follows. (1) The equilibrium constant between the two kinds of excited states in thermal equilibrium and their dipole moments in various solvents have been determined by means of picosecond quantitative transient spectroscopy. (2) Rapid and slow formations of the Y state have been observed in 2-propanol solution. The rapid formation of the Y state may be caused by the excitation of ADMA molecules with weak intramolecular charge-transfer character in the ground state due to the interaction with 2-propanol. A slight reorientation of the solvent in close contact with ADMA will be sufficient, for its electronic structure becomes practically the same as that of the Y state and will be followed by a more extensive reorganization of the surrounding solvent molecules as well as a geometrical structural change of ADMA. (3) In the slow formation process in 2-propanol solution, any specific strong interaction between ADMA and polar solvent molecules may not exist at the moment of excitation, and the reorientation of solvent molecules and the twisting motion of

excited ADMA will be coupled with each other, leading to the extensive charge separation. Although the Y state formation mechanism in other polar solvents examined in this work may be analogous to the case of 2-propanol solution, not only the "rapid" process but also the "slow" process in those solvents may be much faster than in 2-propanol, owing to their low viscosity. (4) The importance of the wide-band picosecond transient absorption spectroscopy for the elucidation of the solvent-induced electronic structure change in the excited composite molecules has been clearly demonstrated.

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Theoretical Studies of the Gas-Phase Proton Affinities of Molecules Containing Phosphorus–Carbon Multiple Bonds

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Theoretical values for the gas-phase proton affinities (PA's) of phosphaethyne, phosphaethene, and phosphabenzene have been obtained from ab initio SCF calculations employing analytic gradient techniques for geometry optimization. The sensitivity of the results to the choice of basis set and to the inclusion of correlation is discussed. The PA's for P-site and C-site protonation are found to be nearly equal in both phosphaethene and phosphabenzene at the split-valence SCF level; however, polarization functions and electron correlation both act to favor P-site protonation over C-site protonation, resulting in an isomerization energy of approximately 50 kJ mol^{-1}. By contrast we find C-site protonation to be strongly favored over P-site protonation for phosphaethyne even at the split-valence SCF level. Comparisons are made to computed and observed PA's both for saturated C–P systems and for saturated and unsaturated C–N systems. The computed order of basicities, $H_3CPH_2 > C_5H_5P > PH_3 > H_2CPH > HCP$ (C-site), differs from that for the corresponding N systems, namely, $C_5H_5N > H_3CNH_2 > H_2CNH \approx NH_3 > HCN$, not only in the lower position of C_5H_5P, as is well-known, but also in the lower position of H_2CPH.

I. Introduction

The gas-phase proton affinities (PA's) of the P and As analogues of pyridine, namely, phosphabenzene and arsabenzene, have been recently determined[1] by the ion cyclotron resonance (ICR) technique to be 820.0 and 792.8 kJ mol^{-1}, respectively, relative to a value of 852.7 kJ mol^{-1} for NH$_3$. These values are significantly less than the PA of pyridine, which is 918.8 kJ mol^{-1}. Perhaps even more interesting, deuterium labeling experiments[1] have indicated that P-site protonation occurs for phosphabenzene, while C-site protonation occurs for arsabenzene.[2] These results have prompted us to carry out a theoretical investigation of the gas-phase PA's and site preferences not only for phosphabenzene (C$_5$H$_5$P) but also for phosphaethene (H$_2$CPH) and phosphaethyne (HCP), all of which contain phosphorus–carbon multiple bonds.

Previous theoretical studies[3-6] of the PA's of phosphorus containing molecules have largely focused upon phosphine and alkyl phosphines, although values for the phosphorus-site (P-site) PA

of H$_2$CPH and HCP have been obtained[3] at the STO-3G and 3-21G levels. Protonation at P in C$_5$H$_5$P was explored earlier by Clark and Scanlan,[6] but without geometry optimization, while Thompson reported[7] partially optimized STO-3G and 4-31G energies for H$_2$CPH but not for the protonated species. A detailed study of HCP and FCP is that of Thompson and Ellams,[8] but

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again no protonated species were considered.

II. Method

The proton affinity (PA) of a base B may be defined as $-\Delta H^{\circ}{}_{298}$ for the gas-phase reaction

$$B + H^+ \rightarrow BH^+ \qquad (1)$$

Thus the PA may be written as

$$PA = -\Delta E_0{}^{el} - \Delta ZPE - \int_0^{298} \Delta C_p \, dT \qquad (2)$$

where $\Delta E_0{}^{el}$ is the electronic energy difference $E(BH^+) - E(B)$, ΔZPE is the zero-point energy difference $ZPE(BH^+) - ZPE(B)$, and ΔC_p of the molar heat capacity difference at constant pressure $\bar{C}_p(BH^+) - \bar{C}_p(B) - \bar{C}_p(H^+)$. If B and BH^+ possess the same number of rotational degrees of freedom and if vibrational and electronic contributions to the difference $\bar{C}_p(BH^+) - \bar{C}_p(B)$ are ignored, then the last term in (2) reduces to the small H^+ contribution of $+5RT/2$, or 6.2 kJ mol^{-1} at 298 K, which has not been included in our calculations. In contexts where a distinction is important, we use the symbols PA to refer to calculated values of $-\Delta E_0{}^{el} - \Delta ZPE$ and PA$_{el}$ to refer to $-\Delta E_0{}^{el}$ alone. In some general contexts we use the symbol PA for the latter, while experimental PA's which are quoted include all contributions to $-\Delta H^{\circ}{}_{298}$.

A wide variety of basis sets were employed in out studies, namely, minimal[9] (STO-3G), split-valence[10,11] (3-21G, 4-31G), and polarization[10,12] [6-21G* (with d orbitals on P), 6-31G* (with d orbitals on C and P), 6-21G**, 6-31G** (with d orbitals on C and P, with p orbitals on H)] basis sets. The geometries of the protonated and unprotonated molecules were optimized by using energy gradients at the SCF (single determinantal) level with various basis sets (see section III). Energy differences were calculated at the Hartree–Fock (HF), second- through fourth-order Møller–Plesset perturbation theory (MP2, MP3, and MP4SDQ), and configuration interaction involving double excitation (CID) levels. Inner shells were excluded from CID calculations, while the unrestricted Hartree–Fock (UHF) method was used for triplet states. Calculations with d polarization functions employed all six second-order Gaussians. A description such as MP2/6-31G* is used to designate the method and basis set employed in an energy calculation. If the geometry was optimized at a level different from the energy calculation, this is denoted by a second energy descriptor, i.e., MP2/6-31G*//HF/3-21G indicates that the energy was calculated at the MP2 level with the 6-31G* basis by using the geometry optimized at the HF/3-21G level. Vibrational frequencies and zero-point energies were computed from analytical second derivatives[13] at the HF/3-21G level. Calculations were made either at the Institute for Molecular Science with the IMSPACK series of programs or at the University of Michigan and Wayne State University with the GAUSSIAN 80 program.[14]

For the smaller molecules, namely, HCP, H$_2$CPH, H$_3$CPH$_2$, PH$_3$, and their protonated forms, we have used a variety of optimized geometries obtained at levels ranging from HF/STO-3G to HF/6-31G*. A number of these geometries, such as the

TABLE I: Calculated Energies for HCP and Energy Differences for Protonated HCP

level	$E(HCP)^a$	PA$_{el}^-$ (P)^{b,c}	PA$_{el}^-$ (C)^b	$\Delta E^{b,d}$
HF/STO-3G	−374.800 66	(734.4)	1013.3	+278.9
HF/4-31G	−378.644 16	(522.8)	764.0	+241.2
HF/6-21G**//HF/4-31G	−379.081 74	(521.6)	747.4	+225.8
HF/3-21G	−377.171 03	(503.8)	746.1	+242.3
HF/6-21G**//HF/3-21G	−379.080 85	(522.4)	748.6	+226.2
MP2/3-21G//HF/3-21G	−377.349 81	(502.1)	670.2	+168.1
HF/6-31G*//HF/3-21G	−379.103 88	(518.9)	747.7	+228.8
MP2/6-31G*//HF/3-21G	−379.344 95	(522.8)	666.4	+143.6
MP4/6-31G*//HF/3-21G	−379.359 55	(528.4)	707.9	+179.5
HF/6-31G*	−379.105 30	(518.7)	746.4	+227.7
MP2/6-31G*//HF/6-31G*	−379.342 94	(522.0)	673.6	+151.6
MP4/6-31G*//HF/6-31G*	−379.358 24	(527.4)	712.1	+184.7
HF/6-31G**//HF/6-31G*	−379.107 44	(527.2)	751.7	+224.5
MP2/6-31G**//HF/6-31G*	−379.350 89	(539.9)	691.8	+151.9
MP4/6-31G**//HF/6-31G*	−379.366 32	(545.3)	730.1	+184.8
−ΔZPE^e		(−14.6)	−24.7	−10.1

^{a} Energy in au; frozen core used for MPn/6-31G*; MP2/3-21G includes all orbitals; MP4 denotes MP4SDQ (see text). ^{b} PA$_{el}$'s and $\Delta E \equiv E(HCPH^+) - E(H_2CP^+)$. ^{e} $\Delta ZPE \equiv ZPE(HCPH^+$ or $H_2CP^+) - ZPE(HCP)$ calculated at HF/3-21G level. The two imaginary frequencies for HCPH$^+$ have been omitted.

HF/3-21G and HF/6-31G* geometries[10b,12b] for the above four neutrals, the HF/3-21G geometries[5] for H$_3$CPH$_3^+$ and PH$_4^+$, as well as a number of the HF/STO-3G geometries, were taken from the literature. Remaining geometries were determined by us. Our major computational levels for molecules with not more than one C atom were HF/6-31G* and MPn/6-31G* (n = 2, 3, 4) energies evaluated at both HF/3-21G and HF/6-31G* optimized geometries. For protonations at the P-site the use of the more economical HF/3-21G geometries yields PA's differing by 1 kJ mol^{-1} or less from those obtained from the more reliable HF/6-31G* geometries. For protonations at the C-site in HCP or H$_2$CPH the PA's obtained with HF/3-21G geometries are 4.5 kJ mol^{-1} less at the MP4/6-31G* level than those obtained with HF/6-31G* geometries. Our conclusion is that the use of HF/3-21G geometries is an adequate approximation in computing PA's for phosphorus-containing molecules and, in fact, better than for nitrogen-containing molecules, where somewhat larger PA differences[15,16] (8.7 kJ mol^{-1} for NH$_3$ at the MP4/6-31G* level) have been noted between the uses of HF/3-21G and HF/6-31G* geometries. For molecules with more than one C atom, such as H$_2$CPCH$_3$, C$_5$H$_5$P, and their protonated forms, we have used HF/3-21G and HF/4-31G geometries, with expected errors, relative to the use of HF/6-31G* geometries, of 1–2 kJ mol^{-1} for P-site protonations and 5–10 kJ mol^{-1} for C-site protonations.

III. Results

A. Phosphaethyne. The first species containing a multiple P–C bond which we consider is phosphaethyne, HCP, which was first prepared[17] in 1961. This molecule has been the subject both of a microwave structural determination[18] and of an extensive theoretical treatment[8] using a variety of basis sets. Studies of the PA have been limited to a consideration[3] of the collinear HCPH$^+$ form and to the use of modest (STO-3G and 3-21G) basis sets.

In Table I we present our results for HCP and protonated HCP. The energies displayed for P-site-protonated HCP are those for collinear HCPH$^+$ and is placed in parentheses to denote that this structure is *not* a local minimum on the potential energy surface but is rather a local maximum characterized by a negative force constant for the H–P–C angle bend. At the HF/3-21G level, the $C_{\infty v}$ maximum for HCPH$^+$ lies 242.4 kJ mol^{-1} above the H$_2$CP$^+$ minimum (C_{2v} symmetry, Figure 1a). The local minimum for

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TABLE II: Calculated Energies for H_2CPH and Energy Differences for Protonated H_2CPH

level	$E(H_2CPH)^a$	$PA_{el}(\text{P-site})^b$	$PA_{el}(\text{C-site})^b$	$\Delta E^{b,c}$
HF/STO-3G	−375.988 53	990.0	1063.6	+73.6
HF/4-31G	−379.815 75	772.7	780.6	+7.9
HF/6-21G**//HF/4-31G	−380.262 11	794.1	761.6	−32.5
HF/3-21G	−378.341 14	750.9	762.8	+11.9
HF/6-21G**//HF/3-21G	−380.261 99	793.9	764.8	−29.1
MP2/3-21G//HF/3-21G	−378.507 57	747.7	712.6	−35.1
HF/6-31G*//HF/3-21G	−380.286 03	790.4	764.9	−25.5
MP2/6-31G*//HF/3-21G	−380.520 46	771.9	711.0	−60.7
MP4/6-31G*//HF/3-21G	−380.549 81	777.0	727.6	−49.4
HF/6-31G*	−380.287 05	790.1	765.8	−24.3
MP2/6-31G*//HF/6-31G*	−380.520 16	772.6	716.5	−56.1
MP4/6-31G*//HF/6-31G*	−380.549 29	777.3	732.1	−45.2
HF/6-31G**//HF/6-31G*	−380.292 94	798.3	771.2	−27.0
MP2/6-31G**//HF/6-31G*	−380.545 82	788.7	733.0	−55.1
MP4/6-31G**//HF/6-31G*	−380.575 49	794.7	748.7	−45.4
$-\Delta ZPE^d$		−24.7	−27.6	−2.9

^{a} Energy in au; frozen core used for MPn/6-31G*; MP3/3-21G includes all orbitals; MP4 denotes MP4SDQ (see text). ^{b} PA_{el}'s and ΔE in kJ mol⁻¹. ^{c} $\Delta E \equiv E(H_2CPH_2^+) - E(H_3CPH^+)$. ^{d} $\Delta ZPE \equiv ZPE(H_2CPH_2^+ \text{ or } H_3CPH^+) - ZPE(H_2CPH)$ calculated at HF/3-21G level.
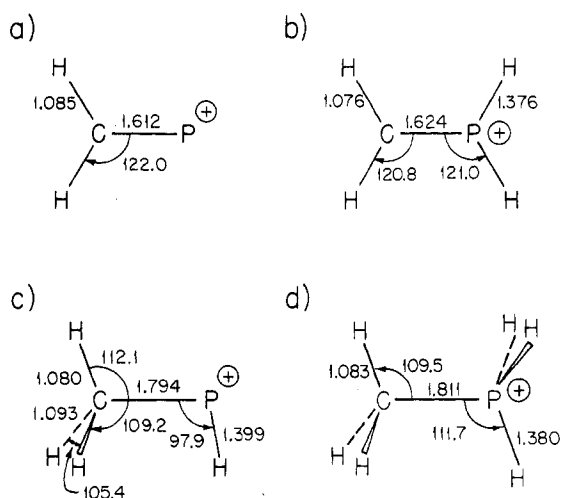

Figure 1. Optimized bond lengths in angstroms and bond angles in degrees obtained at the HF/6-31G* level for (a) C-protonated phosphaethyne, H_2CP^+, symmetry C_{2v}; (b) P-protonated phosphaethene, $H_2CPH_2^+$, symmetry C_{2v}; (c) C-protonated phosphaethene, H_3CPH^+, symmetry C_s; (d) protonated methylphosphine, $H_3CPH_3^+$, symmetry C_{3v}. Structures at the HF/6-31G* level for HCP, H_2CPH, and H_3CPH_2 are given in ref 12b.

HCPH$^+$ possesses an E (trans) planar geometry with an H–P–C angle of 91.8° and is 186.3 kJ mol⁻¹ above H_2CP^+ at HF/3-21G. However, this minimum is only 6.2 kJ mol⁻¹ below the transition structure for HCPH$^+$ → H_2CP^+ (∠HPC = 69.9°). We were unable to locate the HCPH$^+$ minimum or transition structure with the 6-21G* basis, implying that these structures are artifacts of the smaller basis set. Thus we conclude that the only local minimum resulting from the protonation of HCP is the H_2CP^+ species corresponding to C-site protonation, a behavior quite different from the favored protonation of HCN to form collinear HCNH$^+$. Our results are consistent with the observation that phosphaalkynes RCP add HX in solution to form RHCPX, corresponding to C-site protonation. However, some caution is necessary in this interpretation of the addition reaction, since X attack may dominate the site preference. We note that, although the inclusion of polarization functions (HF/6-31G*, HF/6-21G**) and electron correlation (MP2/3-21G, MPn/6-31G*) lowers the energy of HCPH$^+$ relative to H_2CP^+, C-site protonation is still favored by an overwhelming margin.

The difference in zero-point energy between HCP and H_2CP^+ is 24.7 kJ mol⁻¹ at the HF/3-21G level; when this ΔZPE value is combined with the PA_{el} value of 730.1 kJ mol⁻¹ at the MP4/6-31G**//HF/6-31G* level, the proton affinity of HCP is predicted to be 705.4 kJ mol⁻¹, with protonation occurring exclusively at carbon.

B. Phosphaethene and 2-Phosphapropene. In Table II we present our calculated PA's for H_2CPH, a molecule first identified[19] by its microwave spectrum. The P-site- and C-site-protonated forms refer to $H_2CPH_2^+$ and H_3CPH^+, respectively. The former has planar C_{2v} symmetry, the latter has C_s symmetry and an E (trans) conformation (the Z(cis) conformation is 2.6 kJ mol⁻¹ higher in energy at the HF/3-21G level). The optimized cation structures are shown in Figure 1b–c. The results may be summarized as follows: the minimal STO-3G basis set leads, as expected, to an exaggeration of PA_{el} by over 100 kJ mol⁻¹ with a C-site preference of 73.5 kJ mol⁻¹; split-valence basis sets lead to reasonable PA_{el}'s of approximately 770 kJ mol⁻¹ with slight C-site preferences of 7.9 and 11.9 kJ mol⁻¹ for HF/4-31G and HF/3-21G levels, respectively; inclusion of polarization functions *reverses* the site preferences, producing a P-site preference of 25–32 kJ mol⁻¹ at the HF/6-21G**//HF/4-31G, HF/6-21G**//HF/3-21G, and HF/6-31G*//HF/3-21G levels; there is a similar reversal upon consideration of correlation (P-site preferred by 35.1 kJ mol⁻¹ with second-order Møller–Plesset perturbation theory); and finally, the effects of including polarization and correlation are approximately additive, as indicated by the MPn/6-31G*//HF/6-31G* results for n = 2, 3, and 4, where P-site protonation is found to be favored by 50–60 kJ mol⁻¹. These results can be regarded as a calibration of split-valence SCF results: the small C-site preference energy of approximately 10 kJ mol⁻¹ found at this level corresponds to an actual P-site preference of approximately 50 kJ mol⁻¹ when polarization functions and electron correlation are added. Several studies of the importance of these effects for PA's of PH₃ and of nitrogen compounds have been reported.[4,5,15,20,21]

We have calculated the difference in zero-point energies between H_2CPH and each of the protonated forms. At the HF/3-21G level, the ZPE of $H_2CPH_2^+$ is 24.7 kJ mol⁻¹ greater than that of H_2CPH, while that of H_3CPH^+ is 27.6 kJ mol⁻¹ greater than that of H_2CPH. Thus, our conclusion that P-site protonation is favored by about 50 kJ mol⁻¹ over C-site protonation is not significantly affected by the small 3 kJ mol⁻¹ difference in the zero-point energies. When the P-site ΔZPE of 24.7 kJ mol⁻¹ is combined with the PA_{el} value of 794.1 kJ mol⁻¹ at the MP4/6-31G**//HF/6-31G* level, the proton affinity of H_2CPH is predicted to be 769.4 kJ mol⁻¹.

There remains one important consideration in the theoretical description of the protonation of H_2CPH, namely, that the isomer H_3CPH^+ resembles a carbene and thus is a good candidate for having a low-lying, and possibly ground-state, triplet. Indeed, as

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TABLE III: Triplet-Singlet Separations and Bond Angles for RPH$^+$

level	HPH$^+$			H$_3$CPH$^+$		
	ΔE^a	$\angle$T	$\angle$S	ΔE^a	$\angle$T	$\angle$S
HF/3-21G	−24.9	124.0^b	96.3^b	−12.0	125.4	98.4
HF/6-21G*//HF/3-21G	0.0			+12.5		
HF/6-21G*	+1.0	121.4^c	94.4^c	+12.4	122.5	98.0
HF/6-21G**//HF/6-21G*	−0.3			+8.2		
MP2/6-21G**//HF/6-21G*	+44.1			+60.5		
MP3/6-21G**//HF/6-21G*	+54.7					
CID/6-21G**//HF/6-21G*	+54.3					

^{a} $\Delta E \equiv E(\text{UHF triplet}) - E(\text{RHF singlet})$ in kJ mol^{-1}. ^{b} P–H bond lengths of 1.398 and 1.423 for triplet (T) and singlet (S), in Å. ^{c} P–H bond lengths of 1.386 and 1.400 for triplet (T) and singlet (S), in Å.

TABLE IV: Calculated HF/4-31G Energies for C$_5$H$_5$P and Protonated C$_5$H$_5$P

molecule	symmetry	E, au	ΔE, kJ mol^{-1}
C$_5$H$_5$P	C_{2v}	−532.272 06	+819.0^a
C$_5$H$_5$PH$^+$	C_{2v}	−532.584 07	0
α-C$_5$H$_6$P$^+$	C_s	−532.583 19	+2.4
γ-C$_5$H$_6$P$^+$	C_{2v}	−532.579 59	+11.8

^{a} HF/3-21G value is +796.2 kJ mol^{-1}.

shown in Table III the triplet state of H$_3$CPH$^+$ is found to be 12.0 kJ mol^{-1} below the singlet at the HF/3-21G level. Recalculation of the energy at the HF/6-21G*//HF/3-21G level (polarization functions used for P only) reverses the order, placing the singlet lower by 12.5 kJ mol^{-1}, a result only slightly affected (0.1 kJ mol^{-1}) by reoptimization of geometries at the HF/6-21G* level (Table III). The energy preference for the singlet increases significantly to 60.5 kJ mol^{-1} when correlation is included at the MP2/6-21G**//HF/6-21G* level. For the smaller HPH$^+$ molecule the results are similar, with the triplet favored by 24.9 kJ mol^{-1} at the HF/3-21G level, but the singlet favored over the triplet by about 54.5 kJ mol^{-1} at either the MP3/6-21G**//HF/6-21G* or CID/6-21G**//HF/6-21G* levels. This separation is about 10 kJ mol^{-1} greater than that calculated at the MP2 level. Assuming a similar 10 kJ mol^{-1} difference between the CID and MP2 values for the triplet–singlet energy difference, we predict the singlet state of H$_3$CPH$^+$ ($\angle$CPH = 98°) to be more stable than the triplet ($\angle$CPH = 122°) by approximately 70 kJ mol^{-1}. It is interesting to note the similarity of the H$_3$CPH$^+$ results with those reported[22,23] for H$_3$CSiH, where calculations using polarization basis sets and including correlation show the singlet to lie approximately 100 kJ mol^{-1} below the triplet.

From this detailed study of the protonation of H$_2$CHP in which the effects of polarization functions, correlation, and zero-point energy differences have been explicitly considered, we conclude that P-site gas-phase protonation should be preferred over C-site protonation. This result is at first glance at odds with the observation[24] that substituted phosphaethenes RR'C=PR'' in solution add HX to form RR'HC–PXR'', corresponding to protonation at the C-site. It may well be that the site preference for the addition of X$^-$ dominates the site preference for the addition of H$^+$ or that the addition is kinetically rather than thermodynamically controlled.

The calculations on phosphaethene may be considered prototypes for the protonation of phosphabenzene (section IIIC). The species 2-phosphapropene, H$_2$CPCH$_3$, is perhaps a better model since the phosphorus is connected to two carbons, one by a double bond and the other by a single bond, thus resembling a resonance structure for phosphabenzene. At the HF/3-21G level the C-site protonated product H$_3$CPCH$_3$$^+$ is 32.6 kJ mol^{-1} more stable than the P-site product H$_2$CPHCH$_3$$^+$. Although the methylsubstitution on the phosphorus of H$_2$CPH enhances the apparent preference for C-site protonation, the above energy difference is not large
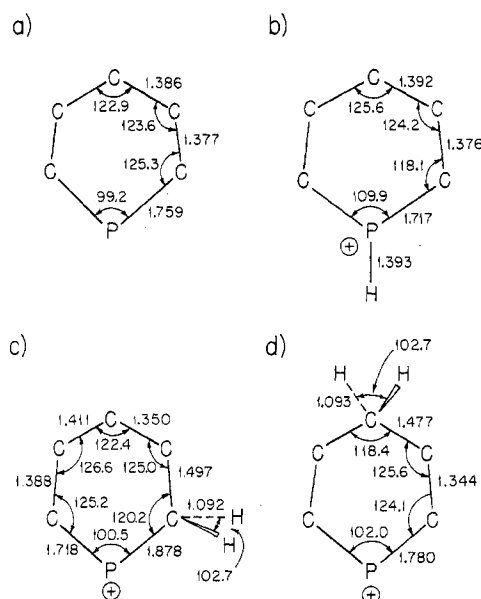

Figure 2. Optimized bond lengths in angstroms and bond angles in degrees obtained at the HF/4-31G level for (a) phosphabenzene, C$_5$H$_5$P, C_{2v} symmetry; (b) P-protonated phosphabenzene, C$_5$H$_5$PH$^+$, C_{2v} symmetry; (c) α-C-protonated phosphabenzene, C$_5$H$_6$P$^+$, C_s symmetry; (d) γ-C-protonated phosphabenzene, C$_5$H$_6$P$^+$, C_{2v} symmetry. Hydrogen atoms have been omitted from the figures except at the protonation sites. The optimized C–H bond lengths range from 1.069 to 1.075 Å.

enough to constitute a reliable prediction of a C-site preference. In fact, by assuming the same 60 kJ mol^{-1} shift found for H$_2$CPH when polarization functions and correlation are included, we actually predict P-site protonation to be favored for H$_2$CPCH$_3$ by 25–30 kJ mol^{-1}.

C. Phosphabenzene. In Table IV we present HF/4-31G energies for phosphabenzene C$_5$H$_5$P and for three protonated forms, namely, those corresponding to P-site, α-C-site, and γ-C-site protonation. The corresponding optimized geometries are shown in Figure 2. Calculations have also been made at the HF/3-21G level for C$_5$H$_5$P and C$_5$H$_5$PH$^+$ (P-site). Previous theoretical studies[6,25,26] of this molecule have largely been focused upon orbital energies and their comparisons to observed ionization energies. When the HF/4-31G energy differences are used, the calculated PA$_{el}$ for C$_5$H$_5$P, uncorrected for correlation effects and for zero-point energy differences, is 819.0 kJ mol^{-1} as compared to the observed[1] PA value of 820.0 kJ mol^{-1}. This calculated PA$_{el}$ is for P-site protonation and is slightly larger than the corresponding HF/3-21G value of 796.2 kJ mol^{-1}. The α-C and γ-C protonated forms are calculated to be less stable by 2.4 and 11.8 kJ mol^{-1}, respectively. While it is pleasing that agreement with experiment is obtained both in respect to the protonation site preference and to the PA value, there are reasons to be very

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cautious in attaching significance to such a small (2.4 kJ mol^{-1}) computed energy difference as a reliable indication of the site preference. Indeed this difference is comparable to the computed difference in ZPE's (2.9 kJ mol^{-1}) between C-protonated and P-protonated H_2CPH, although if this difference were transferable to the C_5H_5P protonation products, its sign (Table II) would increase the stability of $C_5H_5PH^+$ relative to α-$C_5H_6P^+$.

We note from Figure 2 that the "local" molecular structure about the P atom in $C_5H_5PH^+$ is very different from that about the P atom in α-$C_5H_6P^+$ or γ-$C_5H_6P^+$. In the latter two species the C–P–C bond angles are 100 and 102°, respectively, not much larger than the computed 99° value for C_5H_5P itself (the observed[27] microwave value for C_5H_5P is 101°), while the value for $C_5H_5PH^+$ is 110°. Thus the addition of polarization functions, particularly d functions for P, as well as the inclusion of correlation effects, might well affect the energy difference between $C_5H_5PH^+$ and α-$C_5H_6P^+$, as we found for $H_2CPH_2^+$ and H_3CPH^+. By contrast we expect that our split-valence SCF result of 9.4 kJ mol^{-1} for the energy difference between α-$C_5H_6P^+$ and γ-$C_5H_6P^+$ to be a reasonably reliable estimation of this difference since the two isomers are otherwise very similar in their geometrical and electronic structures. As it is not feasible for us to carry out extensive ab initio studies including polarization functions and correlation effects on a molecule as large as C_5H_5P or its protonated forms, we have instead estimated these corrections from our studies on smaller molecules containing P–C multiple bonds. For H_2CPH a 60 kJ mol^{-1} shift in the site preference energy was found when polarization functions and correlation are included. If H_2CPH is taken as a model for C_5H_5P and a similar 60 kJ mol^{-1} shift in site preference is assumed, then the small P-site preference of 2.4 kJ mol^{-1} for C_5H_5P at the HF/4-31G level translates to an estimated 60 kJ mol^{-1} P-site preference when polarization functions and correlation are included.

A better model for C_5H_5P, although one for which we have less extensive results than for H_2CPH, is 2-phosphapropene, H_2CP-CH_3. The HF/3-21G P-site PA_{el}'s for H_2CPCH_3 and C_5H_5P are very similar, namely, 801.2 and 796.2 kJ mol^{-1}, respectively, despite the fact that the C–P–C bond angle in H_2CPCH_3 increases from 102.8 to 124.4° upon protonation, while the angle in C_5H_5P only increases from 99.8 to 109.9° (HF/3-21G angles for C_5H_5P and $C_5H_6P^+$; the HF/4-31G angles in Figure 2 are similar). Thus the low PA value for C_5H_5P, as compared to the saturated $(H_3C)_2PH$ (see section IVA), does not appear to be principally a consequence of the geometrical constraints in the ring compound but rather of the character of the carbon-phosphorus multiple bond.

IV. Discussion

A. Comparisons to Nitrogen Compounds and to Saturated Carbon–Phosphorus Compounds. In Table V we present a comparison of our computed PA_{el}'s for HCP, H_2CPH, H_2CPCH_3, and C_5H_5P to similarly computed values[3,16] for the corresponding nitrogen containing molecules. Also presented are computed PA_{el}'s for the saturated molecules[3,5,16] XH_3, H_3CXH_2, and $(H_3C)_2XH$, with X = N or P, and experimental PA's as available.[1,28] [The PA's for many of the molecules have been the subjects of numerous theoretical studies.[3–5,15,20,21,29]] The results given at the higher levels of calculation for PH_3 and H_3CPH_2 are new to this study and match those described in detail for HCP and H_2CPH. The HF/6-31G* geometry of $H_3CPH_3^+$ is shown in Figure 1d, that for PH_4^+ has P–H = 1.380 Å, while those for PH_3 and H_3CPH_2 have been previously published.[12b] We first note some comparisons of computational interest:

(1) Split-valence PA_{el} values such as those at the HF/4-31G and HF/3-21G levels underestimate the PA's for P-containing molecules but overestimate the PA's for N-containing molecules,

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TABLE V: Proton Affinities^a for Unsaturated and Saturated C–N and C–P Systems

molecule	X	site	HF/4-31G	HF/3-21G	HF/6-21G**//HF/3-21G	HF/6-31G*	MP4/6-31G*//HF/6-31G*^{f}	MP4/6-31G**//HF/6-31G*^{f}	$-\Delta$ZPE	calcd^i	exptl^i
HCX	N	N	762.3	765.2^b	765.9	745.2^e	734.3^e	749.8^g	−33.4	716.4	736.3
	P	P	(522.8)^c	(503.8)	(522.4)	(518.7)	(527.4)	(545.3)	(−14.6)	(530.7)	
		C	764.0	764.1	748.6	746.4	712.1	730.1	−24.7	705.4	
H$_2$CXH	N	N	964.4	966.2^b	958.0	931.3^e	912.8^e	926.3^g	−40.6	885.7	918.8
	P	P	772.7	750.9	793.9	790.1	777.3	794.1	−24.7	769.4	820.0
		C	780.6	762.8	764.8	765.8	732.1	748.7	−27.6	721.1	
H$_2$CXCH$_3$	N	N		992.0							
	P	P		801.2							
		C		833.9							
C$_5$H$_5$X	N	N	1014.2	1009.2							
	P	P	819.0	796.2							
		C	816.6								
XH$_3$	N	N	924.7	949.4^b	953.8	909.5^e	912.1^e	923.8^g	−43.5	880.3	852.7
	P	P	784.5	771.1^b	821.9	823.4	810.0	833.1^h	−31.0	802.1	790.3
H$_3$CXH$_2$	N	N	969.0	991.4^b	988.9	954.8^e	954.8^e	965.7^g	−42.7	923.0	890.3
	P	P	841.8	827.9^d	889.1	890.4	875.5		−29.2		850.6
(H$_3$C)$_2$XH	N	N		1018.8^d							917.9
	P	P		875.7^d							901.6

^{a} $PA_{el} = -\Delta E_0$, el values except as noted. ^{b} Reference 3. ^{c} Based on energies for the unstable collinear HCPH$^+$ structure. ^{d} Reference 5, which also includes HF/6-31G*//HF/3-21G* values of 984.1 and 944.7 kJ mol^{-1} for $(H_3C)_2$NH and $(H_3C)_2$PH, respectively. ^{e} Reference 15. ^{f} MP4 denotes MP4SDQ. ^{g} Reference 16. ^{h} Reference 33. ^{i} MP4/6-31G**//HF/3-21G including ΔZPE//HF/3-21G. ^{j} References 1 and 28; PA(NH$_3$) taken as 852.7 kJ mol^{-1}.

indicating the difference in the effects of polarization functions and correlation between the first and second row. These differences are described further in section IVC.

(2) The C-site PA_{el}'s for unsaturated C–P systems[30] are more sensitive to inclusion of correlation than are the P-site PA's, reflecting the larger electronic and geometrical (Figures 1 and 2) changes accompanying C-site protonation. Correlation at the MP4SDQ level reduces the C-site HF/6-31G* or HF/6-31G*//HF/3-21G PA_{el}'s for HCP and H_2CPH by approximately 40 kJ mol⁻¹ (Tables I and II).

(3) As suggested in section II, the use of HF/3-21G geometries is a good approximation to the use of HF/6-31G* geometries in computing PA_{el}'s at the HF/6-31G* or MPn/6-31G* levels. The differences between the MP4/6-31G*//HF/6-31G* and MP4/6-31G*//HF/3-21G PA_{el}'s (in kJ mol⁻¹) are +4.2, +0.3, +4.5, −0.8, and +1.2 for HCP (C-site), H_2CPH (P-site), H_2CPH (C-site), PH_3, and H_3CPH$_2$, respectively, indicating that the use of HF/3-21G geometries is an especially good approximation for P-site PA_{el}'s. The corresponding differences[16] in N-site PA_{el}'s are (in kJ mol⁻¹) −7.1, −1.0, −6.7, and −2.9 for HCN, H_2CNH, NH_3, and H_3CNH$_2$, respectively.

Some comparisons of more chemical interest which we note from Table V include the following:

(1) The triple-bonded system HCP is very different from HCN in that while N-site protonation is strongly favored for HCN, to form linear HCNH⁺, C-site protonation is strongly favored for HCP, to form H_2CP⁺. Interestingly the PA_{el}'s of HCN and HCP, although referring to different protonation processes, are similar, with both being approximately 700 kJ mol⁻¹.

(2) All of the molecules with C–P multiple bonds have comparatively small calculated PA_{el}'s, the largest (at the HF/3-21G level) being 801.2 kJ mol⁻¹ for H_2CPCH$_3$. By contrast the values for the molecules with C–N multiple bonds are closer to those for molecules with C–N single bonds, with the well-known exception of HCN.

(3) The general level of agreement with experiment of the PA's obtained by combining the better PA_{el} values with ΔZPE values is pleasing; experimental data do not appear to be available for HCP, H_2CNH, or H_2CPH, so that the calculated values constitute predictions (see section IVC).

(4) The difference between the X-site (X = N or P) PA_{el}'s in HCX or H_2CXH (Table V) is reflected in the difference between the C-site PA_{el}'s in these molecules as compared to those for HCCH or H_2CCH$_2$ (not tabulated). At the HF/6-21G**//HF/3-21G level, the C-site PA_{el}'s for HCX are 703.0, 484.2, and 748.6 kJ mol⁻¹ for X = CH, N, and P, respectively, while those for H_2CXH are 731.4, 562.6, and 764.8 kJ mol⁻¹ for X = CH, N, and P, respectively. In both series there is a large drop in the C-site PA_{el} accompanying the rise in the X-site PA_{el} when N replaces CH; opposite shifts occur when P replaces CH, suggesting a simple explanation in terms of charge density shifts away from C when N replaces CH but toward C when P replaces CH. (The N-site PA_{el} for H_2CNH has been previously calculated by several groups.[3,15,29])

(5) Unlike the well-known increase[1,3,5] in P-site PA's by approximately 50 kJ mol⁻¹ when an H bonded to P is replaced by CH$_3$, we note a *decrease* when 2 H's bonded to P are replaced by a CH$_2$: 20.2 kJ mol⁻¹ for PH_3 to H_2CPH and 26.7 kJ mol⁻¹ for H_3CPH$_2$ to H_2CPCH$_3$, based on HF/3-21G PA_{el} values, or better, 26.4 kJ mol⁻¹ for PH_3 to H_2CPH based on MP4/6-31G*//HF/6-31G* values combined with ΔZPE values. The modest *increase* in PA_{el} in going from PH_3 to H_2CPCH$_3$ (30.1 kJ mol⁻¹, HF/3-21G) or from PH_3 to C_5H_5P (25.1 kJ mol⁻¹,
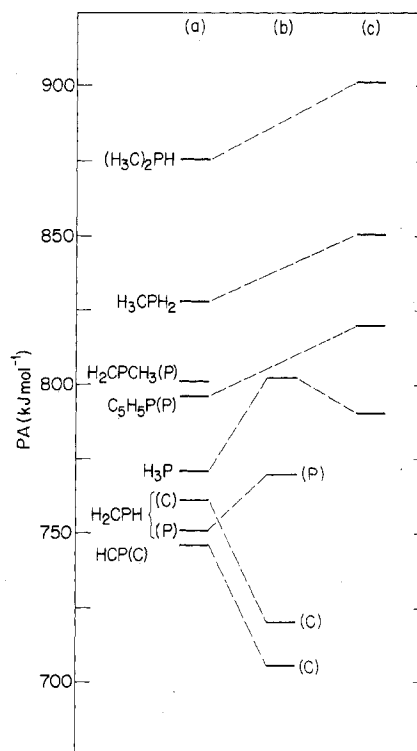

Figure 3. Comparison of calculated PA's in kJ mol⁻¹ at the levels (a) HF/3-21G ($-\Delta E_0^{el}$ or PA_{el}) and (b) MP4/6-31G**//HF/6-31G* (including ΔZPE//HF/3-21G) to experimental PA's (c) from ref 1 and 28. The letters P and C in parentheses denote protonation sites. MP4 denotes MP4SDQ. The calculated PH_3 value at the MP4 level is from ref 33.

HF/3-21G; 29.7 kJ mol⁻¹, ICR[1]) reflects the combination of these two opposing effects, as both methylene and methyl substitutions are in effect being made. The methylene substitution effect for N compounds is considerably less,[16] there being a slight increase in going from NH_3 to H_2CNH of 0.7 kJ mol⁻¹ at the MP4/6-31G*//HF/6-31G* level without the ΔZPE correction and 8.6 kJ mol⁻¹ with the correction.

B. Comparisons to Silicon Compounds. It is interesting to note the close similarity between our results for H_2CPH$_2$⁺ and H_3CPH⁺ and those reported for the isoelectronic neutral molecules H_2CSiH$_2$ and H_3CSiH. As summarized in a recent review,[31] the trends in the isomerization energy parallel our results, namely, that H_3CSiH is found to be strongly preferred over H_2CSiH$_2$ at a minimal basis set level, less strongly preferred at a split-valence level, even less so at a split-valence plus polarization level, and finally a near equivalence in energy, with a very slight preference for H_2CSiH$_2$, when correlation is included via large CI in calculations using double ζ plus polarization basis sets.[22,23] In both cases (X = P⁺, Si), polarization functions and electron correlation lower the energy of H_2CXH$_2$ more than H_3CXH. However, the phosphorus calculations lead to a more definitive conclusion concerning the more stable isomer, since basis sets and correlation effects widen the energy gap for H_2CPH$_2$⁺/H_3CPH⁺ but narrow it for H_2CSiH/H_3CSiH.

Our calculations show that the preference for P-site protonation is approximately 10 kJ mol⁻¹ greater for C_5H_5P than for H_2CPH. These results can be extrapolated to the comparison of silabenzene and silaethene, suggesting that the Si site preference in C_5H_6Si is ca. 10 kJ mol⁻¹ greater than in H_2CSiH$_2$. Since H_2CSiH$_2$ and H_3CSiH are nearly equal in energy,[22,23,31] this implies that silabenzene, isostructural with C_5H_5PH⁺, should be more stable by approximately 10 kJ mol⁻¹ than the isomer isostructural with α-C_5H_5P⁺. A study of silabenzene has been reported,[32] showing it to be more stable than 4-silacyclohexadienylidene, but did not

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(30) C-site protonation of H_2CXH (X = N or P) to form H_3CXH⁺ may be viewed as isomerization of H_2CXH to H_3CX followed by P-site protonation. At the HF/6-21G**//HF/3-21G level the isomerization energies are 333.8 and 144.5 kJ mol⁻¹ for X = N and P, respectively, with H_3CX taken as a spin singlet with C_s symmetry (ground state is a triplet). The decrease of 188.8 kJ mol⁻¹ in the isomerization energy in going from N to P is close to the increase of 202.2 kJ mol⁻¹ in the C-site PA_{el}, implying that the difference in C-site PA_{el}'s of H_2CXH for X = N and P is essentially given by the isomerization energy difference.

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(32) Schlegel, H. B.; Coleman, B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 6499.

report results for α-C_5H_6Si or γ-C_5H_6Si.

C. Comparisons to Experiment. Our ab initio studies of the gas-phase proton affinities for both saturated and unsaturated C-P systems are summarized in Figure 3, in which we compare calculated PA values at the levels (a) HF/3-21G (PA_{el} only) and (b) MP4/6-31G**//HF/6-31G* (including ΔZPE//HF/3-21G) to experimental values (c) as available.[1] The calculated MP4 value (b) shown for PH_3 is the PA_{el} value of Del Bene et al.[33] combined with our ΔZPE value (Table V). This is the only phosphorus species for which we have available both a PA_{el} value at the MP4/6-31G**//HF/6-31G* level and an experimental value. The calculated PA, including ΔZPE, is approximately 12 kJ mol^{-1} greater than the observed value; if the correction $5RT/2$ were to be added to the former, the difference would be increased to 18 kJ mol^{-1}, indicating that residual errors in the calculation are somewhat larger than the probable uncertainty of ± 8 kJ mol^{-1} in the reference PA value[1] for NH_3 used in calibrating the experimental scale. We expect that our comparably calculated PA values for HCP and H_2CPH are of similar accuracy. For the remaining molecules, namely, C_5H_5P, H_2CPCH_3, and $(H_3C)_2PH$, the PA_{el} values from HF/3-21G or HF/4-31G calculations are part of a scale of relative PA values which agree with the observed relative values (as available) to within 5–10 kJ mol^{-1}.

It is important to recognize that close agreement between calculated and observed PA's may result in part from a cancellation of errors. A shortcoming in many calculations is the omission of p-type polarization functions for H atoms. In Tables I and II we see that MP4/6-31G**//HF/6-31G* PA_{el}'s for HCP (C-site) and H_2CPH (P site) are respectively 18.0 and 16.6 kJ mol^{-1} higher than the MP4/6-31G*//HF/6-31G* values. We do not have MP4/6-31G** results for H_3CPH_2, but for PH_3 the increase upon including polarization functions is similar to the HCP and H_2CPH increases, namely, 23.1 kJ mol^{-1}, based on unpublished 6-31G** results[33] and our 6-31G* results in Table V. For N-containing molecules the increases are smaller. From a combination of published and unpublished results,[15,16] the differences between MP4/6-31G**//HF/6-31G* and MP4/6-31G*//HF/6-31G* PA_{el}'s (in kJ mol^{-1}) are +15.5, +13.5, +11.7, and +10.9, for HCN, H_2CNH, NH_3, and H_3CNH_2. Thus we conclude that calculated PA's are increased by 15–25 kJ mol^{-1} for P-containing molecules and 10–15 kJ mol^{-1} for N-containing molecules by the inclusion of polarization functions for H atoms. The reason that PA_{el} values obtained without these functions agree better with observed PA's for P-containing molecules than for

N-containing molecules is that for the former the increases described above are roughly cancelled by the $-\Delta ZPE + 5RT/2$ contributions, while for the latter the increase when combined with $-\Delta ZPE + 5RT/2$ makes a net negative 20–30 kJ mol^{-1} contribution, so that PA_{el} values overestimate PA's by this amount.

V. Summary

Our studies of protonation site preferences indicate that while C-site protonation is strongly favored for HCP, P-site protonation is somewhat favored for H_2CPH and by inference for C_5H_5P, assuming similar basis set and correlation effects as found for H_2CPH. This agrees with the site preference found for C_5H_5P from ICR experiments.[1] Also for C_5H_5P we find a preference of 9.5 kJ mol^{-1} for α-C protonation over γ-C protonation. This result should not be very sensitive to further refinements and, therefore, should be a reliable guide to the choice of C sites[34] in C_5H_5As, where carbon protonation is observed[1] to be favored over heteroatom protonation. The computed order of proton affinities, $H_3CPH_2 > C_5H_5P > PH_3 > H_2CPH > HCP$ (C-site), differs from that for the corresponding N systems,[3,15,29] namely, $C_5H_5N > H_3CNH_2 > H_2CNH \approx NH_3 > HCN$, not only in the lower position of C_5H_5P, as is known from experiment,[1,28] but also in the lower position of H_2CPH.

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