosphorus* **1973,** *3*, 15.
(9) Vande Griend, L. J.; Verkade, J. G. *Inorg. Nucl. Chem. Lett.* **1973,** *9*, 1137.
(10) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971,** *22*, 527.
(11) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, Jr., R. T.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977,** *99*, 5417. For a more complete discussion of the proton affinities of the methyl phosphines, see: Staley, R. H.; Beauchamp, J. L. *Ibid.* **1974,** *96*, 6252.
(12) Bowers, M. T.; Aue, D. H.; Webb, H. M.; McIver, Jr., R. T. *J. Am. Chem. Soc.* **1971,** *93*, 4314.
(13) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 47.
(14) Staley, R. H.; Kleckner, J. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976,** *98*, 2081.
(15) Henderson, W. G.; Taagepera, M.; Holtz, D.; McIver, Jr., R. T.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1972,** *94*, 4729.
(16) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1972,** *94*, 4726.
(17) McMahon, T. B.; Beauchamp, J. L. *Rev. Sci. Instrum.* **1972,** *43*, 509.
(18) Denney, D. B.; Varga, S. C. *Phosphorus* **1973,** *2*, 245.
(19) Verkade, J. G.; Hutteman, T. J.; Fung, M. K.; King, R. W. *Inorg. Chem.* **1965,** *4*, 83.
(20) Moedritzer, K.; Maier, L.; Groenweghe, L. C. D. *J. Chem. Eng. Data* **1962,** *7*, 307.
(21) Mosbo, J. A.; Verkade, J. G. *J. Am. Chem. Soc.* **1973,** *95*, 4659.
(22) Cowley, A. H.; Lattman, M.; Montag, R. A.; Verkade, J. G. *Inorg. Chim. Acta Lett.* **1977,** *25*, L151.
(23) Cowley, A. H.; Goodman, D. W.; Kuebler, N. A.; Sanchez, M.; Verkade, J. G. *Inorg. Chem.* **1977,** *16*, 854.
(24) Cowley, A. H.; Lattman, M.; Verkade, J. G., submitted for publication.
(25) Yarbrough, L. M.; Hall, M. B. *Inorg. Chem.* **1978,** *17*, 2269. These authors have also carried out ab initio MO calculations which show the first PE band of the bicyclic phosphite **3** to be mainly phosphorus in character [*J. Chem. Soc., Chem. Commun.* **1978,** 161].
(26) Verkade, J. G. *Bioinorg. Chem.* **1974,** *3*, 165.
(27) Hudson, R. F.; Verkade, J. G. *Tetrahedron Lett.* **1975,** 3231.
(28) Verkade, J. G. *Coord. Chem. Rev.* **1972,** *9*, 1.

Nucleophilic Reactions of Anions with Trimethyl Phosphate in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

Ronald V. Hodges, S. A. Sullivan, and J. L. Beauchamp*

Contribution No. 5690 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received July 25, 1978*

Abstract: The gas-phase ion-molecule reactions of several negative ions (SF_6^-, SF_5^-, SO_2F^-, F_2^-, F^-, CF_3Cl^-, Cl^-, CD_3O^-, DNO^-, OH^-, and NH_2^-) with trimethyl phosphate are investigated using ion cyclotron resonance techniques. Nucleophilic attack on $OP(OCH_3)_3$ occurs chiefly at carbon, resulting in displacement of $O_2P(OCH_3)_2^-$. This behavior contrasts with that observed in solution, where attack at phosphorus is favored for hard nucleophiles. This difference is ascribed to solvation energetics for the intermediates involved in the two reactions. The failure of SF_6^- to transfer F^- to $OP(OCH_3)_3$ places an upper limit of 11 ± 8 kcal/mol on the fluoride affinity of $OP(OCH_3)_3$). The significance of the results for the negative chemical ionization mass spectrometry of phosphorus esters is briefly discussed.

Bimolecular nucleophilic substitution reactions occupy an important place in the chemistry of phosphorus compounds.[1] All classes of phosphorus compounds are susceptible to nucleophilic attack. The esters of phosphoric acid are of special interest because of their biological significance. Some are essential to life processes, while the toxicology of others has

0002-7863/80/1502-0935$01.00/0