J. Am. Chem. Soc. 1988, 110, 6964–6967

Phosphaethene. Synthesis by Vacuum Gas–Solid Reaction (VGSR) and Characterization by Photoelectron Spectroscopy[1]

Sylvie Lacombe,[†] Danielle Gonbeau,[†] Jean-Luc Cabioch,[‡] Bruno Pellerin,[‡] Jean-Marc Denis,[‡] and Geneviève Pfister-Guillouzo[*,†]

Contribution from the Laboratoire de Physico-Chimie Moléculaire, UA 474, Université de Pau et des Pays de l'Adour, Avenue de l'Université, 64000 Pau, France, and the Groupe de Recherches de Physicochimie Structurale, UA 704, Avenue du Général Leclerc, 35042 Rennes, France.

Received January 4, 1988

Abstract: Phosphaethene, the unstable parent compound in the phosphaalkenes series, has been thoroughly investigated using theoretical calculations. For the first time, its electronic structure is evidenced from its photoelectron spectrum. The PE spectra of phosphaethene and 1-phosphapropene, generated in the gas phase by the respective vacuum dehydrochlorination of chloromethylphosphine and 1-chloroethylphosphine, have been recorded in situ by the use of a vacuum device directly coupled to the spectrophotometer. The vertical $\pi_{P{=}C}$ and n_p ionization energies are observed respectively at 10.30 and 10.70 eV for phosphaethene and at 9.75 and 10.35 eV for 1-phosphapropene. The band's characterizations are discussed through correlations with the corresponding imines and with substituted phosphaalkenes and are confirmed by ab initio theoretical calculations. The results indicate a rather significant energetic separation between the two first $\pi_{P{=}C}$ and n_p ionic states.

1. Introduction

Phosphaethene ($CH_2{=}PH$) is the unstable parent compound in the series of the extensively studies phosphaalkenes.[2] It was first tentatively identified by Hopkinson et al.[3] by observation of a single microwave transition at 31.067 MHz. This identification was confirmed by a complete assignment of the microwave spectra of phosphaethene and isotopic species. In these reports phosphaethene was generated by flash-thermolysis of either dimethylphosphine[4] or trimethylsilylmethylphosphine.[5] The recent work of some of us[6a] concerning the preparation of phosphaethene by a gas–solid dehydrochlorination of chloromethylphosphine (VGSR) and its characterization by NMR and mass spectrometry enabled us to record its photoelectron spectrum (PES), by use of a vacuum device directly coupled to the spectrometer.[7] This study thus constitutes the first experimental characterization of the electronic structure of phosphaethene which up to now could only be inferred from spectral data on substituted compounds[8] or from theoretical calculations.[9] Our experimental results on phosphaethene (**1**) and 1-phosphapropene (**2**) generated by the respective dehydrochlorination of chloromethylphosphine and 1-chloroethylphosphine have been supplemented by a theoretical study of the ionization potentials of phosphaethene.

2. Experimental Section

Photoelectron spectra were recorded on an Helectros 0078 spectrometer connected to a microcomputer system supplemented by a digital analogic converter (DAC). The spectrometer was coupled to the vacuum device where the VGSR were performed, so that the gaseous flow was continuously analyzed.

Chloromethylphosphine[6a] and 1-chloroethylphosphine[6b] were prepared by reduction of the corresponding phosphonates according to the reported methods. These chlorophosphines were then slowly distilled at 243 K over a 30-cm length of solid K_2CO_3 at 373 K (carefully powdered and dried by extensive heating at 473 K under vacuum). A cold trap cooled to 153 K for phosphaethene and 178 K for 1-phosphapropene was inserted between K_2CO_3 and the spectrometer to get rid of the unreacted starting compounds. In both cases the pressure in the device amounted to 10^{-3} mbar before vaporization of the phosphine.

The calculations were performed with the Monstergauss program.[10] The split-valence 4.31G basis set was used, augmented by one set of d polarization functions on phosphorus ($\delta_p{}^d = 0.57$)[11] (set A) and by one set of diffuse functions on phosphorus (set B).[12]

In light of the size of system, we were led to use a method of pseudo-potentials[13] (PS HONDO program[14]) for the rigorous calculation of ionization potentials. The pseudo-potentials and the double-zeta (ζ) quality basis set previously determined[15] were adopted including d polarization and s diffuse type functions for phosphorus. The energies of ionic states were evaluated by a configuration interaction method iteratively combining variation and perturbation (CIPSI algorithm[16]). A subspace S_0 was constructed iteratively in order to obtain a plurideterminant zero-order function. To evaluate the remaining correlation energy a second-order Moller–Plesset perturbation method was used (all mono- and biexcited determinants of S_0). In some cases, in order to evaluate the correlation energy as accurately as possible a technique for extrapolating a variational correlation energy was used.[17] To estimate the participation of quadriexcited determinants to S_0, corrections were calculated as proposed initially by Davidson.[18]

[†] University of Pau.

[‡] University of Rennes.

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Table I. Calculated Vertical Ionization Potentials of Phosphaethene

	IP (eV)					
	Koopmans[9a]	CIPSI		extrapolation[17]	extrapolation + correction[18]	extrapolation + correction[18]
ionic state	set A	set A	set B	diagonalization	$(1 - C_0^2)(E_i - E_0)$	$[(1 - C_0^2)(2C_0^2 - 1)](E_i - E_0)$
$^2A''$	9.63	10.03	10.05	10.02	9.97	9.94
$^2A'$	10.43	9.91	9.85	10.19	9.92	9.77

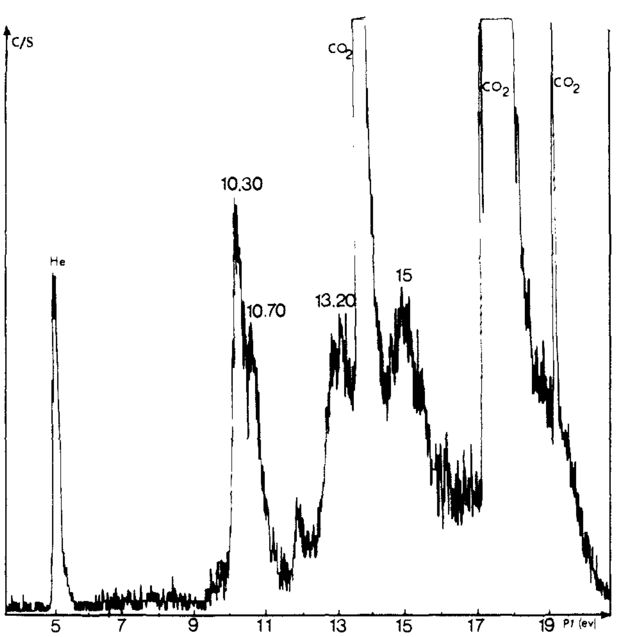


Figure 1. Photoelectron spectrum of phosphaethene.

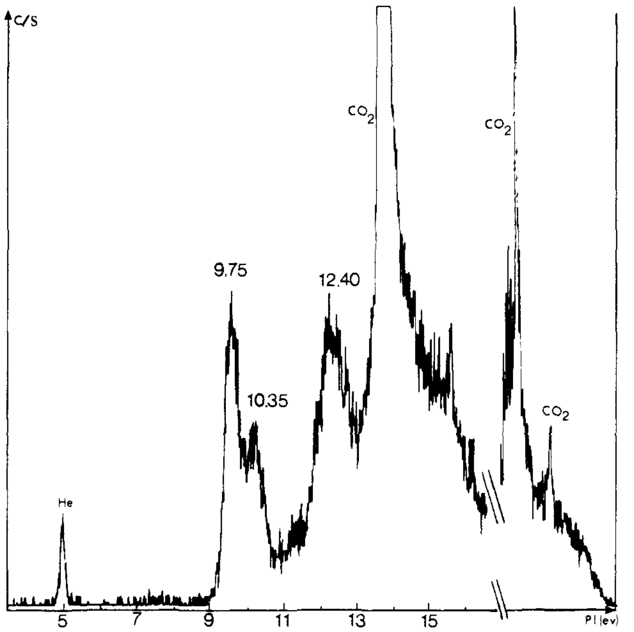


Figure 2. Photoelectron spectrum of 1-phosphapropene.

3. Photoelectronic Spectra

In the VGSR conditions, phosphaethene (**1**) was generated very cleanly as indicated by its photoelectron spectrum (Figure 1). The only other reaction product is carbon dioxyde (ionizations at 13.78, 17.59, and 18.08 eV). When the trap is warmed, no side-product is detected except unreacted chlorophosphine. For 1-phosphapropene (**2**), we also observe in the PE spectrum (Figure 2), besides the bands of the phosphaalkene, the presence of carbon dioxide.

In both cases the reaction proceeds very cleanly, and the detection of CO_2 is indicative of the effectiveness of the dehydrochlorination. The initial pressure in the apparatus is an important parameter. It should be pointed out that after a few minutes the pressure in the photoelectron spectrometer begins to decay and no more signal is obtained.

For both phosphaalkenes, two first bands are observed at 10.30 and 10.70 eV for phosphaethene (**1**) and 9.75 and 10.35 eV for 1-phosphapropene (**2**). The former one always appear thinner than the latter, which is rather broad and poorly resolved. Besides the bands of CO_2 we notice other ionizations at 13.20 and 15 eV for **1**. In the case of the substituted compound **2**, the ionizations of CO_2 are rather strong but two broad bands are observed at 12.40 eV and between 14 and 15 eV. In this part of the spectrum only the skeleton is concerned and the problem arises primarily from the attribution of the two first bands. Without taking their order into account, it may be assumed that they result from the ejection of an electron from the $\pi_{P=C}$ bond ($^2A''$ ionic state) and from the lone pair of the phosphorus atom ($^2A'$ ionic state).

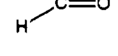
These results may be compared to the photoelectron spectrum of 2-phosphapropene reported by Bock and Bankmann.[8c] In this case, two very close first bands were obtained at 9.69 and 9.97 eV, and were attributed respectively, on the basis of MNDO eigenvalues (Koopman's approximation), to $^2A''$ and $^2A'$ radical cation states.

4. Discussion of Results

From ab initio calculations with different basis sets,[9a-c] the same attribution has been proposed for phosphaethene with the order $^2A''$, $^2A'$. The energetic gap between the two first orbitals $\pi_{P=C}$ and n_p has been estimated to 0.8 eV.[9a] Nevertheless, the results of Peyerimhoff[9c] on the isovalent molecules $H_2C=NH$, $H_2C=PH$, $H_2Si=NH$, and $H_2Si=PH$ have led, with a complete configuration interaction (MRD-CI calculation), to two close ionic states $^2A'(n_\infty)$ and $^2A''(\pi_\infty)$ respectively calculated at 10.29 and 10.11 eV for $CH_2=PH$. Moreover, these authors have pointed out that the $^2A''$ ionic state was always underestimated by about 0.2 eV under these conditions and they thus assume that the two first ionization potentials are superimposed.

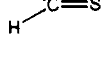
Our own results are displayed in Table I and give rise to the same conclusion. The calculations have been performed with the CIPSI algorithm followed by an extrapolation method and corrections according to Davidson.[18] We have used 4.31G basis sets supplemented with either polarization orbitals (set A) or both polarization and diffuse orbitals (set B). As Cederbaum et al. already mentioned for H_2S or $H_2C=S$,[19] the experimental results are not in agreement with the calculations for $CH_2=PH$. This problem appear to be common to molecules bearing second-row atoms.

According to these inadequate theoretical results, it seems reasonable to turn back to experimental considerations to explain the spectra. For formaldehyde, thioformaldehyde, or methanimine, the analysis of the vibrational spacings has unambiguously led to the attribution of the $^2A''$ and $^2A'$ ionic states. In the case of the $^2A''$ state (bonding electron) a pronounced vibrational progression is expected, the stretching vibration ν_{CX} of the ionic state being much smaller than that of the ground state.



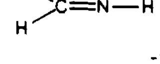
$\nu_{C=O} \sim 1700\ cm^{-1}$

$\nu^+_{C=O} \sim 1210\ cm^{-1}$ [20]



$\nu_{C=S} \sim 1200\ cm^{-1}$

$\nu^+_{C=S} \sim 840\ cm^{-1}$ [21]



$\nu_{C=N} \sim 1600\ cm^{-1}$

$\nu^+_{C=N} \sim 1300\ cm^{-1}$ [22]

For the $^2A'$ state (nonbonding electron) of formaldehyde or

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Table II. Ab Initio Calculated (Koopmans' Approximation)[25] and Observed Ionization Potentials of Phosphaalkenes

$H{-}P{=}CH_2$			$CH_3{-}P{=}CH_2$			$HP{=}CHCH_3$		
nature of MO	calcd	exptl	nature of MO	calcd	exptl[8c]	nature of MO	calcd	exptl
$\pi_{P=C}$ ($^2A''$)	9.63	10.30	$\pi_{P=C}$	9.29	9.69	$\pi_{P=C}$	9.11	9.75
n_P ($^2A'$)	10.43	10.70	n_P	9.92	9.97	n_P	10.26	10.35
$\sigma_{H\text{-}P\text{-}C\text{-}H}$	14.02	13.20	σ_{HCPCH}	13.21	12.42	σ_{HCCPH}, σ_{CH_3}	13.32	12.75
			σ_{CH3}	15.14	13.9	$\sigma_{C(H)\text{-}C}$	14.37	
			π_{CH3}	15.23	14.4	π_{CH_3}	15.42	
σ_{CH_2}	16.51	15.00	π_{CH_2}	16.20	15.5	σ_{HCCPH}, σ_{CH_3}	16.70	

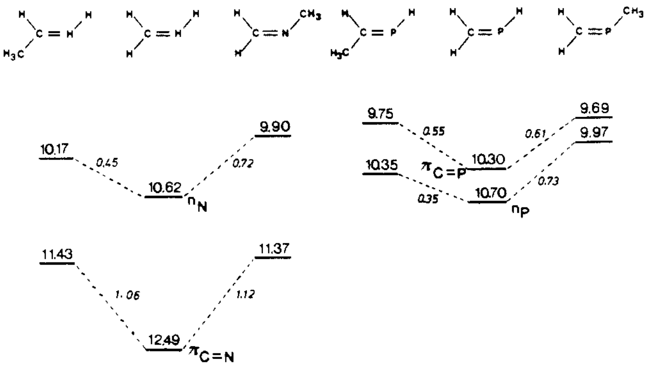

Figure 3. Correlation between the vertical ionization potentials of imines and phosphaalkenes.

thioformaldehyde sharp bands are observed, whereas in the case of the imine the band is broad and displays a structure arising from the ν_6 vibration (CNH knicking) of the ion amounting to 500 cm^{-1} (ν_{CNH} of the ground state, 1344 cm^{-1}). In our recording conditions the vibrational structures are poorly resolved, in agreement with the recent work of Ohno.[23] As a matter of fact, the $\nu_{C=P}$ stretching wavenumber of $CH_2{=}PCl$ is observed at 980 cm^{-1}, and the ν_6 (CPH knicking) in $CF_2{=}PH$ at 485 cm^{-1}, so that it may be assumed that the vibrational frequencies of the ionic states are weak.

Our characterization of the two first bands is based on methylation effects (either at carbon or phosphorus) and on the comparison with the corresponding imines. The spectrum of methanimine has been first obtained by Peel and Willett,[24] and has recently been described with those of substituted imines by Bock and Dammel.[22] The first striking difference between methanimine and phosphaethene concerns the shapes of the two first bands; the latter is broader and less strong than the former for the phosphorus compound, in contrast with the spectrum of the imine. This observation suggests a reverse ionization order.

Starting from this assumption, methylation effects have been analyzed as displayed in Figure 3, and seem to be consistent with the proposed order $^2A''$, $^2A'$. We notice that the energies of the $^2A'$ ionic states undergo the same type of variation, with a more pronounced effect for a P or N methylation than for a C methylation. The energetic differences between the $^2A''$ ionic states are found to be more important for the imines than for the phosphorus compounds, but for the two types of molecules the $^2A''$ ionic states of the methylated derivatives (either at carbon or heteroatom) are observed at the same energy level: 11.43 and 11.37 eV for imines and 9.75 and 9.69 eV for phosphaalkenes. The less important destabilization observed for phosphaethene results from the pronounced diffuse character of the $\pi_{P=C}$ orbital (Figure 4) leading to a weaker electronic delocalization for the methylated derivatives $^2A''$ ionic states.

This diffuse character, originating from the $2p\pi$–$3p\pi$ overlap, may account for the much weaker energy of the $\pi_{P=C}$ orbital relative to the $\pi_{N=C}$. Moreover, the important s character of the lone pair of phosphorus, inferred from the value of the CPH angle of 97°4′[5b] and 95°5′[4] determined from microwave values, still favors the reverse order of the ionization potentials with respect to the imines (Figure 5).

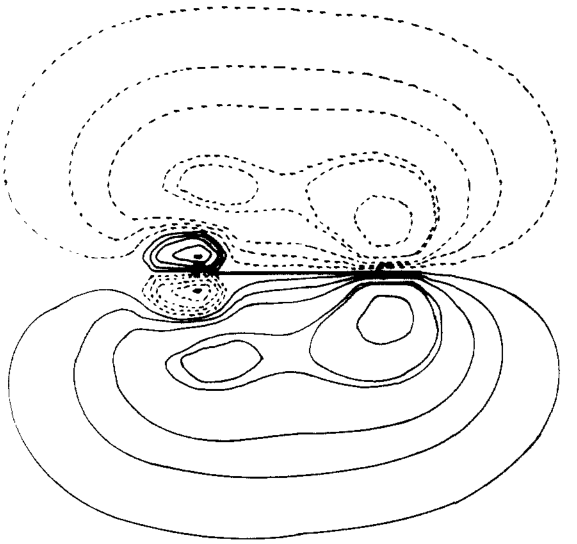

Figure 4. Wave-function contours of the $\pi_{P=C}$ orbital. Wave-function contours are associated with the values ±0.02, ±0.05, ±0.08, ±0.13, ±0.14, and ±0.2.

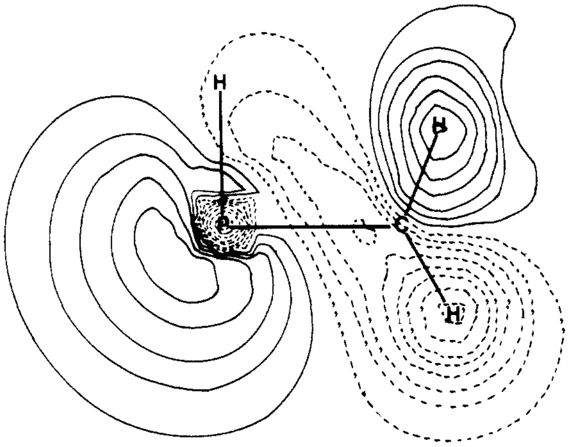

Figure 5. Wave-function contours of the lone pair of phosphorus. Wave-function contours are associated with the values ±0.02, ±0.05, ±0.08, ±0.13, ±0.18, ±0.23, and ±0.28.

Thus our attribution order of the two first ionic states is in agreement with the results of Koopmans' calculations (Table II). In this table all the orbital energies for the other experimental bands are also displayed. It is noticeable from our results (Tables I and II) that the electronic correlation plays an important role in the $^2A'$ ionic state. Nevertheless, with the bases used and with the up-to-date configuration interactions, the electronic reorganization of the ion and the correlation effects are miscalculated for the $^2A''$ ionic state. This problem, general to second-row atoms

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involved in π double bonds, is under investigation.

5. Conclusion

From these results, a significant energetic separation between the $^2A''$ and $^2A'$ ionic states is evidenced for both phosphaethene and 2-phosphapropene. This should lead for these compounds to an enhanced reactivity of the P=C double bond as compared with the phosphorus lone pair toward transition metals (η^2 P=C bonded complexes[26]). To our knowledge, the behavior of phosphaalkenes toward complexation has been achieved only on heavily substituted compounds,[27] and no experimental data on the ability of phosphaethene to form either η^1 or η^2 complex are available. Further photoelectronic studies on substituted phosphaalkenes are under investigation in order to complete these results.

Acknowledgment. We thank Mrs Maryse Simon for her efficient technical assistance during the course of this work. This project is financially supported by the CNRS (ATP: Synthetic processes under extreme physical conditions).

Registry No. 1, 61183-53-7; **2**, 107257-40-9.

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Infrared Vibrational Circular Dichroism of Alanine in the Midinfrared Region: Isotopic Effects

Max Diem

Contribution from the Department of Chemistry, City University of New York, Hunter College, 695 Park Avenue, New York, New York 10021. *Received January 11, 1988*

Abstract: The infrared vibrational circular dichroism (VCD) spectra of L-alanine (L-Ala) and L-alanine-N-d_3 (L-Ala-N-d_3) in water and deuteroxide are reported between 900 and 1700 cm^{-1}. Large VCD signals are observed in vibrations associated with the C–H deformation modes of the methine hydrogen, whereas the other vibrations exhibit small, but certainly observable, VCD. The methine deformation vibrations do change significantly upon N-deuteriation of the molecule, both in terms of their frequencies and vibrational and VCD intensities.

Infrared (vibrational) circular dichroism, the differential absorption of left and right circularly polarized infrared radiation by molecular vibrational transitions, has recently been used by a number of researchers as a new probe for peptide and nucleotide conformation.[1-3] So far, conformational sensitivity for peptides was established in the amide I and amide II (1550–1700 cm^{-1}) spectral region in peptides,[2,3] and in the same wavenumber range in a number of model polynucleotides.[1] In the former case, the interaction of peptide linkages gives rise to distinct positive/negative couplets, which can, in principle, be related to conformation via the coupled oscillator model. Similarly, the interaction of certain base vibrations in the nucleotides produces pronounced couplets, which are indicative of the orientation of the coupling dipoles.

For very small peptides, such as dipeptides, we have shown recently[4] that the amide I and II vibrations do not produce significant VCD intensities, thus giving further evidence that the VCD intensities observed in large peptides are due to a coupling mechanism. However, we found very large VCD intensities[4] in the amide III spectral region (1270–1330 cm^{-1}). This region was previously studied in detail via investigation of the vibrational spectra of six isotopically substituted alanine dipeptides, and it was established that the "amide III" vibration is a delocalized, coupled vibration of an N–H deformation and adjacent C–H deformations.[5]

Although this vibrational study explains the observed VCD in terms of the vibrations involved, there is, to date, no explanation for the large intensity observed in the amide III region. A coupled oscillator or a simple fixed partial charge model calculation yields for the C*–H stretching or deformation vibrations, or the coupled amide III mode, VCD intensities that are about one order of magnitude lower than the observed values.[6a] Thus, the origin of the large intensity has to be investigated further. In the following paper, we report the VCD results of the monomeric molecule, alanine, between 800 and 1700 cm^{-1} in aqueous solution, with special emphasis on the C–H deformation region (1250–1350 cm^{-1}), to shed light on the origin of the large VCD intensities in these modes.

Both alanine and alanine-N-d_3 in H_2O and D_2O, respectively, were investigated. For both species, the VCD spectra are dominated by signals due to the methine C–H deformation vibrations, which exhibit very large VCD intensities in both species, whereas the remaining vibrations exhibit much smaller VCD intensities. This behavior is similar to the one observed in alanine in the C–H *stretching* range,[6] where the only large signal is due to the methine stretching vibration, at 2950 cm^{-1}. It was this large intensity of the methine stretching vibration in alanine, and all other α-amino

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