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Ionization potentials of heteroalkenes: a comparative study

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Methanimine, methylenephosphine and methylenearsine have been prepared in the gas phase and the gaseous flow has been analyzed by spectroscopy. Photoelectron spectra have been recorded and we report here a comparative study on these spectra. This comparison has been extended to the corresponding derivatives with a triple bond: hydrogen cyanide and methylidynephosphine. Estimation by theoretical calculations of the ionization potentials of the unknown methylidynearsine has been proposed. Copyright © 2004 John Wiley & Sons, Ltd.

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INTRODUCTION

Main-group elements chemistry is currently the subject of intense study, particularly multiple bond compounds between carbon and pnictogen atoms[1,2] (for reviews see Refs 3–5). These species are interesting from both the theoretical point of view and the synthetic view, because of the possibility of obtaining new ligands in coordination chemistry or good precursors in materials chemistry. Moreover, a typical question concerns the real analogy between the isoelectronic low-coordinate phosphorus or arsenic compounds and nitrogen compounds. Here, we consider double and triple bond derivatives.

RESULTS AND DISCUSSION

From a synthetic point of view, naked compounds are scarce and, in principle, thermodynamic and/or kinetic effects are required to support the stability of such compounds. Owing to the reactivity of non-crowded molecules, only appropriate reactions coupled with specific techniques are available to do these studies. In the gas phase, flash vacuum pyrolysis (FVP)[6–8] can be used to generate reactive species. Vacuum gas–solid reactions (VGSRs) are also useful.[9–11]

Methanimine ($H_2C{=}NH$) has been prepared by FVP starting from the methylazide.[12] Dehydrohalogenation of *N*-methyl-*N*-chloramine on potassium t-butoxide in VGSR conditions[13] or dehydrocyanation of aminoacetonitrile on solid potassium hydroxide[14] also lead to the expected product. This kinetically unstabilized compound can, however, be condensed in a trap cooled by liquid nitrogen and then vaporized *in vacuo* ($<10^{-1}$ mbar). Methylenephosphine ($H_2C{=}PH$) is more highly reactive. It has been prepared by dehydrohalogenation of chloromethylphosphine on potassium carbonate heated at 80 °C in VGSR conditions.[15] This compound is too unstable to be condensed and revaporized, and the gaseous flow should be analyzed directly. Methylenearsine ($H_2C{=}AsH$) has only been recently characterized. It has been prepared by dehydrohalogenation of chloromethylarsine on sodium carbonate at 50 °C (Scheme 1).[16] This reaction is very sensitive to each parameter. The use of potassium carbonate instead of sodium carbonate or a higher temperature of dehydrohalogenation leads to the competitive reaction of reduction and the formation of methylarsine.

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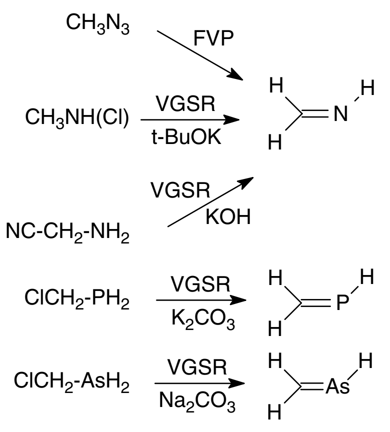

Scheme 1.

To analyze such compounds, the quartz tube heated at high temperature (FVP experiments) or the reactor containing the solid base (VGSR experiments) is connected directly to the spectrometer. The distance between the synthesis zone and the analyzer system should be as short as possible in order to avoid reorganization or polymerization of the species. Mass spectrometry (MS) is naturally useful to determine the molecular mass and the characteristic fragmentations of molecules, but knowledge of the electronic properties is only accessible using a spectroscopic method, like UV photoelectron spectroscopy (UV-PES). Moreover, comparison between these experimental data and calculations is required to ensure consistency in the assignments of the PES spectra and to compare the geometrical and electronic structures.

The first photoelectronic spectrum of methanimine was recorded by Peel and willet[17] in 1975 and shows a first broad band at 10.6 eV and a stronger second one at 12.5 eV. The first ionization potential (IP) corresponds to the ejection of electrons located on the nitrogen lone pair, and the next IP to the ionization of the π orbital.

Later, Pfister-Guillouzo and co-workers[15] obtained the first experimental characterization of the electronic structure of methylenephosphine using VGSR/UV-PES coupling. The attribution of the first two ionic states is based on substituent effects (methyl) and on comparison with the corresponding imines. The spectra have a difference concerning the shape of the first two ionizations. This first observation suggests a reverse ionization order. In fact, owing to the diffuse character ($2p\pi-3p\pi$ overlap) the energy of the $\pi_{P=C}$ orbital must be weaker relative to that of the $\pi_{N=C}$. Moreover, phosphorus hybridization (more s character than in the nitrogen atom) agrees with this destabilization. The bond at 10.3 eV was assigned to the ionization of a π orbital and the bond at 10.7 eV was attributed to the ejection of the phosphorus lone-pair electrons.

What is the behaviour of the analogous arsenic compound? Only recently, some 20 years after the synthesis of the methylenephosphine, we reported the synthesis of the methylenearsine formed by dehydrohalogenation of gaseous chloromethylarsine on a solid base using VGSR conditions.[16] The characterization was performed in the gaseous phase by high-resolution MS (HRMS) and UV-PES. These spectroscopic data are compared with the photoelectron spectrum of methylenephosphine. In this case, the first band at 9.7 eV was attributed to the ejection of an electron from the $\pi_{C=As}$ orbital and the second band, at 10.3 eV, was attributed to the orbital corresponding to the n_{As} arsenic lone pair. The destabilization of the first band corresponds to a slightly more diffuse character of the double carbon–arsenic bond than that of carbon–phosphorus. Table 1 summarizes the data corresponding to the first two experimental IPs of methanimine, methylenephosphine and methylenearsine. These experimental data emphasize the electronic similarity between arsenic and phosphorus species, as well as the more diffuse character of the $\pi_{C=As}$ orbital originating from the $2p\pi-4p\pi$ overlap and weaker energy (0.6 eV) of this double bond relative to the phosphorus analogue ($2p\pi-3p\pi$). Moreover, the destabilization of the n_{As} orbital compared with the $\pi_{C=As}$ orbital is weaker than that observed for the corresponding orbitals of the phosphorus analogue. This can be explained as being due to the compromise between the increasing s-character of the arsenic lone pair and its slightly smaller electronegativity. A significant separation (0.6 eV) of the first two ionic states (0.4 eV for the methylenephosphine) may also lead to the increased reactivity of this double-bond system.

A comparison with the corresponding alkynyl compounds can be performed. Their kinetic stabilities are higher. Hydrogen cyanide (H–C≡N) has been known for a very long time, and methylidynephosphine (H–C≡P) was first synthesized by Gier[18] in 1961. The nature of the triple bonds between the heteroatom and carbon atoms has been investigated extensively, but a challenge remains: no information exists regarding methylidynearsine (H–C≡As). The same order between the first two attributions is found in the case of hydrogen cyanide and methylidynephosphine, i.e. the first ionization energy (IE) is assigned to the ejection of an electron from the degenerated π orbital and the second one is assigned to the ejection of an electron from the lone pair orbital. In contrast with the double bond derivatives, the small split between the two bands is identical (0.4 eV). Nevertheless, the greater diffuse character of the π_{CP} bond compared with π_{CN} explains the observed destabilization. Table 2 lists the experimental and theoretical IPs for HC≡N

Table 1. Comparison of experimental IPs for methanimine, methylenephosphine and methylenearsine and the nature of molecular orbitals

	IP (eV)		
Nature of MO[a]	$H_2C{=}NH$	$H_2C{=}PH$	$H_2C{=}AsH$
$\pi_{C=Pn}$	12.5	10.3	9.7
n_{Pn}	10.6	10.7	10.3

[a] Pn: N, As, P.

Table 2. Geometrical parameters (B3LYP/6-311G**) of $\mathrm{H{-}C\,{\equiv}N}$, $\mathrm{H{-}C{\equiv}P}$ and $\mathrm{H{-}C{\equiv}As}$, comparison of experimental and calculated values of IPs for $\mathrm{H{-}C{\equiv}N}$ and $\mathrm{H{-}C{\equiv}P}$, and calculated IPs for $\mathrm{H{-}C{=}As}$

		$\mathrm{H{-}C{\equiv}N}$	$\mathrm{H{-}C{\equiv}P}$	$\mathrm{H{-}C{\equiv}As}$
C–H (Å)		1.066	1.072	1.075
C≡Y (Å)		1.149	1.539	1.649
OVGF	$\pi_{C\equiv Y}$	13.47	10.49	9.82
	n_Y	13.84	12.58	13.07
TDDFT	$\pi_{C\equiv Y}$	13.73[a]	10.76[a]	10.165[a]
	n_Y	13.87	12.965	12.69
CASPT2	$\pi_{C\equiv Y}$	13.53	10.57	10.09
	n_Y	13.5	12.36	12.16
Khon–Sham energy	$\pi_{C\equiv Y}$	10.06	7.73	7.42
	n_Y	10.55	10.00	9.75
Estimated IP	x shift	3.54	3.06	2.74
	$\pi_{C\equiv Y}$	13.6[b]	10.79[b]	10.165[a]
	n_Y	14.09	13.06	12.49
Experiment	$\pi_{C\equiv Y}$	13.6	10.79	
	n_Y	14.05	12.86	

[a] Δ SCF value.
[b] Experimental IP.

and $\mathrm{HC{\equiv}P}$ and the calculated IP for $\mathrm{HC{\equiv}As}$. Calculations are required for the consistency of the assignments on the experimental spectra, but they are also useful because they allow us to predict the IP for a new compound. Reliability between experiment and calculations is found for these three compounds. We note that use of the outer-valence Green's function (OVGF) method gives a good estimation of the gap value between the first two ionization energies (e.g. for $\mathrm{HC{\equiv}P}$: experiment 2.07 eV; OVGF, 2.09 eV; time-dependent density functional theory (TDDFT): 2.2 eV; CASPT2, 1.79 eV), but TDDFT gives IPs closer to the observed values. So, considering this information, we can reasonably estimate a first band at around 10.1 eV for the $\mathrm{HC{\equiv}As}$ molecule, due to the ejection of electrons localized on the degenerated π system, and a second one near 12.5 eV arising from ionization of the arsenic lone pair.

CONCLUSIONS

Many photoelectron spectra of substituted alkyl, aryl and halogeno-phosphaalkenes and -alkynes have been reported,[19–22] but not so many for arsenic derivatives.[23,24] We mentioned some examples here in which it is clear that, to obtain spectra of less hindered compounds, coupling with a specific device is necessary; the success depends on the availability of the precursor. Investigations to find good conditions to generate $\mathrm{HC{\equiv}As}$ are in progress in our groups.

COMPUTATIONAL DETAILS

The calculations were performed using the Gaussian 98[25] and MOLCAS[26] (for CASPT2) program packages. The 6-311G(d,p) basis set was used for all calculations, since the inclusion of polarization functions is necessary for an accurate description of the neutral molecules containing an arsenic atom and their cations. Geometry optimizations were carried out at the DFT level of theory with the B3LYP[29–31] functional and confirmed as true minima via frequency analysis, which was also used to calculate zero-point energies without scaling. IE were calculated with Δ SCF-DFT i.e. ($\mathrm{IE}{=}E_{\mathrm{cation}}{-}E_{\mathrm{neut.mol.}}$). To calculate the first ionic states, the TDDFT[32,33] approach was used. The vertical IPs were also calculated at the *ab initio* level according to the OVGF[34,35] method. CASPT2[26] refers to multiconfigurational self-consistent field *ab initio* calculations in which all excitations are taken into account in a certain orbital space (the active space), with second-order perturbation corrections added afterwards. We also proceeded to the commonly employed method involving "shifting" of the B3LYP/6-311G (d,p) Kohn–Sham energies. Indeed, recent studies[36,37] have shown that ε_i^{KS} could be linked up to experimental vertical IPs ($\mathrm{IP_v}$) by a uniform shift $x = |-\varepsilon_i(\mathrm{HOMO}) - \mathrm{IP}_v^{exp}|$.

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