

A THEORETICAL STUDY OF THE GAS-PHASE BASICITY OF MOLECULES CONTAINING ARSENIC—CARBON MULTIPLE BONDS

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ABSTRACT

Gas-phase proton affinities are calculated using ab initio methods for the unknown unsaturated molecules H_2CA_sH and HCAs as well as for AsH_3 . The results parallel those previously found by us for the corresponding phosphorus compounds, in that the order of basicities is $AsH_3 > H_2CA_sH > HCAs$. For H_2CA_sH the C-site and As-site PA's are nearly equal, while for HCAs protonation is predicted to occur only at C.

INTRODUCTION

We have recently presented the results of ab initio studies of the gas-phase basicities [1] and acidities [2] of molecules containing phosphorus—carbon multiple bonds. The molecules considered in one or both studies were phosphacetyne (HCP), phosphacetylene (H_2CPH), 2-phosphapropene (H_2CPCH_3), and phosphabenzene (C_5H_5P), with comparisons being made to the saturated compounds H_3CPH_2 and PH_3 , to the corresponding unsaturated and saturated nitrogen compounds, and to selected hydrocarbons. In this present communication we report our ab initio results for the gas-phase basicities of arsaethyne (HCAs) and arsaethene (H_2CA_sH). While these molecules are at present unknown, the latter should serve as a model for the known arsabenzene (C_5H_5As), whose proton affinity (PA) has been reported [3] to be $792.8 \text{ kJ mol}^{-1}$, greater than that of AsH_3 ($763.0 \text{ kJ mol}^{-1}$) but less than that of $(H_3C)_3As$ ($887.8 \text{ kJ mol}^{-1}$). These values are all somewhat less than those for the phosphorus counterparts, namely 820.0, 790.4, and $941.4 \text{ kJ mol}^{-1}$ for C_5H_5P , PH_3 and $(H_3C)_3P$, respectively. In addition it has been reported from deuterium labeling experiments [3] that while the protonation of C_5H_5P takes place at the P-site, that of C_5H_5As takes place at a C-site. A key result from our theoretical study [1] of the PA's of H_2CPH , H_2CPCH_3 , and C_5H_5P was that P-site and C-site PA's were nearly equal in each of these molecules, with a preference of approximately 50 kJ mol^{-1} for P-site protonation demonstrated for H_2CPH in calculations employing polarization basis sets and incorporating electron correlation effects. By contrast HCP was found to protonate only at the C-site, the collinear $HCPH^+$ form being a local maximum rather than a minimum. A shallow minimum corresponding to a

bent HCPH⁺ was thought to be a computational artifact. These results differ greatly from those for HCN and H₂CNH, as N-site protonation is strongly favored in both of these cases.

METHOD

In our study [1] we noted that energies computed at the self-consistent field (SCF or HF) level with split-valence basis sets such as 3-21G or 4-31G provided much better PA's for P-containing molecules than they did for N-containing molecules. As a starting point we have used the recently published STO-3G basis set [4] for As (5 *d* functions used for the 3*d* shell rather than 6 second-order gaussians) to calculate PA's for HCAs and H₂CAs (C-site and As-site in each case) as well as for AsH₃. As described below, calculations were then made using a split valence basis set. All calculations were made with the GAUSSIAN 80 program [5], with molecular geometries determined using the analytic gradient optimization method at the self-consistent field (SCF or HF) level. The PA of a base B is taken as $-\Delta H_{298}^0$ for the reaction $B + H^+ \rightarrow BH^+$; for our present purposes the PA is approximated by the electronic energy difference $-\Delta E_0^{el} = E^{el}(B) - E^{el}(BH^+)$, as the zero-point energy correction and the difference between ΔH_{298} and ΔE_0 together would make a contribution of only -20 to -25 kJ mol⁻¹ to the PA, an amount comparable to or less than the residual errors in our calculations.

RESULTS AND DISCUSSION

Figure 1 displays the HF/STO-3G optimized geometries for HCAs, H₂CAs⁺, H₂CAsH, H₂CAsH₂⁺, and H₃CAsH⁺. The parameters at this level are shown in parentheses. The collinear HCAsH⁺ was found, as was the case for HCPH⁺, to be a maximum with respect to a bending mode. The ab initio energies and energy differences are given in Tables 1 and 2, respectively, together with the values for AsH₃ and AsH₄⁺. The published [3] HF/STO-3G bond length and bond angle for AsH₃ are 1.457 Å and 94.0°, while our bond length for AsH₄⁺ is 1.465 Å. The HF/STO-3G PA for AsH₃ of 1004.9 kJ mol⁻¹ is, as expected, very high but slightly below the HF/STO-3G value of 1020.1 kJ mol⁻¹ for PH₃ [6]. The calculated difference of 15.2 kJ mol⁻¹ is somewhat higher than the observed difference of 27.4 kJ mol⁻¹ [7]. In order to improve the calculations to approximately the HF/3-21G level, which has been shown [1] to give a good description of relative PA's for P-containing molecules, we have simply separated the gaussian primitives constituting the 4*s* and 4*p* valence basis functions for As into sets of two and one, respectively. This splitting of valence orbitals of a minimal basis set without reoptimization is not without precedent; this procedure was employed by Sakai et al. [8] in expanding their MINI basis sets to MIDI basis sets. In our case it produces a "3-21G-like" basis set, albeit not one with optimized exponents and coefficients. The designation 3-21G will be

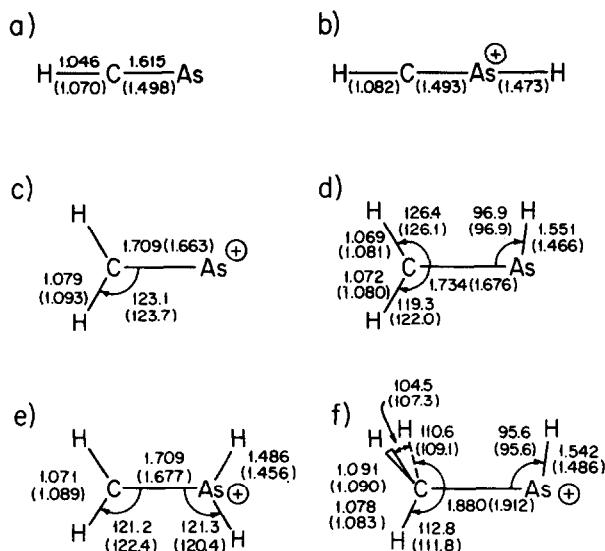


Fig. 1. Optimized bond lengths in Å and bond angles in degrees obtained at the HF/3-21G and HF/STO-3G levels (the latter values given in parentheses) for: (a) HCAs, symmetry $C_{\infty v}$; (b) HCAsH⁺, symmetry $C_{\infty v}$ (a local maximum); (c) H₂CA⁺, symmetry C_{2v} ; (d) H₂CAH, symmetry C_s ; (e) H₂CAH₂⁺, symmetry C_{2v} ; (f) H₃CAH⁺, symmetry C_s . The designation 3-21G refers to standard 3-21G basis sets for H and C combined with the 3-21G-like basis set for As as described in the text.

used to refer to this As basis set used in combination with standard 3-21G basis functions for C and H. We have used this basis set in several ways: first, to recalculate the HF energies at the HF/STO-3G geometries (results in Tables 1 and 2 designated HF/3-21G//HF/STO-3G); second, to reoptimize geometries (results designated as HF/3-21G); and finally, to incorporate correlation effects at the second-order Møller-Plesset (MP2) perturbation theory level (results designated as MP2/3-21G//HF/3-21G).

TABLE 1

Ab initio energies^a for neutrals and cations

Molecule	Symmetry	HF/STO-3G	HF/3-21G/ /HF/STO-3G ^d	HF/3-21G ^d	MP2/3-21G/ /HF/3-21G ^d
AsH ₃	C_{3v}	-2211.01403 ^b	-2211.28995	-2211.29577	-2211.35750
AsH ₃ ⁺	T_d	-2211.39684	-2211.61830	-2211.61882	-2211.68890
H ₂ CA ⁺	C_s	-2248.37113	-2248.94434	-2248.94972	-2249.10851
H ₂ CAH ₂ ⁺	C_{2v}	-2248.74313	-2249.25151	-2249.25362	-2249.41663
H ₃ CAH ⁺	C_s	-2248.77080	-2249.27545	-2249.27708	-2249.42036
HCA ⁺	$C_{\infty v}$	-2247.1983 ^c	-2247.75643	-2247.77483	-2247.94685
HCAH ⁺	$C_{\infty v}$ ^c	(-2247.48000)	—	—	—
H ₂ CA ⁺	C_{2v}	-2247.56658	-2248.08791	-2248.08978	-2248.23685

^aEnergies in au. ^bRef. 3. ^cLocal maximum with respect to a bending mode. ^dThe designation "3-21G" refers to standard 3-21G basis sets for H and C combined with the 3-21G-like basis set for As as described in the text.

TABLE 2

Calculated gas-phase proton affinities^a

Molecule	Site	HF/STO-3G	HF/3-21G//HF/STO-3G ^c	HF/3-21G ^c	MP2/3-21G//HF/3-21G ^c
AsH ₃	As	1004.9	861.9	848.0	869.9
H ₂ CAsH	As	976.5	806.3	797.7	808.8
	C	1049.1	869.2	859.3	818.6
HCAs	As	(739.3) ^b	—	—	—
	C	966.6	870.1	826.7	761.2

^a $-\Delta E_0^{\text{el}} = E(\text{B}) - E(\text{BH}^+)$ in kJ mol^{-1} . ^bCollinear protonated form is a local maximum.

^cThe designation "3-21G" refers to standard 3-21G basis sets for H and C combined with the 3-21G-like basis set for As as described in the text.

Our reoptimized bond length and bond angle for AsH₃ are 1.534 Å and 93.5°, while the bond length for AsH₄⁺ is 1.484 Å. These bond lengths are larger than the HF/STO-3G values; for AsH₃ the parameters are close to the HF/STO values of 1.528 Å and 93.6° [9] and to the observed values of 1.511 Å and 92.1° [10].

As a test of the above procedure for generating a 3-21G-like basis set, we followed the same procedure for PH₃ and PH₄⁺. In the latter case we find a "HF/3-21G" PA of 830.3 kJ mol^{-1} , higher than the 771.3 kJ mol^{-1} value obtained with the standard 3-21G basis set [11] but much lower than the HF/STO-3G value of 1020.1 kJ mol^{-1} [6]. It should be noted that the approximately 60 kJ mol^{-1} difference between these two "HF/3-21G" values for PH₃ reflects both a difference in optimized geometries as well as a difference in the basis set used for the energy calculations. The P—H bond lengths computed with the non-optimum "3-21G" basis set are longer than the HF/STO-3G values [6] by 0.057 and 0.022 Å for PH₃ and PH₄⁺, respectively, and slightly longer, by 0.015 and 0.012 Å, respectively than reported HF/3-21G values [6, 11]. Our conclusion is that the separation of the STO-3G valence orbitals into two basis functions each produces a reasonably satisfactory approximation to accepted 3-21G results.

In Fig. 1 we show the HF/3-21G structural parameters. Longer C—As bonds are obtained than at the HF/STO-3G level for each molecular species except H₃CAsH⁺. A measure of the relationship between C—As and C—P unsaturated bond distances is given by the microwave values [12, 13] of 1.85 and 1.733 Å for C₅H₅As and C₅H₅P, respectively; combined with the microwave C—P value [14] of 1.673 Å for H₂CPH, a value of approximately 1.79 Å might be expected to obtain for C—As in the unknown H₂CAsH. Our HF/3-21G value of 1.734 Å is closer to this estimate than is our HF/STO-3G value of 1.676 Å.

Our HF/3-21G PA value of 848.0 kJ mol^{-1} (Table 2) for AsH₃ is too high compared to the observed 763.0 kJ mol^{-1} value [7], but is expected to be in the correct position relative to the calculated value (797.9 kJ mol^{-1} for the

As-site in H_2CAsH). We have previously noted [1] a “methylene” effect, namely the reduction of P-site PA’s by approximately 25 kJ mol^{-1} when 2H’s are replaced by a CH_2 . Our results suggest that this effect may be even greater for As-site PA’s.

Comparisons of As-site and C-site PA’s in As—C systems must be made carefully, as the effects of including polarization functions and of considering electron correlation affect the two types of PA’s differently. Paralleling our experience [1] in comparing P-site and C-site PA’s in P—C systems, we note from Table 2 that the C-site PA’s of both H_2CAsH and HCAs are significantly reduced by electron correlation at the MP2 level, while there is a smaller effect (an increase) in the As-site PA’s of H_2CAsH and AsH_3 . As a consequence the As- and C-site PA’s of H_2CAsH are computed to be nearly the same; in view of the limitations in the present level of calculation we cannot claim to have established that H_3CAsH^+ is more stable than $\text{H}_2\text{CAsH}_2^+$. These limitations include the lack of polarization functions in our basis set and no consideration of correlation beyond the MP2 approximation. We do note, however, that whereas H_3CPH^+ is incorrectly favored over H_2CPH_2^+ at the HF/3-21G level, even MP2/3-21G//HF/3-21G calculations [15] are sufficient to give H_2CPH_2^+ as the correctly favored form. (By “correct” we mean the form found to be favored in our best calculations [1], such as MP4/6-31G**//HF/6-31G*.) Thus it may be, as suggested by the observed [3] C-site protonation of $\text{C}_5\text{H}_5\text{As}$, that C-site protonation is indeed favored for H_2CAsH .

SUMMARY

Our ab initio studies of the gas-phase proton affinities of AsH_3 , H_2CAsH , and HCAs at the minimal and split-valence SCF levels yields a basicity order $\text{AsH}_3 > \text{H}_2\text{CAsH}$ (As-site) $\approx \text{H}_2\text{CAsH}$ (C-site) $> \text{HCAs}$ (C-site), with As-site protonation of HCAs yielding an unstable structure. As this order is the same as that which we found [1] for the corresponding P-systems both in comparable ab initio calculations (HF/3-21G, HF/4-31G) and in our most rigorous calculations (MP4/6-31G**//HF/6-31G* including ΔZPE //HF/3-21G contributions), we conclude that our order for the As-systems is correct. The corresponding order for N-systems is somewhat different [16] with H_2CNH (N-site) $\approx \text{NH}_3 > \text{HCN}$ (N-site) (C-site protonation very unfavorable). Our present level of calculation is not sufficiently accurate to establish with certainty the relative stabilities of $\text{H}_2\text{CAsH}_2^+$ and H_3CAsH^+ , although our results suggest that the energy difference between these forms may be less than the 50 kJ mol^{-1} calculated [1] for the phosphorus analogs.

The results that the As-site PA’s in the unsaturated As—C compounds are, like those of their P analogues, smaller than those of their N analogues and that the C-site PA’s in these As—C compounds are enhanced as compared either to N—C compounds or to hydrocarbons are correlated with the charge distributions as given by Mulliken population analyses. While the

details are basis set dependent and not to be used as a quantitative measure of the distributions, the general trends are clear. Comparing the HF/3-21G-like results for H₂CAsH and HCAs to HF/3-21G results for H₂CXH and HCX (X = CH, N, P), we note that Mulliken charges on As are approximately +0.6 for each molecule, slightly more positive than the +0.5 charges on P for the P-systems, but very much more positive than the -0.6 to -0.4 charges on N for the N systems. Correspondingly, the charges on C atoms in these As-C systems are quite negative, approximately -0.9, slightly more so than in the P-C systems, but much more so than the values of approximately -0.3 for H₂CCH₂ and HCCH or the approximately neutral values in the N-C systems. Thus it is not surprising that there is experimental evidence [3] that the unsaturated C₅H₅As protonates at a C-site rather than at the As-site.

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