The Gas-Phase Acidity of HCP, CH_3CP, HCAs, and CH_3CAs: An Unexpected Enhanced Acidity of the Methyl Group

Otilia Mó,[a] Manuel Yáñez,*[a] Jean-Claude Guillemin,[b] El Hassan Riague,[b]
Jean-François Gal,[c] Pierre-Charles Maria,[c] and Christine Dubin Poliart[c]

Dedicated to Dr. Ing. Michèle Decouzon on the occasion of her retirement

Abstract: The gas-phase acidities of methylidynephosphine, $HC{\equiv}P$, ethylidynephosphine, $CH_3C{\equiv}P$, and ethylidynearsine, $CH_3C{\equiv}As$, have been measured by means of Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometry and calculated at the CCSD(T)/6-311+G(3df,2p)//QCISD/6-311+G(df,p) level of theory. An analysis of these results shows that, in contrast to the well-known fact that $HC{\equiv}N$ is a stronger acid than $CH_3C{\equiv}N$, $CH_3C{\equiv}P$ and $CH_3C{\equiv}As$ are more acidic than $HC{\equiv}P$ and $HC{\equiv}As$, respectively. The most important consequence of this unexpected effect is that while $HC{\equiv}P$ and $HC{\equiv}As$ are found to be weaker acids than $HC{\equiv}N$, the opposite trend is found for the corresponding methyl derivatives, the acidity of which increases as $CH_3C{\equiv}N < CH_3C{\equiv}P < CH_3C{\equiv}As$. Also the effects of deprotonation on the structures and the vibrational frequencies of $HC{\equiv}X$ and $CH_3C{\equiv}X$ (X = N, P, As) compounds are qualitatively similar, but quantitatively very different for nitrogen- as compared with phosphorus- and arsenic-containing compounds. A rationalization of these differences in terms of the bonding differences is presented.

Keywords: acidity · arsenic · gas-phase reactions · nitrogen · phosphorus

Introduction

The capacity of second- and third-row atoms to form multiple bonds has been an intriguing problem in chemistry, and although the characteristics of compounds with $C{\equiv}N$ triple bonds (nitriles) have been well-known for a very long time, this is not true for the corresponding phosphorus- and arsenic-containing analogues. One of the reasons is that compounds such as methylidynephosphine **1**, HCP, and ethylidynephosphine **2**, CH_3CP, are of low stability,[1] so their experimental scrutiny is difficult. These difficulties increase significantly when one moves down the group, and for instance, although the ethylidynearsine **4** derivative, CH_3CAs, could be synthesized,[2] this is not the case for the corresponding unsubstituted compound, methylidynearsine **3**, HCAs. In our groups we have been working recently[3–6] on the characterization of the intrinsic reactivity of low-stability compounds, which contain second-, third-, and fourth-row atoms such as P, As, Si, Ge, and Sn. Along this line, the aim of this paper is to provide, for the first time, quantitative information, from both the experimental and the theoretical viewpoints, on the gas-phase acidity of HCP, CH_3CP, HCAs, and CH_3CAs. The experimental determination of the acidity of simple phosphaalkynes and arsaalkynes in the gas-phase by FTICR is not by any means, a trivial matter. Although these compounds are isoelectronic species of hydrogen cyanide and acetonitrile, two of them, HCP and CH_3CAs, are very unstable compounds in the condensed phase: they decompose into oligomeric products at less than −110 °C for the first one and around −140 °C for the arsenic derivative. So, the vaporization of pure samples in the ICR spectrometer was extremely challenging and led to substantial experimental modifications of the synthesis protocol before success was achieved. For the particular case of HCAs, due to these difficulties, the information on its intrinsic acidity will be exclusively theoretical. For the sake of completeness, and in order to be able to analyze the acidity trends down Group 15, we have calculated also the acidity of HCN and CH_3CN, for which several experimental values can be found in the literature.[7–10]

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[a] Prof. M. Yáñez, Prof. O. Mó
Departamento de Química, C-9
Universidad Autónoma de Madrid
Cantoblanco. 28049-Madrid (Spain)
Fax: (+34) 91-397-5238
E-mail: manuel.yanez@uam.es

[b] Prof. J.-C. Guillemin, El H. Riague
Laboratoire de Synthèse et Activation de Biomolécules
UMR-6052 CNRS, ENSCR, 35700 Rennes (France)

[c] Prof. J.-F. Gal, Prof. P.-C. Maria, Dr. C. Dubin Poliart
Chimie des Matériaux Organiques et Métalliques
Université de Nice-Sophia Antipolis
Parc Valrose, 06108 Nice Cedex 2 (France)

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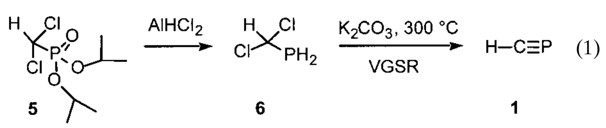
Experimental Section

Safety considerations: Phosphorus and arsenic derivatives are pyrophoric, potentially highly toxic compounds. All reactions and handling should be carried out in a well-ventilated fumehood.

Chemicals

Methylidynephosphine 1:[1] Compound 1 was prepared in a two-step sequence starting from the dichloromethylphosphonic acid, diisopropyl ester **5**. The chemoselective reduction of compound **5** led to the dichloromethylphosphine **6**. The bisdehydrohalogenation of **6** on potassium carbonate at 300 °C under vacuum gas–solid reaction (VGSR) conditions[1, 2, 11] led to a very pure sample of methylidynephosphine **1** [Eq. (1)].

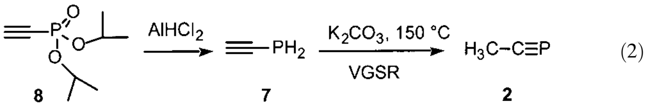


(1)

The preparation of the phosphine **6** was however modified to obtain a pure sample free of any low-boiling-point solvent: $LiAlH_4$ (133 mg, 3.5 mmol) and diethyleneglycol dibutyl ether (20 mL) were introduced into a two-necked flask (50 mL) under nitrogen. The suspension was cooled at −30 °C, and $AlCl_3$ (1.3 g, 10 mmol) was introduced by portions. The flask was then fitted on a vacuum line (10^{-1} mbar) equipped with two traps. It was degassed and allowed to warm to 0 °C and then cooled to −60 °C. The flask was isolated from the vacuum line by a stopcock, and phosphonate **5** (623 mg, 2.5 mmol) diluted in diethyleneglycol dibutyl ether (10 mL) was slowly introduced into the reducing mixture. At the end of the addition, the stopcock was opened to allow the distillation of phosphine **6**, and the cold bath for the flask was removed. The first cold trap (−70 °C) removed selectively the less volatile impurities from the gaseous flow, and phosphine **6** was selectively trapped in a pure form in the second trap cooled at −90 °C. Yield: 73 %.

After vaporization of phosphine **6** from K_2CO_3, pure methylidynephosphine **1** was trapped in a trap cooled at 77 K and kept at this temperature. This trap was then fitted on the mass spectrometer, and the cold bath was very slowly removed to maintain the trap at the lowest temperature of vaporization of the methylidynephosphine **1**. The oligomerization of a part of the product cannot be avoided.

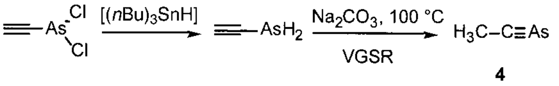
Ethylidynephosphine 2:[11] The ethylidynephosphine **2** [Eq. (2)] was prepared by reduction of the ethynylphosphonic acid, diisopropyl ester **8**[12] followed by the base-induced rearrangement of the ethynylphosphine **7**[13] with potassium carbonate at 150 °C under VGSR conditions.[11] The use of the diisopropyl ester **8** (and not the corresponding diethyl ester) was necessary to obtain the phosphine free of alcohol. The less volatile impurities were removed in vacuo (10^{-1} mbar) with a trap cooled at −100 °C, and the phosphine **7** was selectively trapped at −120 °C.



(2)

The trap containing the ethylidynephosphine **2** was fitted on the mass spectrometer, the temperature of the cold bath was allowed to warm to −70 °C, and the phosphaalkyne **2** was slowly distilled under vacuum.

Ethylidynearsine 4:[2] Compound **4** [Eq. (3)] was prepared by the two-step sequence as previously reported.[2] However, an experimental procedure similar to the one used for HCP was not good enough to inhibit the complete decomposition of pure ethylidynearsine **4** before vaporization in the mass spectrometer. Consequently the last step of the experimental procedure was modified as follows: tetrabutylstannane (20 mL) and small amounts of duroquinone (a radical inhibitor) were introduced into the trap, which was then degassed. The trap was immersed in a liquid nitrogen bath and shaken during cooling to freeze the solvent on the walls. The trap was fitted on the vacuum line (10^{-1} mbar), and ethylidynearsine **4**, synthesized by rearrangement of the ethynylarsine, was condensed in the cold trap on the frozen solvent. At the end of the reaction, the cell was disconnected from the vacuum line and quickly allowed to warm up to the melting point of the solvent (−100 °C). After a few seconds of shaking to mix the arsaalkyne **4** with the solvent, the cell was immersed in a cold bath (−60 °C) and fitted onto the mass spectrometer. Under these conditions, a slow vaporization of pure ethylidynearsine **4** occurred in vacuo.



(3)

FTICR measurements and results: Proton-transfer equilibrium measurements were conducted on an electromagnet Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer built at the University of Nice-Sophia Antipolis, using the methodology described previously.[4, 5]

Negative ions were generated by proton abstraction from the neutral reactants by tBuO$^-$. This anion was obtained by electron ionization at 0.1 eV (nominal) of tBuONO, introduced into the spectrometer at a partial pressure of about 10^{-5} Pa. The proton-transfer reactions were monitored for 2–10 s. The equilibrium constants K were determined from the reaction in Equation (4), and the relative acidities were calculated from Equation (5).

$$AH + Ref^- \xrightarrow{K} RefH + A^- \tag{4}$$

$$\Delta\Delta G^o_{acid} = -RT\ln K \tag{5}$$

Absolute gas-phase acidities (Gibbs energies at 298.15 K for the reaction: $AH \rightarrow A^- + H^+$) were referenced to the values of the NIST Standard Reference Database.[14] Equilibrium constants were obtained at an ICR cell temperature of 338 K, while tabulated ΔG^o_{acid} of reference compounds referred to the standard temperature of 298.15 K. Temperature corrections were considered as minor as compared with other experimental uncertainties, therefore ΔG^o_{acid} for the compounds under scrutiny were reported at 298.15 K in Table 1 without such temperature corrections.

Table 1. Experimental gas-phase acidities for methylidynephosphine **1**, ethylidynephosphine **2**, and ethylidynearsine **4** (kJ mol^{-1}, 298.15 K).

AH	RefH	ΔG^o_{acid}(RefH)[a]	$\Delta\Delta G^o_{acid}$[b]	ΔG^o_{acid}(AH)[c]
HC≡P	MeCN	1528 ± 8.4	≪0	
	Me_2CO	1514 ± 8.4	≈0	
	EtCHO	1501 ± 8.4	>0	
	CF_3CH_2OH	1482 ± 8.4	≫0	1514 ± 8.4
CH_3C≡P	MeCN	1528 ± 8.4	≪0	
	MeCHO	1502 ± 8.4	−0.08 ± 0.29	
	MeCOCH=CH_2	1492 ± 8.4	1.16 ± 0.17	
	CF_3CH_2OH	1482 ± 8.4	≫0	1498 ± 8.4
CH_3C≡As	CF_3CH_2OH	1482 ± 8.4	−9.10 ± 0.27	
	pyrrole	1468 ± 8.4	2.30 ± 0.39	
	MeSH	1467 ± 8.4	1.15 ± 0.56	1470 ± 8.4

[a] Reference [14]. [b] Gibbs energies for the reaction $AH + Ref^- \rightarrow A^- + RefH$ (338 K). [c] The indicated uncertainty corresponds to the uncertainty on the reference acidities.

The reversibility of proton exchange between neutral acids and the negative ions was checked by careful selection of each ion participating in the equilibrium, followed by a reaction delay of 0.5 to 2 s. Only the results concerning pairs of ion/neutral acid that react significantly in the practical time frame of the experiments are reported here.

For proton-transfer equilibrium determination, variable pressure ratios between the unknown acid under study and the reference compound, differing by at least a factor of three, were used with total pressures in the range 2×10^{-5} to 8×10^{-5} Pa (as read on a Bayard Alpert ion gauge). Relative (to N_2) sensitivities S_r of the Bayard Alpert gauge have been estimated using the Bartmess and Georgiadis equation [Eq (6)].[15]

$$S_r = 0.36\,\alpha + 0.30 \tag{6}$$

The molecular polarizability α was taken as α(ahc), calculated using the atomic hybrid component (τ) approach of Miller.[16] For phosphorus and arsenic, we used τ values estimated from experimental S_r previously measured in our laboratory for phosphine[17] and arsine[3] by using a spinning rotor gauge (Leybold Vakuum GmbH, Cologne, Germany).[18]

For methylidynephosphine **1**, no precise equilibrium constant could be determined, because of difficulties in handling this unstable compound. It was found that acetone was close in acidity. Reversible exchange was observed with butanone, but no equilibrium constant could be determined. The acidity of methylidynephosphine **1** reported in Table 1 was confirmed by bracketing experiments with acetonitrile, propanal, and 1,1,1-trifluoroethanol. Ethylidynephosphine **2** was also bracketed by observing the reaction with acetonitrile and 1,1,1-trifluoroethanol. An equilibrium constant with methylvinylketone was successfully obtained, but proton transfer with ethanal was slow, leading to a larger uncertainty. Nevertheless the average of the two absolute acidities corresponding to these references is reported, with the status of a semiquantitative bracketing. The relative acidity of ethylidynearsine **4** was measured against three reference acids. Despite the reduced precision of the equilibrium constants attributed to a partial decomposition of the compound during experiments, the resulting relative acidities led to rather consistent absolute acidities, which were averaged.

Computational Methods

It has been shown that the G2 method[19] is, in general, well suited for the calculation of gas-phase basicities and acidities.[20] However, the accuracy of this approach was a little poorer when the systems included second- and third-row heteroatoms.[1, 21] This can be critical in our particular case, because, as we shall show in forthcoming sections, the acidity gap between the unsubstituted parent compound and the methyl-substituted one is, in some cases, rather small, and of the same order as expected from the G2 method accuracy.

One of the critical points of the method used was sometimes associated with the reliability of the structures used, in this particular case that of the anion produced upon deprotonation of the neutral species, mainly in the case of the methyl derivatives. Hence, we decided to use a high-level procedure based on the use of the QCISD method[22] together with a very flexible 6-311 + G(df,p) basis set expansion for the geometry optimizations of both neutral and anionic systems. The corresponding harmonic vibrational frequencies have been evaluated at the same level of theory. In this way, we checked that the optimized structures found corresponded to local minima of the potential energy surface with all frequencies being real. The zero-point energy was used unscaled. Nevertheless, if the scale factor, 0.98, proposed by Scott and Radom[23] for QCISD calculations using smaller basis sets was employed, the effect on the calculated acidity was typically 1 $kJ\,mol^{-1}$ or smaller. The final energies were obtained in the framework of the coupled-cluster theory[24, 25] CCSD(T)/6-311 + G(3df,2p) through single-point calculations using the aforementioned QCISD-optimized geometries.

We have also considered it of interest to explore the performance of the widely used B3LYP approach[26, 27] for this particular set of compounds. Indeed, for other related systems it has been found that the B3LYP method, when used with an extended 6-311 + G(3df,2p) basis set on B3LYP/6-31 + G(d) optimized geometries, yielded proton affinities and acidities close to the experimental values. Hence, the same approach will be used here to be compared with the CCSD(T) calculations and with the experimental results.

The bonding of the species under investigation will be analyzed by means of the atoms in molecules (AIM) theory of Bader.[28] For this purpose we have located the relevant bond critical points and we have evaluated the electron density at them. The net atomic charges have been obtained using the NBO partition technique.[29] All these analyses were carried out on the QCISD/6-311 + G(df,p) optimized geometries.

Results and Discussion

The optimized geometries of the systems under investigation are shown in Figure 1. The total energies and the calculated intrinsic acidities have been summarized in Table 2. The calculated harmonic vibrational frequencies are given in Table 3.

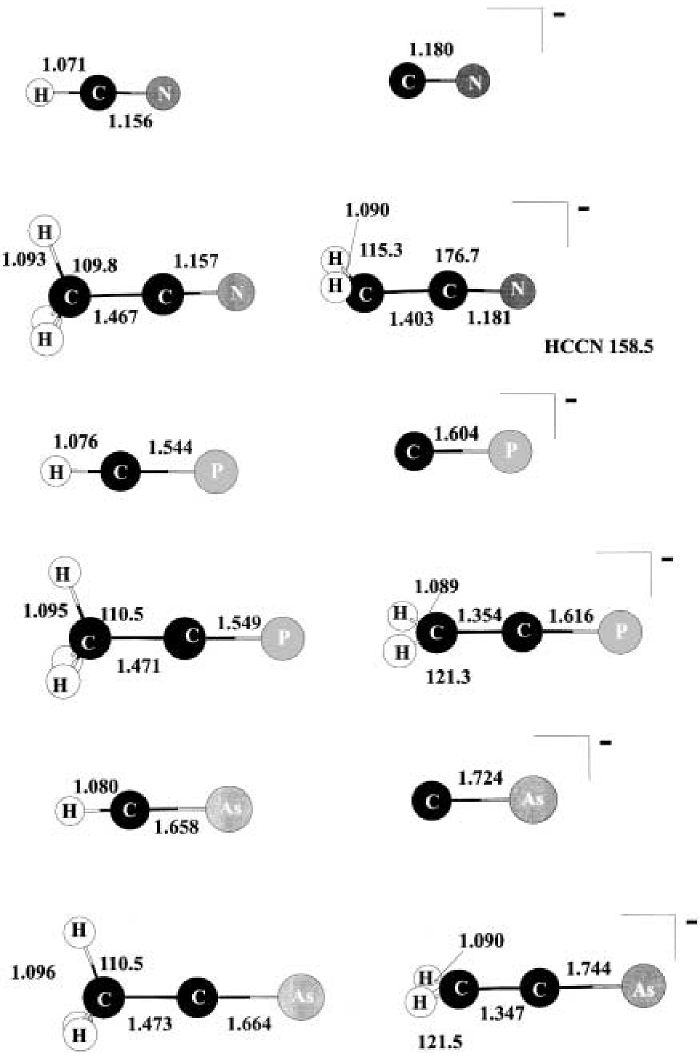


Figure 1. QCISD/6-311 + G(df,p) optimized geometries. Bond lengths in Å and bond angles in degrees.

Structural aspects: An inspection of Figure 1 clearly indicates that the deprotonation of the acids under investigation has a similar qualitative effect on the structure of the system. In all HCX compounds, the loss of a proton induces a lengthening of the CX bond. Similarly, as could be anticipated, for CH_3CX compounds, the deprotonation process results in a shortening of the C–C bond and in a lengthening of the C–X linkage since this process leads from a $CH_3C{\equiv}X$ structure toward the $^-CH_2{-}C{\equiv}X \leftrightarrow [CH_2{=}C{=}X]^-$ mesomeric forms. However, as reflected by the calculated charge densities at the C–C and C–X bond critical points, these effects are quantitatively different for N as compared with P- or As-containing compounds (see Table 4). In fact, these results indicate that while on going from CH_3CN to $[CH_2{=}C{=}N]^-$ the charge density at the CC bond critical point increases by 10 %; for the P- and As-containing analogues this increase is 18 % and 21 %, respectively. Consistently, the shortening of the C–C bond upon deprotonation of CH_3CX (X = P, As) is almost

Table 2. Total energies [E, hartrees], zero-point energies [ZPE, hartrees], entropies [cal mol^{-1}], and calculated acidities [ΔG^{o}_{acid}(AH), kJ mol^{-1}].

System	$E^{[a]}$				ΔG^{o}_{acid}(AH)		
	CCSD(T)	B3LYP	ZPE[b]	S[b]	CCSD(T)	B3LYP	Exp.
HC≡N	– 93.27477	– 93.46011	0.016143	48.183	1435	1433	1427 ± 8.8,[c] 1438 ± 8.4[d]
C≡N$^-$	– 92.70708	– 92.89321	0.004802	47.043			
CH_3C≡N	– 132.52496	– 132.80462	0.045585	60.353	1538	1520	1528 ± 8.4,[d] 1530 ± 8.4,[e] 1523 ± 11[f]
CH_2C≡N$^-$	– 131.91467	– 132.16518	0.030717	59.387			
HC≡P	– 379.47924	– 380.04134	0.013682	51.428	1510	1513	1514 ± 8.4[g]
C≡P$^-$	– 378.88363	– 379.44389	0.002729	50.382			
CH_3C≡P	– 418.72673	– 419.38235	0.042657	63.517	1498	1478	1498 ± 8.4[g]
CH_2C≡P$^-$	– 418.13207	– 418.79446	0.028311	62.567			
HC≡As	– 2272.87233	– 2274.53321	0.013014	54.205	1499	1499	–
C≡As$^-$	– 2272.28098	– 2273.94102	0.002240	53.182			
CH_3C≡As	– 2312.11945	– 2313.87466	0.041927	66.168	1476	1459	1470 ± 8.4[g]
CH_2C≡As$^-$	– 2311.53364	– 2313.29412	0.027767	65.240			

[a] Values obtained using a 6-311 + G(3df,2p) basis set. [b] Values obtained at the QCISD/6-311 + G(df,p) level. [c] Value taken from reference [10]. [d] Value taken from reference [8]. [e] Value taken from reference [9]. [f] Value taken from reference [7]. [g] This work.

Table 3. Harmonic vibrational frequencies [cm^{-1}] and assignments.

	HCX							CH_3CX					
Assignm.	X = N		X = P		X = As		Assignm.	X = N		X = P		X = As	
	HCN	CN$^-$	HCP	CP$^-$	HCAs	CAs$^-$		CH_3CN	CH_2CN^-	CH_3CP	CH_2CP^-	CH_3CAs	CH_2CAs^-
HCX bend	726	–	652	–	635	–	CCX bending	358	544	283	375	275	364
CX stretch	2163	2108	1327	1198	1097	983	CC stretch	933	1043	756	1640	633	1616
CH stretch	3471	–	3375	–	3344	–	CH_3 rocking	1069	–	1031	–	1021	–
							CH_3 umbrella	1431	–	1413	–	1400	–
							CH_3 deform.	1493	–	1478	–	1481	–
							CH_2 twisting	–	413	–	323	–	297
							CH_2 wagging	–	467	–	503	–	562
							CH_2 rocking	–	1075	–	1006	–	985
							CH_2 scissors	–	1451	–	1434	–	1418
							CX stretch	2353	2153	1616	806	1482	633
							CH stretch	3094	3128	3066	3134	3060	3121
								3142	3201	3142	3204	3136	3189

Table 4. Charge densities [e au^{-3}] at the bond critical points of the CH_3CX (X = N, P, As) acids and their conjugated bases.

Bond	CH_3CN	CH_2CN^-	CH_3CP	CH_2CP^-	CH_3CAs	CH_2CAs^-
CC	0.260	0.287	0.266	0.314	0.265	0.321
CX	0.478	0.449	0.200	0.179	0.195	0.170
CH	0.277	0.271	0.271	0.271	0.275	0.266

twice that calculated for CH_3CN. At the same time, the blue shifting of the C–C stretching frequency observed for the reference base with respect to the corresponding acid is also significantly larger for P- and As-containing compounds (884 and 983 cm^{-1}, respectively) than for CH_3CN (110 cm^{-1}; see Table 3). Table 4 also indicates that the charge density at the CN bond critical point of CH_3CN decreases by about 6% upon deprotonation. Again this decrease is higher (10 and 12%, respectively) for the P and As derivatives. As a consequence, the lengthening of both the CP and the CAs bonds of CH_3CP and CH_3CAs is almost three times that predicted for the CN bond of CH_3CN. In all cases the C–X stretching frequency appears red shifted; the shifting is much larger for P- and As-containing compounds (129 and 114 cm^{-1}) than for the corresponding N-containing analogues (55 cm^{-1}; see Table 3).

Hence, in summary, although upon deprotonation, the CC bond becomes reinforced, and the C–X becomes weaker, these effects increase in the order N ≪ P < As. This can be understood if one takes into account that, as a result of a less efficient overlap between the 2p orbitals of C and the 3p and the 4p orbitals of P and As, respectively, the C≡P and the C≡As bonds are already weaker than the C≡N bond in the neutral acid. Hence, on going from the triple to the double bond, the destabilization is only slightly larger for P and As than for N. Hence, the main effect is the strong stabilization of the C–C bond for P and As as compared with N, reflected in a larger double bond character of this linkage in $[CH_2CP]^-$ and $[CH_2CAs]^-$ than in $[CH_2CN]^-$. In this respect it is worth noting that while the $[CH_2{=}C{=}X]^-$ (X = P, As) are strictly planar C_{2v} structures, at both the QCISD and the B3LYP levels of theory, the $[CH_2{=}C{=}N]^-$ anion is not (see Figure 1); the HCCN dihedral angle is 158° at the QCISD/6-311 + G(df,p) level and 161° at the B3LYP/6-31 + G(d,p) level. This is also consistent with the fact that the CH_2 wagging, which involves a pyramidalization of the terminal sp^2 carbon, has a much higher frequency for $[CH_2CP]^-$ and $[CH_2CAs]^-$ than for $[CH_2CN]^-$ (see Table 3), while the opposite trend is observed as far as the CCX bending mode is concerned.

Gas-phase acidities: The first conspicuous fact from Table 2 is the good agreement between the values calculated at the CCSD(T) level and the experimental ones, when available. It can also be observed that, although the B3LYP estimates for the acidity of the unsubstituted parent compounds are in very good agreement with both the CCSD(T) and the experimental values, the B3LYP approach significantly overestimates the acidity of the methyl-substituted derivatives.

For the particular case of HCN, two different experimental gas-phase acidities can be found in the literature.[8, 10] Although our theoretical estimate lies within the experimental uncertainty of both values, the agreement is much better with the value reported by Bartmess et al.[8] Three different experimental values of the gas-phase acidity of the methyl derivative, CH_3CN, have been published.[7–9] All values are slightly smaller than the calculated one. However, most importantly, both theory and experiment indicate that the intrinsic acidity of HCN is significantly higher than that of the CH_3CN derivative. This result is particularly relevant, because, as we will discuss later for the phosphorus- and arsenic-containing analogues, the opposite effect is found. In fact, the values in both Tables 1 and 2, indicate that CH_3CP is slightly more acidic than HCP. Something similar is predicted, on theoretical grounds for the As derivatives.

As expected, HCP and HCAs are predicted to be weaker acids in the gas phase than HCN, just reflecting the fact that the heterolytic dissociation energy of the C–H bond is smaller for HCN than for HCP or HCAs, due to the much higher electronegativity of the nitrogen atom. There is not however a regular trend, because HCAs is predicted to be a slightly stronger acid than HCP (see Table 2); this is likely to reflect the ability of the more voluminous As atom to accommodate a negative charge. Quite surprisingly, the behavior is just the opposite as far as the methyl derivatives are concerned. Indeed, on the one hand, both CH_3CP and CH_3CAs are found to be stronger acids than CH_3CN, and on the other hand, there is a regular trend in the relative acidities of these systems which increases following the sequence $CH_3CN < CH_3CP < CH_3CAs$.

In order to gain some understanding about the origin of the acidity changes observed on going from $HC{\equiv}X$ to $CH_3C{\equiv}X$ compounds as a function of the nature of the heteroatom, we have used the following isodesmic reactions [Eqs. (7) and (8)].

$$HCX + CH_3{-}C{\equiv}CH \rightarrow CH_3CX + HC{\equiv}CH \quad (X = N, P, As) \tag{7}$$

$$CX^- + CH_3{-}C{\equiv}CH \rightarrow CH_2CX^- + HC{\equiv}CH \quad (X = N, P, As) \tag{8}$$

These measure the effect of replacing a hydrogen atom by a methyl group on the stability of the acid and on the stability of the corresponding conjugate base, respectively. The results obtained are shown in Figure 2. It can be observed that P- and As-containing systems exhibit significant differences with respect to the nitrogen-containing analogues. In the first place, while the acid stability increases slightly on going from $HC{\equiv}X$ to $CH_3C{\equiv}X$ for X = N, it decreases also slightly when X = P or As. However, the most significant differences affect the relative stability of the conjugated bases. Indeed, the P and As-containing anions are slightly stabilized on going from CX^- to $^-CH_2CX$, while the nitrogen analogue is strongly destabilized. The main consequence is that CH_3CP is predicted to be a much stronger acid than CH_3CN. Also importantly, the stabilizing effect is also higher for As than for P compounds, and accordingly the acidity of CH_3CAs is larger than that of CH_3CP. Identical conclusions are obtained when using the CH_3CH_3 and CH_4 saturated compounds as reference systems in isodesmic reactions (7) and (8).

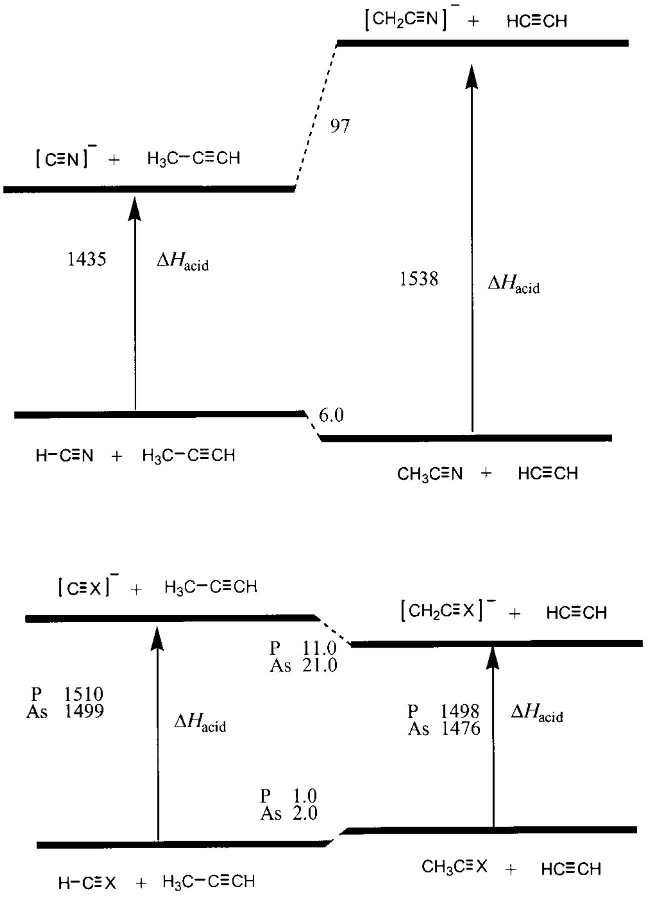


Figure 2. CCSD(T)/6-311 + G(3df,2p)//QCISD/6-311 + G(df,p) relative enthalpies involved in the deprotonation process of $HC{\equiv}X$ (X = N, P, As) and their methyl derivatives. All values in kJ mol^{-1}.

These trends are consistent with the structural changes induced by the deprotonation process which have been discussed above. From the energetic point of view, there are two opposite effects, the reinforcement of the C–C bond, which leads to a stabilization of the system and the weakening of the C–X linkage, which tends to destabilize the anion. For CH_3CN, the latter effect dominates, since we are changing from a very strong CN triple bond to a CN double bond. Conversely, for CH_3CP and CH_3CAs, the reinforcement of the C–C bond dominates, in agreement with the arguments given in the preceding section.

Conclusion

The results of our combined experimental and theoretical study show that HCP and HCAs are weaker acids in the gas phase than HCN, as a direct consequence of the much higher electronegativity of N as compared with that of P or As. Interestingly, although the gas-phase acidity of HCAs could not be measured due to the difficulties inherent in the synthesis of this compound, our high-level ab initio calculations predict this compound to be slightly more acidic than the phosphorus-containing analogue.

Quite unexpectedly, we have found, both on experimental and theoretical grounds, that the acidity trends are reversed when one considers the CH_3CX methyl-substituted derivatives; CH_3CN is the weakest acid of the three. A theoretical analysis of these results in terms of the enthalpies associated with appropriate isodesmic reactions indicates that the most significant difference between the N derivative and the P and As ones is associated with the relative stability of the conjugated base. While for P- and As-containing acids a small stabilization of the anion produced upon deprotonation is observed on going from $HC{\equiv}X$ to $CH_3C{\equiv}X$ compounds, for the N-containing analogue a significant destabilization of the system is predicted. This destabilization is associated with a sizable weakening of the $C{\equiv}N$ bond.

This picture is consistent with the effects of the deprotonation on the structure and on the vibrational frequencies of HCX and CH_3CX ($X = N$, P, As) compounds. These effects are qualitatively similar for all the systems investigated, but quantitatively very different for nitrogen- than for phosphorus- and arsenic-containing compounds.

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