Core-Ionization Energies and the Anomalous Basicity of Arsabenzene and Phosphabenzene

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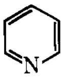
Abstract: To help understand the anomalously low basicity of arsabenzene and phosphabenzene we have investigated the correlation between the core-ionization energies and proton affinities for arsabenzene, phosphabenzene, arsine, trimethylarsine, phosphine, and the methylphosphines. The results support the view that the low basicity is due to the inability of the aromatic compounds to undergo geometric rearrangement on protonation. Comparison of the Auger kinetic energies with core-ionization energies gives an estimate of 0.45 eV for the stabilization energy due to the resonance delocalization of the charge on phosphine following core ionization. Further comparison of these quantities indicates that a methyl group and an aromatic ring are both electron donating compared to hydrogen.

Introduction

The recent synthesis[2-4] of the pyridine homologues shown below has made it possible to see how the properties of heterobenzenes vary with changes in the heteroatom. A variety of spectral techniques[5-7] indicate that there are similar aromatic properties throughout the series. Structural studies show that **1–4** have planar C_{2v} rings with typical aromatic C–C bond lengths (1.40 ± 0.03 Å).[8]



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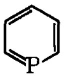

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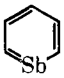

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In contrast, chemical studies have shown the heavier heterobenzenes to be markedly different from pyridine. The chemistry of pyridine is dominated by its basicity. However, in solution **2–5** show no basic properties.[5] These qualitative solution-phase observations are reflected in the gas-phase proton affinities of phosphabenzene and arsabenzene.[9] For nitrogen compounds, the proton affinity (or gas-phase basicity) increases in the order NH_3, CH_3NH_2, $(CH_3)_2NH$, pyridine, $(CH_3)_3N$, whereas for phosphorus the order is PH_3, phosphabenzene, CH_3PH_2, $(CH_3)_2PH$, $(CH_3)_3P$. For arsenic the complete series has not been studied, but the proton affinity of arsabenzene is only slightly greater than that of arsine. A quantitative comparison of the proton affinities of these compounds indicates that the proton affinities of phosphabenzene and arsabenzene are about 80 kJ/mol less than would be expected from the systematic behavior of the other compounds.

The source of this anomalously low basicity is uncertain. It has been suggested that the phosphorus lone pair may be too diffuse to form a strong bond to a proton.[10] Alternatively it has been argued that the ring structure of phosphabenzene prevents necessary changes in geometry on protonation.[5] These two explanations are, however, closely related to one another. In phosphine, for instance, the HPH bond angle is 93°; the corresponding bond hybridization is predominantly p^3 with little s participation. The lone pair is almost pure s and is, therefore, diffuse, that is, spread over a wide range of angles. For a strong bond to form with an added proton, the lone pair must become more directed and, hence, must acquire additional p character. The P–H bonds must take on more s character and the bond angles shift to the tetrahedral angle (as required also by the symmetry of the PH_4^+ ion). In phosphabenzene, however, the rigidity of the rest of the ring prevents a change in the CPC angle and prevents a decrease in the diffuseness of the lone pair through rehybridization. A strong bond cannot form.

A number of correlations have established that proton affinities (basicities) are closely related to core-ionization energies.[11-17] Since core ionization is a vertical process, it is sensitive only to the electronegativity of the atom ionized (that is, to its electronic ability to accept positive charge), to the electronegativity of the surrounding atoms, and to the ability of the surrounding atoms to delocalize the positive charge. Protonation, on the other hand, is adiabatic and depends not only on the factors just mentioned, but also on the ability of the molecule to undergo geometric rearrangement. The failure of the proton-affinity-core-ionization point for a compound to fall on the correlation line established by other compounds suggests that it undergoes different geometric rearrangements than do the reference compounds.[14] A comparison of the proton-affinity and core-ionization data for phosphabenzene and arsabenzene with those for phosphines and arsines should give information on the importance of geometric rearrangement in the protonation of these substances. We report here on such a comparison.

Experimental Section

Sample Preparation. Arsabenzene and phosphabenzene were synthesized according to methods described by Ashe.[2] Phosphine was prepared by reaction of calcium phosphide with water and purified by distillation under vacuum. Trimethylarsine was purchased from Strem Chemicals, Inc., and used without further purification. Arsine was obtained from one of our colleagues.

Measurements. X-ray photoelectron spectra and Auger spectra of the gaseous substances were measured in the Oregon State University cylindrical mirror analyzer.[18] Aluminum Kα radiation was used to excite the arsenic samples. For the phosphorus samples we used an anode containing both aluminum and silver. The aluminum X-rays provided the phosphorus 2p photoelectron spectra while the silver Lα X-rays excited the KLL Auger transitions.

For the arsenic measurements the sample gases were mixed with argon for calibration.[19] The argon 2p line is close to the arsenic $L_2M_{4,5}M_{4,5}$ Auger peaks and to the arsenic 3s photoemission peak, and, consequently, the spectrum for calibrant and sample could be run in one sweep. Typical results for the three arsenic compounds are shown in Figure 1. The value of the spectrometer constant was determined by comparison of the positions of the argon 2p and LMM Auger peaks, which were run simultaneously. The spectra were also run without argon, in order to establish the shape of the Auger spectrum without interference from the Al K$\alpha_{3,4}$ satellite of the argon spectrum.

The phosphorus samples were run mixed with neon; the neon Auger

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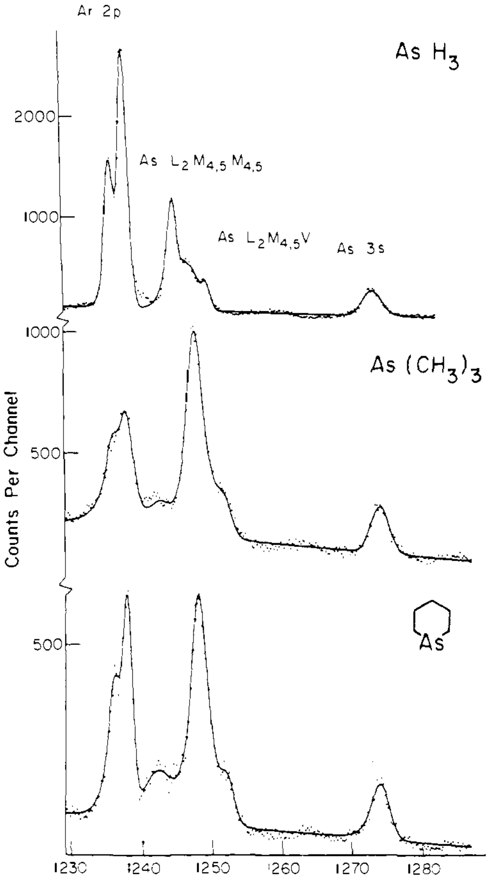

Figure 1. Argon 2p, arsenic LMM Auger, and arsenic 3s electron spectra for arsine, trimethylarsine, and arsabenzene. The argon was included for calibration purposes. The solid lines represent least-squares fits to the data.

(^{1}D) line[19] and the neon 1s line[19] excited by silver Lα_1 radiation (2984.31 eV[20]) were used for calibration.

Peak positions were determined by least-squares fits of Gaussian functions to the data; the solid lines in Figure 1 represent these fits. The ionization potentials and Auger kinetic energies are summarized in Table I. Except for arsine, each result is the average of at least two measurements; the root mean square difference between duplicate measurements is 0.1 eV.

Discussion

There are well-established linear correlations between core-ionization potentials and proton affinities (or Lewis basicities) for oxygen, nitrogen, and phosphorus compounds.[11-17] In general, the slope of these lines is close to minus one. The reason for this relationship is that removal of an electron from an atom is electrically equivalent to addition of a proton; the principal difference between the two processes is that electron removal is vertical whereas proton addition is adiabatic. If, however, there is no change in geometry during protonation, or if all molecules of a given series of compounds undergo similar geometrical changes on protonation, then we expect to find good correlations between proton affinities and core-ionization energies. For molecules containing oxygen and nitrogen the geometry of the protonated species is similar to that of the neutral species. A good linear correlation with slope minus one has been reported by Cavell and Allison[16] for nitrogen compounds, including pyridine. For the phosphines[14] the slope of the correlation has been reported to be −0.6; the deviation from unity has been attributed to the substantial geometric change that occurs on protonation of the phosphines.

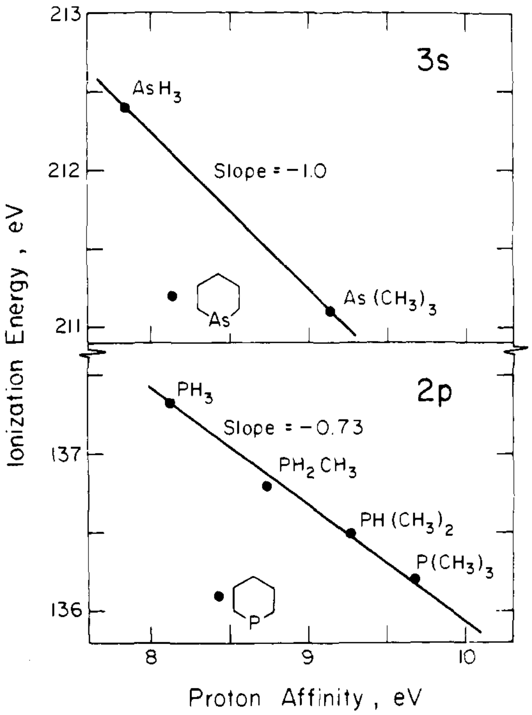

Figure 2. Correlation between core-ionization energy and proton affinity for arsenic and phosphorus compounds. The arsenic data and the points for phosphabenzene and phosphine are from this work. The other phosphorus points are from ref 14, normalized to our data at phosphine.

Table I. Core-Ionization Energies and Auger Kinetic Energies for Arsenic and Phosphorus Compounds

compd	core-ionization energy, eV[a]	Auger kinetic energy, eV[b]
AsH_3	212.4	1245.1
$As(CH_3)_3$	211.1	1247.9
arsabenzene	211.2	1248.2
PH_3	137.3	1841.4
phosphabenzene	136.1	1845.3

[a] 3s for arsenic. 2p multiplet average for phosphorus. [b] $L_2M_{4,5}M_{4,5}(^1G)$ for arsenic. KLL (^{1}D) for phosphorus.

The correlations between proton affinity and core-ionization potential for arsenic and phosphorus compounds are shown in Figure 2. For proton affinities we have used the data reported by Hodges, Beauchamp, and Ashe.[9,21] The arsenic core-ionization energies are those we have measured. For the phosphorus compounds we have used the shifts reported by Mills, Martin, and Shirley,[14] normalized to our absolute value for phosphine. We note first that the data for phosphines and arsines fall on lines with slopes −0.73 and −1.0, respectively. The difference between the slope of −0.73 given here and that of −0.6, reported by Mills, Martin, and Shirley, arises from our use of more recent values of the proton affinities. The difference in slope between the phosphorus and arsenic compounds is surprising, since the arsines and phosphines both undergo the same sort of geometric change on protonation.

The significant point to be noted in Figure 2 is the large deviation of the arsabenzene and phosphabenzene points from the lines established by the arsines and phosphines. In particular, the proton affinities are substantially lower than would be expected from the core-ionization energies. The situation here is in contrast to that for the corresponding nitrogen compounds, where the aliphatic and aromatic amines all fall on the same correlation line.[16]

For the nitrogen compounds, the bond angles (HNH, HNC,

Table II. Relative Relaxation Energies for Arsenic Compounds Derived from Auger and Core-Ionization Energies

compd	ΔR, eV
AsH_3	0
$As(CH_3)_3$	0.75
arsabenzene	0.95

and CNC) in the unprotonated species are close to those of the protonated species. No geometric rearrangement takes place and, hence, the data for the aliphatic and aromatic compounds are on the same line. For the phosphorus and arsenic compounds, the bond angles change significantly on protonation of the aliphatic species; a stabilization of the protonated species results from this rearrangement. A similar rearrangement is not possible for arsabenzene and phosphabenzene, with the result that their proton affinities and basicities are anomalously low compared to those of the arsines and phosphines. Comparison of the data for arsabenzene and phosphabenzene with the correlation lines indicates that this molecular rearrangement energy is about 0.9 eV for the arsines and about 1.4 eV for the phosphines. These numbers are only approximate, since, as has been noted by Mills, Martin, and Shirley,[14] the molecular rearrangement energy varies as hydrogen is replaced by methyl in the phosphine series.

For an order of magnitude theoretical estimate of this rearrangement energy, we have done CNDO/2 calculations of the energy of a PH_4^+ ion in two configurations. The first is the tetrahedral geometry, representing the ground state of the ion. In the second, three hydrogens have HPH bond angles of 93.3°, as in neutral phosphine. The fourth hydrogen is at the position of an added proton. This species represents the ion before geometric rearrangement has taken place. For both species the bond length was 1.42 Å. The difference in energy between these two species is 0.5 eV, significantly smaller than our experimental estimate, but of the same magnitude.

Additional information about the source of the basicity can be obtained from a comparison of core-ionization energies with Auger energies.[22-29] The proton affinity depends on three factors: the charge distribution in the original molecule (initial-state effect), charge rearrangement after protonation (final-state effect—the positive charge is delocalized over the molecule), and geometric rearrangement (as discussed above). Since core ionization is a vertical process, the core-ionization energy depends only on the first two of these. The shift in core-ionization energy, ΔE, relative to that in some reference compound, can be written as

$$\Delta E = \Delta E_1 - \Delta R \qquad (1)$$

where ΔE_1 is the shift due to the initial-state charge distribution and ΔR is that due to the rearrangement of the valence electrons to redistribute the positive charge. The Auger kinetic energies also depend on these two quantities. For the Auger kinetic energy, K, the corresponding expression is approximately

$$\Delta K = -\Delta E_1 + 3\Delta R \qquad (2)$$

The sum of the core-ionization-energy shift, ΔE, and the Auger kinetic-energy shift, ΔK, is equal to $2\Delta R$, or twice the contribution of electronic relaxation to the core-ionization shift. It should be noted that the factor 2 depends on an assumption of constant polarizability of the surrounding medium (in the classical derivation of expressions 1 and 2) or on an assumption that certain different Coulomb matrix elements are equal to one another (in the quantal derivation). Experimental evidence suggests that it might be as large as 3.

Inspection of the positions of the various peaks in Figure 1 shows that the Auger 3s spacing is noticeably greater for arsine than for either trimethylarsine or arsabenzene. Values of ΔR (relative to arsine) derived from comparison of the Auger energies and core-ionization energies (using the factor of 2 discussed above) are given in Table II. The electronic relaxation energy for trimethylarsine and arsabenzene is significantly greater than that for arsine. This is the expected result; the species attached to arsenic in trimethylarsine and arsabenzene are much more polarizable than the hydrogens of arsine. It is also to be noted that the relaxation energy for arsabenzene is about 0.2 eV higher than that for trimethylarsine. This result presumably reflects the possibility of resonance delocalization of the positive charge in arsabenzene that is not possible for trimethylarsine. The relaxation due to resonance structures is probably greater than this 0.2-eV difference, since there are three carbons attached to the arsenic in trimethylarsine and only two in arsabenzene. A more appropriate comparison would be between arsabenzene and dimethylarsine. By linear interpolation between arsine and trimethylarsine, we estimate the electronic relaxation-energy shift between dimethylarsine and arsabenzene to be 0.45 eV. This energy represents approximately the extra stability gained by the protonated arsabenzene through resonance delocalization of the positive charge. This value, which corresponds to about 43 kJ/mol, is reasonable. It is large enough to be chemically significant but still small compared to the total resonance stabilization energy of the benzene ring (151 kJ/mol).[30] Phosphabenzene and arsabenzene provide a unique opportunity to measure this effect directly, since (1) they incorporate a readily identifiable heteroatom into the ring, and (2) the Auger transition (which is core to core in second- and third-row atoms) can be used to measure the relaxation.

Equations 1 and 2 can also be solved to give ΔE_1, the part of the shift that is due to the initial state charge distribution. From these equations we have

$$\Delta E_1 = (3\Delta E + \Delta K)/2$$

For trimethylarsine and arsabenzene, relative to arsine, the values of ΔE_1 are −0.55 and −0.25 eV, respectively. From this we conclude that in the neutral molecule the methyl group or the aromatic ring is relatively electron donating compared to hydrogen. Although this result is at odds with the usual ideas about the relative electronegativities of hydrogen and carbon, the same conclusions are reached from similar considerations of germanium compounds,[29] from theoretical calculations on gas-phase acidities and basicities,[31] and from comparisons of experimental core-ionization potentials with gas-phase acidities and basicities.[17]

Summary

For phosphabenzene and arsabenzene the data on the core-ionization energy and proton affinity fall well off the correlation line for the phosphines and arsines. This result is consistent with the belief that the low basicity of phosphabenzene and arsabenzene is due to the inability for these molecules to change their configuration after protonation. From the experimental data it is possible to estimate that the phosphines gain 1.4 eV on rearrangement after protonation and the arsines 0.9 eV.

Comparison of the Auger kinetic energies with the core-ionization energies makes it possible to estimate the relative extra-atomic relaxation energy for the various compounds. Of particular interest is the comparison between arsabenzene and dimethylarsine, which gives a measure of the extra relaxation associated with the resonance delocalization of charge in the aromatic ring.

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Carbon Dioxide Activation. Deoxygenation and Disproportionation of Carbon Dioxide Promoted by Bis(cyclopentadienyl)titanium and -zirconium Derivatives. A Novel Bonding Mode of the Carbonato and a Trimer of the Zirconyl Unit

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Abstract: Carbon dioxide is quantitatively deoxygenated to carbon monoxide by $[Cp_2TiCl]_2$ [$Cp = \eta^5\text{-}C_5H_5$] which is converted to $[Cp_2TiCl]_2O$, while $Cp_2Ti(CO)_2$ promotes the disproportionation of CO_2 to CO and carbonato. This reaction gives rise to a tetranuclear carbonato complex of titanium(III), $[(Cp_2Ti)_2(CO_3)]_2$, in which the $CO_3{}^{2-}$ ligand, engaged in a novel bonding mode, bridges three Cp_2Ti units. The ν_{CO} stretching frequencies for the coordinated $CO_3{}^{2-}$ fall at 1475 m-s and 1425 v-s cm^{-1}, and, as confirmed by the isotopic labeling, the two bands in $[(Cp_2Ti)(^{13}CO_3)_2]_2$ are at 1432 and 1385 cm^{-1}. Carbon dioxide converts $Cp_2Zr(CO)_2$ to the cyclic trimer $(Cp_2ZrO)_3$, which is unprecedented both in cyclopentadienyl and zirconium chemistry. The X-ray structural analysis showed that $(Cp_2ZrO)_3$ contains a six-membered, nearly planar ring, formally derived from the trimerization of the zirconyl unit Zr=O. Noteworthy are both the Zr-O bond distances, which are not significantly different [average value of 1.959 (3) Å], and the Zr-O-Zr bond angles averaging to 142.5 (2)°. These values indicate the presence of a multiple Zr-O bond. Crystallographic details for $[(Cp_2Ti)_2(CO_3)]_2$: space group *Cmca* (orthorhombic), $a = 11.282$ (1) Å, $b = 16.038$ (1) Å, $c = 19.729$ (2) Å, and $Z = 4$. The final R factor is 5.8% for 1508 observed reflections. Crystallographic details for $(Cp_2ZrO)_3{\cdot}C_7H_8$: space group $P2_1/c$ (monoclinic), $a = 10.230$ (1) Å, $b = 18.612$ (2) Å, $c = 17.406$ (2) Å, $\beta = 95.27$ (1)°, and $Z = 4$. The final R factor is 4.3% for 4153 observed reflections.

Introduction

Recently much interest was focused on "model" complexes which could realize fixation and/or elementary transformations of carbon dioxide.[2,3] At present, however, while there are several reports on the insertion reactions of CO_2,[2-4] little is known concerning its fixation, or other metal-promoted transformations, such as disproportionation, dimerization, and deoxygenation. This mainly results from lack of strategy to find complexes able to realize, at the least, CO_2 coordination. In several cases, CO_2 seems to require a bifunctional system, i.e., acid–base, for its fixation and activation,[5] while inorganic chemists normally employ monofunctional complexes in molecular activation processes. The highly basic Ir(I),[6,7] Rh(I),[8] and Ni(0)[9] complexes, which so far have been found to be

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