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Photoelectron Spectrum of Ethylidenearsane: A Revised Assignment

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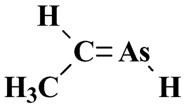
Summary: The interpretation of photoelectron spectrum of ethylidenearsane is based on calculated energies for the first two ionic states. This assignment is coherent with the experimentally observed C-methylation effect.

The kinetically nonstabilized ethylidenearsane and ethylidynearsane, obtained by base-induced rearrangement of vinylarsane and ethynylarsane, respectively, on solid K_2CO_3 under vacuum gas−solid reaction (VGSR) conditions, were characterized by their photoelectron spectra.[1] These spectra were interpreted by analogy with the spectra of their phosphorus analogues.[2]



ethylidenearsane

However, the comparison between the theoretical and experimental IPs, necessary for a reliable identification, was not realized at that time.

Later, we showed for the ethylidenephosphane and the ethylidynephosphane[3] that the density functional methods (BP 98, B3LYP, B3PW91) associated with the 6-311G(dp) basis set gave better results than the HF/MP2 method for the evaluation of ionic state energy ($\mathrm{IP} = E(\mathrm{molecule}) - E(\mathrm{cation\ radical})$), in agreement with the conclusions already drawn by many authors.[4]

We have applied the same methods to the arsenic derivatives, and Table 1 summarizes our main results obtained for the phosphorus and arsenic compounds of low coordination number.

The calculations of these IPs are in excellent agreement with experimental data, the deviations from experiment being less than 0.2 eV.

The ethylidynearsane is characterized by two bands at 9.6 and 12.1 eV.[1]

On the other hand, for ethylidenearsane, a very unstable product, it appears that our assignment of the band at 9.6 eV[1] to the ejection of an electron from the πAs=C orbital is wrong. According to the calculations, this ionization occurs at around 9.3−9.4 eV. In addition, the calculated gap related to ethylidenephosphane (experimental IP 9.75 eV) is 0.4 eV. However, the band observed at 10.3 eV is best associated with the ejection of an electron of the lone pair of the arsenic atom of ethylidenearsane. The phosphorus and arsenic lone pair ionizations are calculated to be very close in energy. The experimental ionization for ethylidenephosphane is observed at 10.35 eV. The very intense band at 9.6 eV is probably due to a hydrolysis product obtained in the rearangement reaction and masks the first ionization.

The analogy often made between the arsa- and phosphaalkene is relative: the pnictogen lone pairs are energetically close, but the energies of the πPn=C orbitals are quite different.

The attribution for ethylidenearsane of a 9.3 eV ionization of the πAs=C orbital, and 10.3 eV ejection of one electron from the arsenic lone pair, is confirmed by the photolelectron spectrum of isopropylidenearsane in which two bands are observed at 8.7 eV (a narrow band) and 9.9 eV (a broader, less intense band) (Figure 1). These values are in good agreement with the calculated values (Table 1). With respect to ethylidenearsane, the C methylation effect is consistent since we observed a greater destabilization for the π ionization (0.6 eV) than for the lone pair (0.4 eV). If we expect a substitution effect of the same order of magnitude for a monomethylation, we can predict for the methylenearsane two ionizations around 9.8 and 10.7 eV, in good agreement with the calculated values for the energies of the first ionic states.[6]

However, the experimental PES characterization of methylenearsane is still a difficult challenge due to its great reactivity. The spectrum recently published[7] appears to correspond to a mixture of products in which the methylenearsane ionizations are not well identified.

Experimental Section

Photoelectron Spectroscopy. The methylvinylarsane was cleanly produced by a chemoselective reduction of the corre-

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[8] Thanks are due to J. C. Guillemin for synthesizing this sample.

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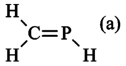
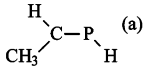
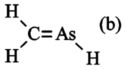
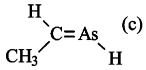
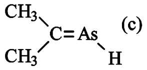
10.1021/om040134b CCC: $30.25

Table 1. Calculated Ionization Energies (eV) (values ΔSCF with 6.311G(dp) basis set) and Experimental IP

					H—C≡P (a)		CH_3—C≡P (a)	
	$^2A''$	$^2A'$	$^2A''$	$^2A'$	Π	$Σ^+$	Π	$Σ^+$
MP2/H.F.	10.11	10.26	9.4	10.09	10.81	13.04	9.85	
B3LYP	10.24	10.51	9.49	10.12	10.76	12.96	9.72	12.11
Exp	10.3	10.7	9.75	10.35	10.8	12.9	9.9	12.1
							$CH_3C≡As$ (c)	
	$^2A''$	$^2A'$	$^2A''$	$^2A'$	$^2A''$	$^2A'$	Π	$Σ^+$
MP2/H.F.			9.05	10.14	8.58	9.61	9.46	11.75
B3LYP	9.72	10.48	9.10	10.16	8.57	9.82	9.38	11.87
Exp	(9.8)	(10.7)	(9.3)	10.30	8.7	9.9	9.6	12.1

[a] Reference 3. [b] Reference 6. [c] Reference 5.

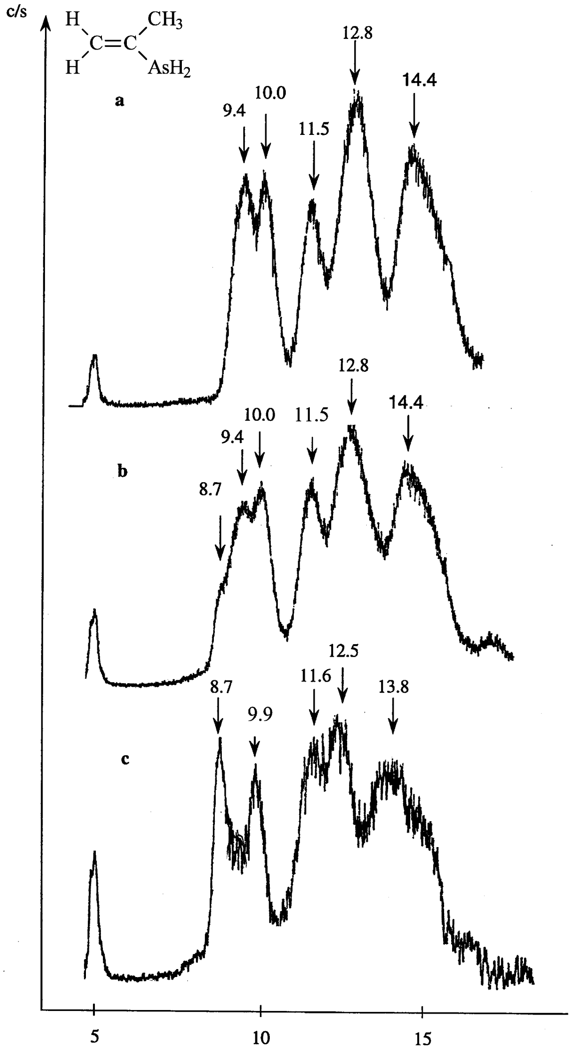


Figure 1. Photoelectron spectra of (a) 1-methylvinylarsane, (b) vaporized over K_2CO_3, and (c) after digital subtraction of spectrum a.

sponding dichloroarsane.[8] The reaction was performed in a vacuum line directly connected via a cryogenic trap to the PES inlet, and the gas flow is directly analyzed. The spectrum is displayed in Figure 1a. The base-induced rearrangement was performed by contacting the gaseous methylvinylarsane with solid potassium carbonate at 373 K in VGSR conditions (cf. ref 1).

The reaction was not complete, but we clearly observe a shoulder at 8.7 eV and an increase of the intensity of the band at 10.0 eV (Figure 1b). The spectrum obtained by digital subtraction of the starting compound shows two well-resolved bands at 8.7 eV (narrow) and 9.9 eV (broad, less intense) (Figure 1c).

The first band is assigned unambiguously to ionization of the πC=As orbital and the larger second one to the ionization of the arsenic lone pair. This attribution is in good agreement with the calculated energies of the ionic states: A″, 8.57 eV; A′, 9.82 eV.

Photoelectron spectra were recorded with a Helectros 0078 spectrometer equipped with a 127° cylindrical analyzer using 21.21 eV He I irradiation as a photon source and monitored by a microcomputer supplemented with a digital analogue converter. Helium autoionization at 4.98 eV and nitrogen ionizations at 15.59 and 16.98 eV were used for calibration.

Computational Details. The calculations were performed using Gaussian-98.[9] Geometry optimizations were performed at both the HF level and DFT level of theory[10] with the B3LYP functional[11] and confirmed as true minima through vibrational analysis. Ionization energies were calculated with the ΔSCF method using energies of neutral and ionized molecules calculated at the MP2/HF and DFT levels of theory with the B3LYP functional at ground state geometries in order to obtain vertical ionizations. The basis set retained was 6.311-G(dp).

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