Organoarsenic Compounds

First Synthesis and Characterization by Mass Spectrometry and UV-Photoelectron Spectroscopy of Methylenearsane**

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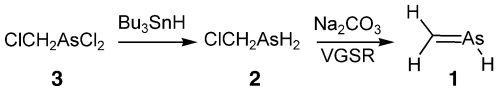
The synthesis of the simplest unsaturated heterocompounds is a particular challenge since most of these compounds are kinetically unstable. Several of the simplest low-coordinated compounds bearing a nitrogen,[1] silicon, phosphorus, or sulfur atom have been prepared[2] but few of the corresponding derivatives with a heteroatom of the following rows of the periodic table have been characterized.[3] Due to a lack of any experimental data, the gas-phase proton affinity,[4] the π-bond strength,[5] or the reactivity trends[6] of the simplest arsaalkene, the methylenearsane **1**, have only been investigated from a theoretical point of view.

We report here the synthesis of the methylenearsane **1**, formed by dehydrohalogenation of gaseous chloromethylarsane on a solid support in a vacuum gas–solid reaction (VGSR).[7] The characterization was performed in the gaseous phase by mass spectrometry and UV photoelectron spectroscopy (UV-PES). Using methylenearsane **1** as an example, we also present the advantages of the very efficient and reliable time-dependent density functional theory (TDDFT) approach for the theoretical evaluation of ionization potentials (IPs).

The synthesis of the chloromethylarsane **2** by chemoselective reduction of the chloromethyl arsonic acid has already been reported,[8] where the latter compound was formed by oxidation of the chloromethyldichloroarsane **3** with aqueous hydrogen peroxide. We reduced **3** directly to the arsane **2** in a 67% yield using tributyl tin hydride.[9] Compound **2** was then vaporized on solid sodium carbonate under VGSR conditions [Eq. (1)]. The gaseous flow was condensed with a co-solvent and then analyzed by ^{1}H NMR spectroscopy. With the temperature of the solid carbonate at 20°C, a small amount of arsane **2** was characterized along with some insoluble oligomeric products. The transformation was complete at a support temperature of 50°C, and at 80°C only the signals corresponding to methylarsane were observed. Attempts to characterize the very reactive species formed in the condensed phase under such conditions by low-temperature NMR (−100°C) or infrared (−196°C) spectroscopy were unsuccessful. Consequently we analyzed the gaseous flow by high-resolution mass spectrometry (HRMS).



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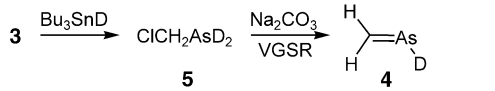
To record the mass spectrum the reactor, which contained the solid support, was connected to the ionization chamber of a high-resolution mass spectrometer. Using sodium carbonate at 20°C as the solid base, the molecular ion of chloromethylarsane **2** was unambiguously observed (calcd for CH_4AsCl: 125.9217; found: 125.922). For a solid-base temperature of 50°C, this compound had completely disappeared from the mass spectrum and a base peak at *m*/*z* 90 attributed to the methylenearsane **1** was observed. The high-resolution mass spectrum confirms the composition of CH_3As for the product (calcd for CH_3As: 89.94507; found: 89.9449). Traces of methylarsane (calcd for CH_5As: 91.96072; found: 91.9608) and carbon dioxide were also observed. Experiments performed with a carbonate heated to 80°C showed the presence of methylarsane as the main product. All these results are consistent with the experiments analyzed by ^{1}H NMR spectroscopy.

On the other hand, reactions performed with a deuterated compound led to the expected results. Under similar experimental conditions, the chloromethylarsane-d_2 **5** gave a compound with a molecular ion at *m*/*z* 91, which we attributed to the methylenearsane-*d* **4** (calcd for CH_2DAs: 90.95134 ; found: 90.9504) [Eq. (2)]. [D_2]Methylarsane, carbon dioxide, and DCl were also observed as minor impurities.



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To corroborate these results, we have chosen UV photoelectron spectroscopy experiments in conjunction with the theoretical evaluation of the ionization potentials, to understand the electronic structure of the methylenearsane **1**.

The UV photoelectron spectra of compounds **1** and **2** are displayed in Figure 1. In the spectrum of chloromethylarsane **2** (Figure 1a), three main ionizations are distinguished: two large peaks at around 9.85 and 12.5–13.1 eV, and a strong and intense band at 11.3 eV with a shoulder at 10.9 eV. In a further experiment, **2** was slowly vaporized over solid sodium carbonate (heated to 65 °C) and the gaseous flow was directly analyzed by UV photoelectron spectroscopy without further purification. The corresponding spectrum (Figure 1b) has a new intense ionization at 9.7 eV with a marked shoulder at 10.3 eV, as well as large peaks at 12.6 and 14.7 eV. The disappearance of the sharp band centered at 11.3 eV corresponding to the precursor **2** can be clearly observed. The ionizations at ≈8.8 and 11.8 eV, which varied in intensity, are attributed to other products (probably traces of methylarsane and oligomeric species). The detection of CO_2 is indicative of the effectiveness of the dehydrochlorination.

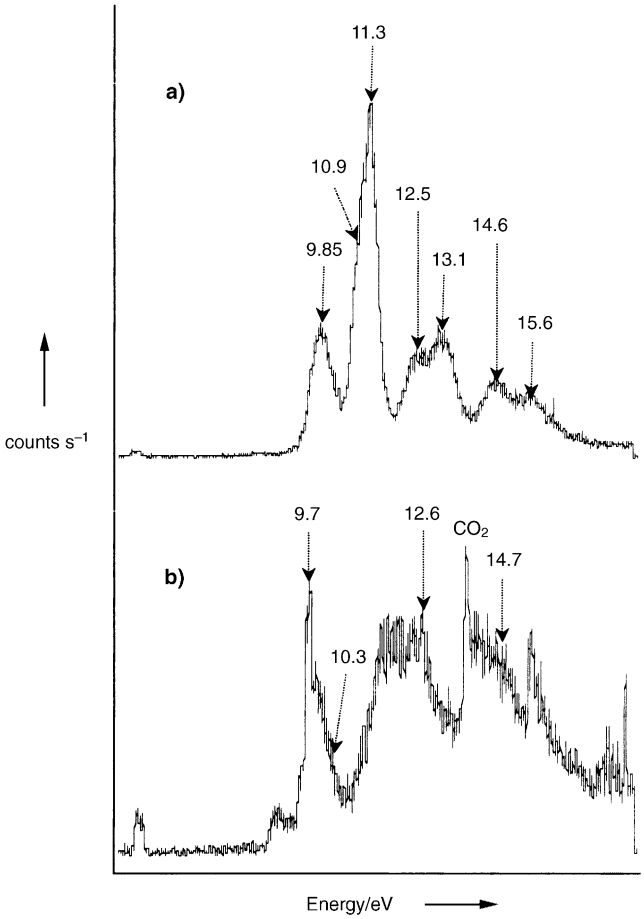

Figure 1. Photoelectron spectra of a) **2**, b) **2** vaporized on Na_2CO_3 (IP in eV).

The photoelectron spectrum of chloromethylarsane **2** was analyzed taking into account the ionization potentials of CH_3AsH_2 (9.50 eV n_{As}, 11.2–12.6 $\sigma_{As\text{-}C}$)[10] and CH_3Cl (11.29 n_{Cl}, 14.42 eV $\sigma_{C\text{-}Cl}$).[11] The first band is essentially assigned to the ejection of an electron from the arsenic lone pair, which is stabilized by 0.35 eV compared to the methylarsane because of the withdrawing effect of the chlorine atom. The next band is principally due to the ionization of the lone pairs of the chlorine atom, and the two large peaks correspond to the ejection of an electron from the σ orbitals.

For compound **1**, the disappearance of the signals corresponding to the chlorine atom lone pairs in the photoelectron spectrum confirms the formation of a nonchlorinated compound. For the methylenephosphane $CH_2{=}PH$,[2b] the vertical $\pi_{P=C}$ and n_P IPs were observed at 10.30 and 10.70 eV, respectively. Considering only these experimental results, we attribute the first band at 9.7 eV to the ejection of an electron from the $\pi_{C=As}$ orbital and the second band at 10.3 eV to the orbital corresponding to the n_{As} arsenic lone pair. The shift of the first band to lower energy relative to methylenephosphane clearly corresponds to a slightly more diffuse character of the carbon–arsenic double bond.

This qualitative interpretation of the PE spectra is not straightforward and comparison of theoretical and experimental IPs is necessary for a reliable identification. Considering that the scope of generally applicable methods for larger and more complicated systems is very limited, we tested the reliability of the TDDFT[12] approach in comparison with OVGF,[13] the more sophisticated CASPT2 calculations,[14] or by "shifting" the calculated Kohn–Sham energies[15] by taking compounds **1** and **2** as simple examples.

Table 1 displays the computed and estimated values of IPs for **1**. The first row of values correspond to the arsenic–carbon double bond, the second row is mainly localized on the arsenic lone pair, and the third and fourth row of figures are associated with simple carbon–arsenic and carbon–hydrogen bonds, respectively. It is worth mentioning that the three methods of calculation of the IPs are in excellent agreement with experimental data, since the deviations from experimental values are less than 0.2 eV. The performance of TDDFT is better than that of OVGF, but is much more favorable than the more expensive CASPT2 caluculations. On the other hand, considering Khon–Sham energies corrected by the uniform shift $x = 2.55$,[15] the estimated values of IPs agree surprisingly well with those calculated by TDDFT and CASPT2. This comparison of experimental IPs of methylenearsane **1** with high-level correlated ab initio calculations

Table 1: Comparison of calculated and experimental ionization potentials (IPs) for **1**; Kohn–Sham (K–S) energies and the nature of molecular orbitals ($x = 2.55$ for estimated IPs; all values in eV).

MOs nature	−K–S energies	IP TDDFT[12]	IP OVGF[13]	IP CASPT2[14]	IP estimated[15]	IP expt
$\pi_{C=As}$ (A″)	7.14	9.72[a]	9.52	9.69	9.7	9.7
n_{As} (A′)	7.76	10.37	10.22	10.13	10.3	10.3
$\sigma_{C\text{-}As}$ (A′)	9.93	12.63	12.64	12.53	12.5	12.6
$\sigma_{C\text{-}H}$ (A′)	12.13	14.74	14.85	14.62	14.7	14.7

[a] value of ΔSCF.

proves the reliability of the TDDFT approach. However, OVGF-computed IPs are also satisfactory.

Table 2 lists the calculated and experimental values for the IPs of **2**. The first and third molecular orbitals correspond to the antibonding and bonding combinations of arsenic and chlorine lone pairs (in the same plane). The second orbital is associated with $n^{\pi}_{Cl,}$ while the fourth IP is mainly due to the ejection of an electron from σ^{-}_{As-H} bond. We note that the first ionic state is slightly underestimated ($\Delta SCF = 9.68$ eV), and as a direct consequence the following TDDFT ionization potentials are slightly too low. For IPs calculated by the OVGF method the first value is also underestimated (9.64 eV). However, values displayed in Table 2 correspond to the conformation in which the arsenic lone pair and the chlorine atom are antiperiplanar, thus allowing free rotation. A similar study performed on compound **3** also gave a very good correlation between TDDFT and the experimental data (see Supporting Information).

Table 2: Calculated and experimental ionization potentials (IPs) for **2** ($x = 2.5$ for estimated IPs; all values in eV).

MOs nature	−K–S energies	IP TDDFT	IP OVGF	IP estimated	IP expt
$n_{As}-n_{Cl}$ (A′)	7.34	9.68[a]	9.64	9.85	9.85
n_{Cl} (A″)	8.37	10.56	11.00	10.9	10.9
$n_{As} + n_{Cl}$ (A′)	8.59	11.28	11.09	11.1	11.3
σ^{-}_{As-H} (A″)	10.09	12.41	12.92	12.6	12.5
$n_{Cl}\ \sigma_{C\text{-}As}$ (A′)	10.50	12.91	13.04	13.0	13.1

[a] Value of ΔSCF.

In summary, the methylenearsane **1** has been prepared by dehydrohalogenation of a chloromethylarsane on solid sodium carbonate and characterized by mass spectrometry and UV photoelectron spectroscopy. The experimental and theoretical data for **1** emphasize an electronic similarity of arsenic and phosphorus double-bonded to the carbon atom, as well as a more diffuse character of the $\pi_{C=As}$ orbital originating from the 2pπ–4pπ overlap and weaker energy (0.6 eV) of this double bond relative to the phosphorus analogue (2pπ–3pπ). Moreover, the destabilization of the n_{As} orbital compared to the $\pi_{C=As}$ orbital is weaker than the one observed for the corresponding orbitals of the phosphorus analogue. This fact can be explained as the compromise between increasing s character of arsenic lone pair and its slightly smaller electronegativity. A significant separation (0.6 eV) of the two first ionic states (0.4 eV for the methylenephosphane) may also lead to the increased reactivity of this double-bond system. On the other hand, the performance of TDDFT method for evaluation of ionization potentials has been successfully demonstrated in the present case.

Experimental Section

All details of the synthesis of compounds **1**–**3**, mass spectrometry, UV-photoelectron spectroscopy, and the quantum chemical procedures employed in this study are given in the Supporting Information.

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