Energy, Offices of Energy Sciences, contract with R.J.W. The rhodium used in these studies was provided on loan from Matthey Bishop, Inc.

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On Correlating Phosphorus Core Binding Energies, Phosphorus Lone Pair Ionization Potentials, and Proton Affinities of Tervalent Phosphorus Compounds

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Abstract: Phosphorus core binding energies have been determined for a wide variety of tervalent phosphorus compounds. These values are compared with literature values of the corresponding lone pair ionization potentials and proton affinities. No single correlation is found between all the core binding energies and the corresponding lone pair ionization potentials or proton affinities, but the lone pair ionization potentials are linearly correlated with the proton affinities. It is concluded that the electronic relaxations accompanying lone-pair ionization and proton attachment are similar in character and energy, whereas the electronic relaxation accompanying core ionization is of a somewhat different type, in which atomic orbital rehybridization plays a relatively unimportant role.

Introduction

Several groups of workers have shown that, for certain compounds of oxygen, nitrogen, and phosphorus with nonbonding "lone-pair" electrons on these atoms, the oxygen, nitrogen, and phosphorus core electron binding energies are linearly correlated with the corresponding proton affinities.[2–4] Indeed, it has been claimed that core binding energy shifts can be used to predict proton affinities.[4] However, there is evidence that such correlation only holds when considering compounds which are very closely related, such as those in a homologous series of compounds.[3] On the other hand, correlations have been observed between "lone pair" ionization potentials and proton affinities[5–8] which appear to be more general than those

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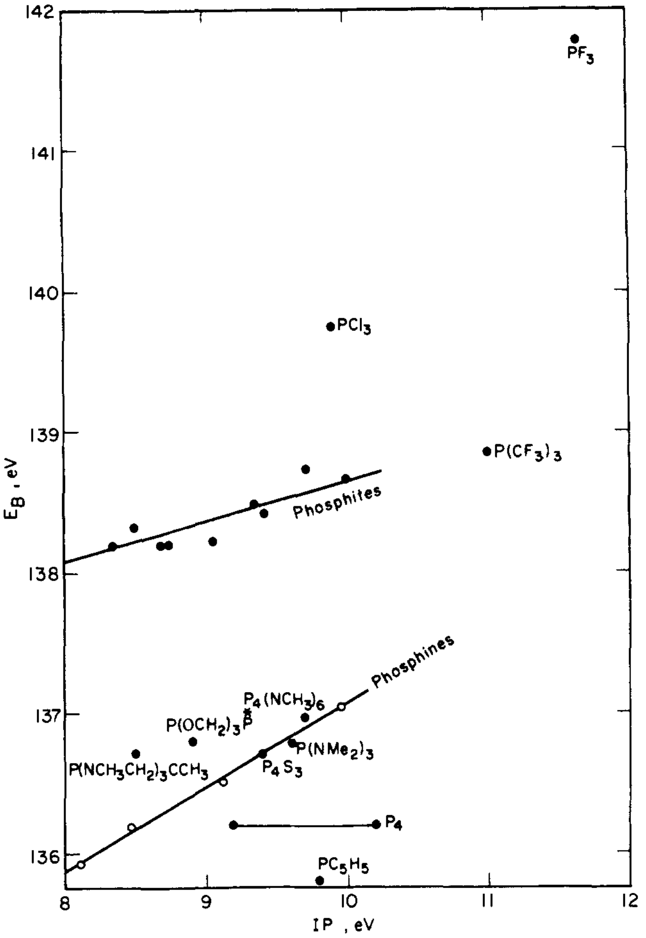

Figure 1. Plot of phosphorus $2p_{3/2}$ binding energy vs. phosphorus lone pair ionization potential for tervalent phosphorus compounds. The open circles correspond to the phosphines, PH_3-$P(CH_3)_3$.

between core binding energies and proton affinities. For example, the ionization potentials of a wide variety of tervalent phosphorus compounds (including phosphite esters, phosphines, and PF_3) are fairly well correlated with the corresponding proton affinities.[8] In this paper we discuss the factors which determine the magnitudes of core binding energies, ionization potentials, and proton affinities, emphasizing the differences between these three types of energy. For illustrative purposes we use data for tervalent phosphorus compounds; however, the principles discussed are applicable to all compounds containing lone-pair electrons.

Data for Tervalent Phosphorus Compounds

To widen the variety of tervalent phosphorus compounds for which core binding energies are known, we have measured the phosphorus $2p_{3/2}$ binding energies of 13 phosphorus compounds. By combining these values with values previously measured in our laboratory[9,10] and with a few other values from the literature,[4,11,12] we obtained phosphorus binding energies for 22 compounds containing phosphorus atoms with valence-shell lone-pair electrons. In this set of compounds, the phosphorus atoms are bonded to groups having a wide range of electronegativity and size, and the bonds to the phosphorus atoms are subject to a wide range of steric constraint. In Table I are listed the phosphorus $2p_{3/2}$ binding energies (E_B) and, where available, literature values for the adiabatic phosphorus lone pair ionization potentials[13-24] (IP) and proton affinities[8,12,19,25] (PA).

Plots of E_B vs. IP, E_B vs. PA, and IP vs. PA are shown in Figures 1, 2, and 3, respectively. Although the points in Figures 1 and 2 are quite scattered, we see that E_B is approximately linearly correlated with IP and PA *for groups of related compounds*, i.e., for the PH_3-$P(CH_3)_3$ series and the phosphite esters. The latter correlations are not very significant because practically any two physical properties of such closely related compounds as the phosphines or the phosphite esters would be expected to be closely correlated. In order to bring all the points in either Figure 1 or Figure 2 onto a single straight line, it would be necessary to make changes as great as several electronvolts in the plotted quantities. Therefore we believe that a reasonable interpretation of Figures 1 and 2 is that there is essentially no single correlation between all the E_B values and either the PA or IP values.

From Figure 3 we see, as has previously been pointed out,[8] that IP and PA are fairly well correlated for tervalent phosphorus compounds. However, the overall correlation is not perfect; it can be seen that the points for the phosphines lie distinctly below the points for the phosphite esters.

We determined the core binding energies of all the atoms (except hydrogen, of course) in each of the phosphorus compounds which we studied by X-ray photoelectron spectroscopy in this research. For the sake of completeness, the nonphosphorus core binding energies are listed in Table II.

Table I. Phosphorus $2p_{3/2}$ Binding Energies, Phosphorus "Lone Pair" Ionization Potentials, and Proton Affinities for Tervalent Phosphorus Compounds

compd	E_B, eV	IP, eV (adiabatic)	PA, eV[a]
PF_3	141.78[b]	11.66[c]	7.15[d]
P_4O_6	139.87[e]		
PCl_3	139.75[b]	9.9[f,g]	
$P(CF_3)_3$	138.85[e]	11.0[f,h]	
$OP(OCH_2)_2CMe$	138.73[e]	9.72[i]	8.69[f]
$\mathbf{P}(OCH_2)_3P$	138.67[e]	10.0[f,k,l]	
$P(OCH_2)_3CMe$	138.48[e]	9.35[i]	9.21[j]
$P(OCHCH_2)_3$	138.41[e]	9.42[i]	9.35[j]
$P(OMe)_3$	138.32[e]	8.50[m]	9.67[j]
$MeOP(OCMe_2)_2$	138.22[e]	9.06[j,n]	9.35[j,n]
$MeOP(OCMe_2)_2CH_2$	138.19[e]	8.34, 8.69, 8.74[j,o]	9.87, 9.75, 9.61[j,o]
$P(OCHMe_2)_3$	138.10[e]		
PH_3	137.04[p]	9.96[q]	8.33[q]
$P_4(NMe)_6$	136.97[e]	9.7[f,r]	
$P(OCH_2)_3\mathbf{P}$	136.80[e]	8.9[f,k,l]	
$P(NMe_2)_3$	136.78[e]	9.6[f,k]	
$P(NMeCH_2)_3CMe$	136.72[e]	8.5[f,k]	
P_4S_3	136.7[r]	9.4[f,t]	
$MePH_2$	136.51[u]	9.12[q]	8.96[q]
P_4	136.2[s]	9.2, 10.2[v]	
Me_2PH	136.19[u]	8.47[q]	9.48[q]
Me_3P	135.93[p]	8.11[j]	9.90[q]
PC_5H_5	135.8[p,w]	9.8[f,x]	8.62[w]

[a] The proton affinities have been corrected to the standard reference $PA(NH_3)$ = 207 kcal/mol (Houle, F.; Beauchamp, J. L., unpublished results). Thus the tabulated PAs are 0.20 eV higher than the literature values. The values plotted in Figures 2 and 3 have not been corrected. [b] Reference 9. [c] Reference 13. [d] Reference 25. [e] This work. [f] Adiabatic value estimated by extrapolation of the straight edge of the UV PES band to the base line, or estimated from the shape of the band. [g] Reference 14. [h] Reference 15. [i] Reference 16. [j] Reference 8. [k] Reference 17. [l] Reassignment of UV PES bands by present authors. [m] Reference 18. [n] Data for $MeOP(OCH_2)_2$. [o] Data for equatorial MeO isomer of $MeOP(OCHMe)_2CH_2$, axial MeO isomer of $MeOP(OCHMe)_2CH_2$, and $MeOP(OCH_2)_2CH_2$, respectively. [p] Reference 10. [q] Reference 19. [r] Reference 20. [s] Reference 11. [t] Reference 21. [u] Reference 4; the P 2p binding energies, relative to PH_3, were used. [v] References 22 and 23. [w] Reference 12. [x] Reference 24.

Energy Contributions to E_B, IP, and PA

Let us consider the energy terms which contribute to changes in E_B, IP, and PA. Each of the three processes,

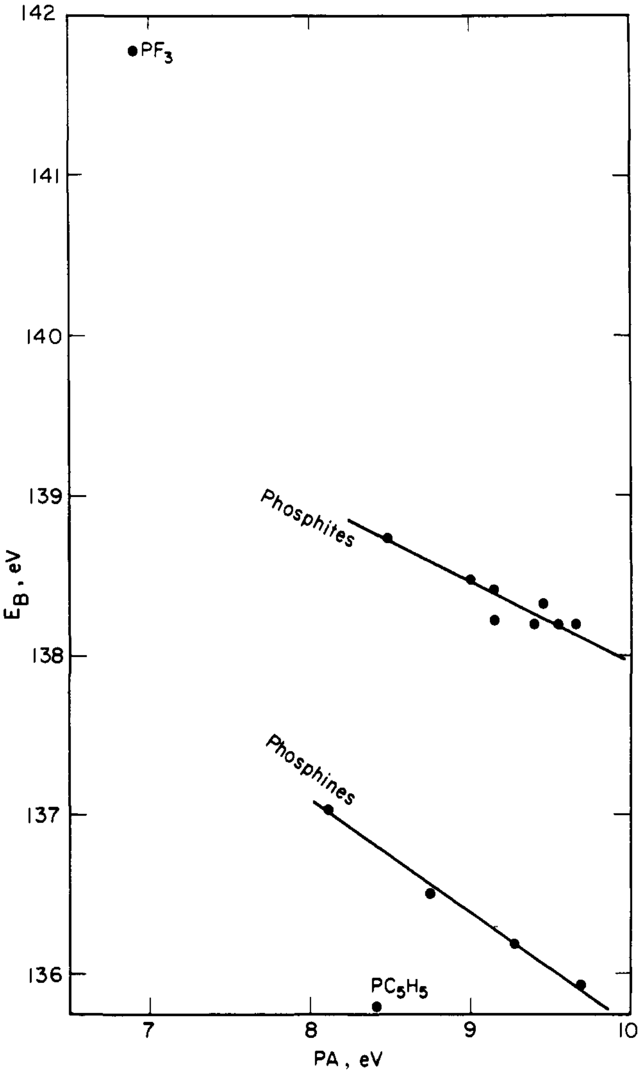

Figure 2. Plot of phosphorus $2p_{3/2}$ binding energy vs. proton affinity for tervalent phosphorus compounds. See footnote *a*, Table I.

namely, core ionization, lone-pair ionization, and proton attachment, can in principle be broken up into three hypothetical steps. (1) In the first step, the atom with the lone pair acquires a *localized* positive charge *without any simultaneous movement of the electrons or nuclei of the molecule.* When the overall process is protonation, this step simply involves the transfer of the proton to the valence shell. When the overall process is ionization, this step may be looked upon as the generation of a positron at a point in the atomic core or valence shell. (2) In the second step, the electrons in the resulting cation respond to the positive charge formed at the lone-pair atom. If the positive charge is due to a proton, electron density shifts toward the proton. If the positive charge is due to a "positron", an electron in the core or lone-pair orbital is annihilated, and the remaining electrons of the molecule shift toward the electron hole. (3) In the third step, bond distances and angles adjust to give the most stable geometric configuration of the cation. This step is applicable only in the case of adiabatic lone-pair ionization and proton attachment.

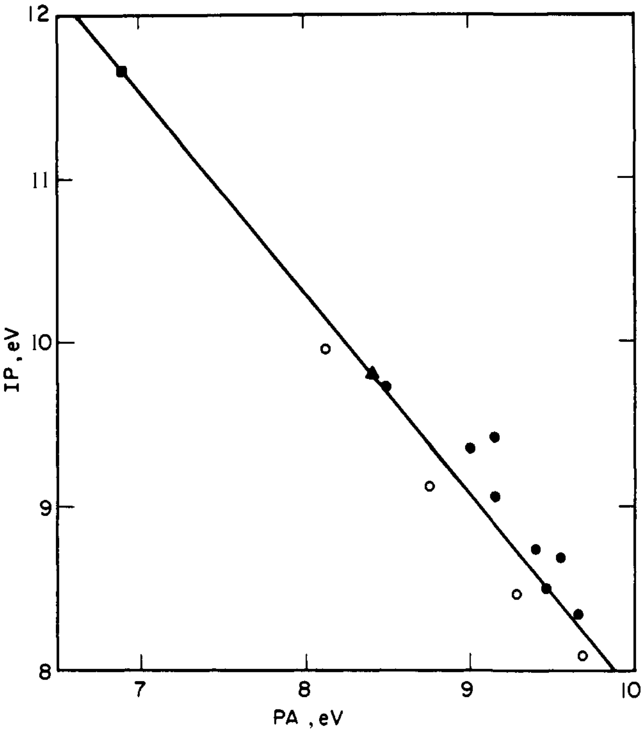

Figure 3. Plot of phosphorus lone pair ionization potential vs. proton affinity for tervalent phosphorus compounds. The solid points correspond to the phosphite esters, the open circles to the phosphines, the triangle to phosphabenzene, and the square to PF_3. See footnote *a*, Table I.

Table II. Nonphosphorus Core Binding Energies

	E_B, eV[a]	
compd	C 1s	O 1s, N 1s, or F 1s
$P(CF_3)_3$	298.88(5)	694.69(3)
P_4O_6		539.25(3)
$OP(OCH_2)_2CMe$	291.34(9) 292.66(3)	538.56(3)
$P(OCH_2)_3P$	292.32(2)	538.42(2)
$P(OCH_2)_3CMe$	291.34(6) 292.41(4)	538.28(3)
$P(OCHCH_2)_3$	290.88(9) 292.38(7)	538.20(5)
$P(OMe)_3$	292.36(3)	538.31(3)
$MeOP(OCMe_2)_2$	290.60(4) 292.31(4)	537.99(5)
$MeOP(OCMe_2)_2CH_2$	290.66(3) 292.36(4)	538.00(3)
$P(OCHMe_2)_3$	290.55(4) 292.10(7)	537.89(4)
$P_4(NMe)_6$	291.26(4)	403.92(3)
$P(NMe_2)_3$	291.15(4)	404.15(4)
$P(NMeCH_2)_3CMe$	290.99(4)	404.14(7)

[a] Uncertainty in last digit indicated parenthetically.

Electrostatic Energy. The energy of the first hypothetical step is essentially an electrostatic interaction energy. On going from one molecule to another, the *change* in this energy is mainly due to changes in the atomic charges of the molecule, especially to the change in the charge of the atom undergoing ionization or protonation. The change in the electrostatic energy has approximately the same magnitude in all three processes because, in each case, it is approximately equal to the change in the energy required to generate a unit positive charge in the "frozen" valence shell of an atom of a particular element. (We remind the reader that, in the valence shell model approximation, the energy of bringing a core electron up to the valence shell is independent of atomic charge.[26]) Thus the poor correlations between E_B and IP and between E_B and PA are not due to differences between the electrostatic energies of these processes. As we shall presently show, the poor correlations are mainly due to differences in the energies of the second hypothetical step—that is, to differences in the electronic relaxation energies.

Electronic Relaxation Energy. The energy of the second hypothetical step (the electronic relaxation energy) is mainly a measure of the energy associated with the flow of electron density to the atom which is ionized or protonated from other atoms in the molecule. In both lone-pair ionization and proton attachment, the electronic relaxation energy is partly a measure of the delocalization of the lone-pair orbital. The lone-pair orbital in some compounds is highly localized on one atom (a phosphorus atom, in our examples) and in others extends over a group of atoms, with a relatively small occupancy on any given atom. When an electron is removed from a highly localized lone-pair orbital, the positive charge ends up mainly on one atom and the electronic relaxation energy is relatively small. However, when an electron is removed from a highly delocalized lone-pair orbital, the resulting positive charge is delocalized, corresponding to a considerable flow of electron density in step 2 and a high electronic relaxation energy. The situation is similar during protonation. Thus, when a delocalized lone-pair orbital is protonated, there is a shift of electron density in this orbital toward the proton, that is, toward the bonding region, just as in lone-pair ionization.

However, electron flow occurs not only within the lone-pair orbital, but within all occupied molecular orbitals located partly on the atom which is ionized or protonated (the lone-pair atom). This flow would take place to a small extent even if the atomic orbital contributions to these molecular orbitals remained constant. However, in general some rehybridization takes place such as to increase the contribution of the lone-pair atom's valence s orbital to the molecular orbitals involved in bonding to other atoms. This rehybridization further increases the effective electronegativity of the atom and increases the electron flow. For example, the lone-pair orbital of PH_3 possesses considerable phosphorus 3s character, corresponding approximately to an $sp^{0.7}$ hybrid, according to ab initio localized orbital calculations.[27,28] Upon removal of one of the lone-pair electrons, considerable stabilization of the ion is achieved by rehybridization to give the lone-pair orbital more p character and the bonding orbitals more s character. Upon protonation of the lone pair to form PH_4^+, a similar rehybridization occurs to shift p character to the lone-pair orbital which has become a bonding orbital. Of course, these rehybridizations are affected by the stereochemical reorganizations which also occur (hypothetical step 3). However, extensive rehybridization occurs even when the nuclear positions are frozen. It should be noted that these remarks regarding rehybridization correspond essentially to recognition of the fact that Koopmans' theorem[29] does not accurately apply to valence-shell ionization.

In view of the similarity of the electron flows which occur in step 2 of lone-pair ionization and protonation, we would expect the electronic relaxation energies associated with these processes to be very similar in magnitude.

In the case of core ionization, the positive hole is completely localized on the lone-pair atom and causes contraction of the valence electron cloud of the atom, with a consequent increase in the effective electronegativity of all the valence atomic orbitals. Because the positive hole is in the atomic core and not in a region of high overlap of the lone-pair orbitals, the polarization and rehybridization of the lone-pair orbital are not as pronounced as in lone-pair ionization or protonation. Supporting evidence for our contention that rehybridization is more pronounced during protonation than during core ionization is presented in Table III. Here we list, for several tervalent phosphorus compounds, the phosphorus 3s density in the lone-pair orbital of the neutral molecule, in the corresponding P-H bonding orbital in the protonated molecule, and in the lone-pair orbital of the core ionized molecule, as calculated by the CNDO/2 method. In making the calculations for the core ionized molecules, we used the equivalent cores approximation;[30] that is, we used the isoelectronic sulfur cation as an analogue of the phosphorus core ionized molecule. It is obvious that both protonation and core ionization cause a reduction of the s character of the lone-pair orbital, but that the reduction is much greater for protonation than for core ionization.

Table III. Phosphorus s Orbital Density of Lone-Pair Orbital, CNDO/2 Calculated[a]

	3s density[b]		
molecule	parent molecule	protonated molecule	core-ionized[c] molecule
PH_3	0.222	0.007	0.109
PF_3	0.419	0.036	0.170
PC_5H_5	0.175	0.052	0.181
$P(CH_3)_3$	0.203	0.000	0.081
$P(OCH_3)_3$	0.240	0.026	0.130

[a] See Experimental Section for a description of the calculational procedure. [b] The square of the coefficient of the phosphorus (or sulfur) 3s orbital in the "lone pair" MO. [c] Calculated for the equivalent cores sulfur cation.

The point to be emphasized is that the electronic relaxations accompanying lone-pair ionization and proton attachment are probably very similar in character and energy, whereas the electronic relaxation accompanying core ionization is of a somewhat different type, in which atomic orbital rehybridization plays a relatively unimportant role.

Stereochemical Relaxation Energy. Core ionization takes place without any simultaneous motion of the nuclei of the molecule, whereas adiabatic lone-pair ionization and proton attachment are processes in which the nuclei move to form the most stable configurations for the resulting ions. That is, the stereochemical relaxation energy is zero for core ionization and finite for both lone-pair ionization and proton attachment. Some idea of the magnitudes of the stereochemical relaxation energies in the latter two processes can be obtained from calculations carried out for phosphine, PH_3. Ab initio calculations[31] show that the energy released when PH_3^+ (lone pair ionized) changes from the unstable configuration corresponding to neutral PH_3 (HPH angle = 93.8°) to the stable ionic configuration (HPH angle = 103°) is 0.27 eV. CNDO/2 calculations[12,32] show that the energy released when PH_4^+ shifts from a configuration in which three of the hydrogens are positioned as they are in PH_3 to the normal tetrahedral PH_4^+ configuration is 0.57 eV. Another estimate of the stereochemical relaxation energy in lone-pair ionization can be obtained from the difference between the vertical and adiabatic ionization potentials. Hodges et al. found that this difference was approximately constant and equal to ~0.6 eV for a large number of phosphites.[8] Thus all the data suggest that stereochemical relaxation energies associated with IP and PA, and the differences between them, are significant but small compared to the apparent discrepancies in Figures 1 and 2. We conclude that the lack of correlation of E_B with IP and with PA is principally due to differences in the electronic relaxation energies.

Discussion

Electron Flow Relaxation. We believe that the points in Figure 1 are widely scattered because, on going from one type of compound to another, the difference between the electronic relaxation energies associated with core ionization and lone-pair ionization changes markedly. We believe that the points in Figure 2 are similarly scattered because of the close analogy between the electronic relaxation processes associated with lone-pair ionization and protonation. Presumably all the points would fall on a single straight line of unit slope if the differences between these relaxation energies ($E_R(E_B) - E_R(\mathrm{IP})$ and $E_R(E_B) - E_R(\mathrm{PA})$) were constant. Because the differences in relaxation energy are probably mainly due to differences in the flow of electron density from the atoms near the phosphorus atom, we believe that for rough comparative purposes the net

Table IV. Electron Flow Accompanying Protonation and Core Ionization, CNDO/2 Calculated[a]

molecule	electron flow during lone pair ionization	electron flow during protonation	electron flow during core ionization[b]
PH_3	0.451	0.496	0.754
PF_3	0.401	0.390	0.519
PCl_3	0.756	0.747	0.898
PC_5H_5		0.604	0.785
$P(CH_3)_3$	0.614	0.616	0.746
$P(OCH_3)_3$, C_3[c]		0.587	0.707
$P(OCH_3)_3$, C_{3v}[c]		0.549	0.686

[a] See Experimental Section for a description of the calculational procedure. [b] Calculated using the equivalent cores approximation. [c] The C_3 structure is the normal structure; the C_{3v} structure is a stand-in for a constrained cyclic phosphite ester.

changes in atomic electron population can be used as measures of the relaxation energies. Thus, letting Q and Q^+ stand for atomic charges in the neutral and ionized molecules, respectively, we represent the flow of electron density during lone-pair ionization by $(1 - Q_P^+ + Q_P)$ and the flow of electron density during protonation by $(1 - Q_H^+ - Q_P^+ + Q_P)$. We represent the flow of electron density during core ionization (using the equivalent cores approximation) by $(1 - Q_S^+ + Q_P)$. These three types of electron flow, calculated by the CNDO/2 method, are presented in Table IV for several tervalent phosphorus compounds. The calculated electron flows are practically identical for lone-pair ionization and protonation, in accord with our expectation that the electronic relaxations during these processes are similar. Unfortunately, we were unable to calculate the lone-pair ionization electron flows for PC_5H_5 and $P(OMe)_3$ by the CNDO/2 method because, according to this method, the lone-pair orbitals of these compounds do not possess the lowest ionization potentials. For each compound in Table IV, the electron flow, and presumably the electronic relaxation energy, is greatest during core ionization. However, the magnitudes of the electron flow and the differences in electron flow between core ionization and the other processes show considerable variation. It is significant that the largest electron flows are found for PCl_3 and the lowest for PF_3. These results probably reflect the high polarizability of chlorine and the low polarizability and high electronegativity of fluorine. It should also be noted that the electron flow during protonation is 0.12 electron units greater for $P(CH_3)_3$ than for PH_3, although the electron flow during core ionization is practically the same for these compounds. This result probably explains the fact that the absolute slopes of the lines through the PH_3-$P(CH_3)_3$ points in Figures 1 and 2 are less than unity.

In an attempt to explain the low slopes of the lines through the phosphite ester points in these figures, we carried out electron-flow calculations for the normal, C_3 symmetry, structure of $P(OCH_3)_3$ and also for a hypothetical C_{3v} structure of $P(OCH_3)_3$ which was used as a stand-in for a constrained cyclic phosphite ester. The data do indicate slightly greater electron flow (greater relaxation energy) during protonation for the normal structure and indicate similar electron flows during core ionization for the two structures. These results are qualitatively in agreement with the fact that $P(OCH_3)_3$ has a relatively low IP and that the cyclic phosphite esters have higher IPs. The facts that the electron flow during protonation is slightly greater for $P(CH_3)_3$ than for PC_5H_5 and that the reverse is true for the electron flow during core ionization are consistent with the positions of the PC_5H_5 points in Figures 1 and 2. However, an abnormally low stereochemical relaxation energy is probably also responsible for the fact that the PC_5H_5 points are well separated from the PH_3-$P(CH_3)_3$ lines.[12]

Delocalization of the Lone-Pair Orbital. The electronic relaxation energy associated with IP and PA is considerably greater for the methylphosphines than for phosphine partly because of greater delocalization of the lone-pair orbital in the methylphosphines. The increased delocalization is obvious from the atomic orbital coefficients of the CNDO/2 wave functions for the molecules; it is due to overlap of the phosphorus lone pair with the C-H bonding electrons and increases with the number of methyl groups attached to the phosphorus atom. Probably a similar lone pair-bonding pair interaction occurs in the case of $P(CF_3)_3$. In PF_3, PCl_3, the phosphite esters, and the phosphorus-nitrogen compounds, delocalization of the "phosphorus lone pair" is caused by repulsion between the lone pairs on the phosphorus atom and the lone pairs on the adjacent electronegative atoms. In fact, the relative ionization potentials of the various phosphite esters can be rationalized by considering the magnitudes of the oxygen lone pair-phosphorus lone pair repulsions.[8,33] One of the oxygen lone pairs is assumed to be in an essentially sp^2 hybrid orbital which overlaps negligibly with the phosphorus lone pair, and the other lone pair is assumed to be in a p orbital perpendicular to the P-O-C plane. In $P(OCH_3)_3$, repulsions between the methyl groups are believed to cause the three P-O-C planes to be oriented such that the oxygen p lone pairs overlap strongly with the phosphorus lone pair, causing the IP to be one of the lowest in the set. In contrast, the carbon atoms in $P(OCH_2)_3P$ are constrained such that the three P-O-C planes coincide at the threefold axis of the molecule; thus the lone p orbitals on the oxygens are orthogonal to the phosphorus lone pair, causing the IP to be relatively high. Phosphites with intermediate degrees of steric constraint have intermediate IPs.

It is not immediately obvious why the relaxation energy associated with the IP of P_4 should be low, particular in view of the fact that the "lone-pair orbitals" of P_4 are, by symmetry, highly delocalized. The $6t_2$ orbital of P_4 is the highest occupied MO which has a symmetry such that it would overlap with a Lewis acid approaching along one of the threefold axes.[22,23] However, there is some uncertainty as to the assignment of the UV photoelectron spectrum of P_4, and so in Figure 1 we have plotted the IPs corresponding to two assignments[22,23] for $6t_2$: 9.2 and 10.2 eV. Calculations[22] show that the $6t_2$ orbital has a moderate electron density between the atoms and therefore is not a strictly nonbonding orbital. The bonding character of this orbital is probably responsible for the high IP. The highest orbital having almost entirely nonbonding character is the $5a_1$ orbital, with an even higher IP of 11.8 eV.

Tetraphosphorus Hexaoxide. The core binding energies of P_4O_6 deserve special comment. Because of structural similarities between this molecule and the phosphite esters, one might have expected the P $2p_{3/2}$ and O 1s binding energies of P_4O_6 to be similar to those of the phosphite esters. However, the P $2p_{3/2}$ and O 1s binding energies are higher by about 1.5 and 1.0 eV, respectively! We know of no good explanation for these data. CNDO/2 calculations yield the atomic charges $q_P = 0.442$ and $q_O = -0.295$ for P_4O_6, and $q_P = 0.427$ and $q_O = -0.268$ for $P(OMe)_3$. Consideration of these charges and the potentials leads to the prediction that the phosphorus binding energies should be very similar and that the oxygen binding energy of $P(OMe)_3$ should be greater than that of P_4O_6. The changes in the phosphorus and nitrogen binding energies in the analogous pair of compounds, $P_4(NMe)_6$ and $P(NMe_2)_3$, are much less pronounced, and even in the opposite direction in the case of the nitrogen binding energies.

Experimental Section

X-ray Photoelectron Spectra. Gas phase X-ray photoelectron spectra were obtained using a GCA/McPherson ESCA 36 spectrometer equipped with an ESCA 36-U gas cell, a magnesium anode, and a cryopump. The experimental procedures and methods for calibrating the spectrometer are described in a recent paper.[34] The measured binding energies were reproducible to within 0.1 eV; in most cases the reproducibility was better than ±0.05 eV. Binding energies were determined from the spectra by a least-squares fitting of the points to Gaussian curves.[35]

Compounds. The cyclic phosphite esters $\overline{OP(OCH_2)_2C}Me$,[33b] $P(OCH_2)_3P$,[36] $P(OCH_2)_3CMe$,[37] $P(OCHCH_2)_3$,[38] $MeOP(OCMe_2)_2$,[39] and $MeOP(OCMe_2)_2CH_2$[40] were prepared and purified by literature methods. The acyclic phosphite esters $P(OMe)_3$ and $P(OCHMe_2)_3$ as well as $P(NMe_2)_3$ were obtained from Aldrich and distilled under nitrogen before use. The bicyclic aminophosphine $P(NMeCH_2)_3CMe$[41] was prepared and purified following a literature report. The compounds were judged sufficiently pure when they showed one spot by thin layer chromatography or when they displayed ^{31}P NMR, ^1H NMR, and mass spectra (high resolution) consistent with only the presence of the desired compound. The P_4O_6 was kindly provided by Professor J. Mills; it melted at 23.9–24.1 °C (lit.[42] 23.8 °C). The $P(CF_3)_3$ was a gift from R. A. Andersen. The vapor pressure at 0 °C was 399 Torr (lit.[43] 400 Torr). The tetraphosphorus hexamethylhexaimide was prepared by the method of Holmes and Forstner;[44] it melted at 121–122 °C (lit. 122–123 °C) and its infrared spectrum agreed with the literature. All transfers of the compounds were carried out under an inert atmosphere.

CNDO Calculations. The calculations were performed using the CNDO/2 program as modified by Sherwood.[45] Literature structural data were used for the molecules PH_3,[46] PF_3,[47] PCl_3,[48] PC_5H_5,[49] PMe_3,[50] $P(OMe)_3$,[51] and P_4O_6.[52] The normal C_3 form of $P(OMe)_3$ was assumed to have the conformation corresponding to the following atomic coordinates (Å): P(0.0, 0.0, 0.0); O(1.390, 0.0, −0.819) (−0.695, 1.203, −0.819) (−0.695, −1.203, −0.819); C(1.571, 0.931, −1.876) (−1.591, 0.895, −1.876) (0.021, −1.826, −1.876); H(2.552, 0.814, −2.336) (1,491, 1.955, −1.512) (0.819, 0.791, −2.653) (−1.981, 1.803, −2.336) (−2.439, 0.313, −1.512) (−1.094, 0.313, −2.653) (−0.571, −2.617, −2.336) (0.948, −2.268, −1.512) (0.276, −1.104, −2.653). The C_{3v} form of $P(OMe)_3$ was assumed to have the following atomic coordinates (Å): C(1.357, 0.0, −2.239) (−0.678, 1.175, −2.239) (−0.678, −1.175, −2.239); H(1.357, −1.018, −2.629) (2.224, 0.517, −2.649) (0.462, 0.501, −2.609) (0.203, 1.684, −2.629) (−1.560, 1.668, −2.649) (−0.665, 0.150, −2.609) (−1.560, −0.666, −2.629) (−0.665, −2.185, −2.649) (0.203, −0.651, −2.609). The data in Tables II and III for the protonated molecules were calculated by placing the proton on the principal molecular axis with a P–H distance of 1.414 Å, as in PH_4^+.[53] The equivalent cores sulfur cations were assumed to have structures identical with those of the parent phosphorus compounds.

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