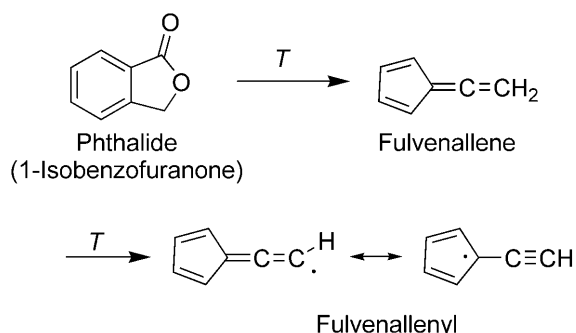


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Photoionization of C_7H_6 and C_7H_5 : Observation of the Fulvenallenyl RadicalMichael Steinbauer,^[a] Patrick Hemberger,^[a] Ingo Fischer,^{*[a]} and Andras Bodi^[b]

Species of the composition C_7H_n are known intermediates in combustion processes.^[1] One out of five C_7H_5 isomers, fulvenallenyl, was recently computed to be a resonance-stabilized radical^[2] expected to be long-lived and to play an important role in the formation of soot and polycyclic aromatic hydrocarbons.^[3] Thus, its structural and thermochemical characterization is relevant for the combustion community. A C_7H_5 species was previously observed in a toluene flame,^[4] but could not be unambiguously assigned to a specific isomer. Herein we report the direct observation of fulvenallenyl in a threshold photoelectron spectrum (TPES) obtained using synchrotron radiation. We also report a TPES of the C_7H_6 isomer fulvenallene together with an accurate ionization energy (I_E) of both species. Such data on reactive species are necessary for their isomer-selective detection in flames.^[5]

Fulvenallene as well as fulvenallenyl were produced by flash pyrolysis^[6] of phthalide according to Scheme 1. This approach has been used before^[7] to record conventional photoelectron spectra of fulvenallene, an unstable species despite being a closed-shell molecule.



Scheme 1. Flash pyrolysis of phthalide yields fulvenallene. At higher temperatures the fulvenallenyl radical is produced by further H-atom abstraction.

Figure 1 shows mass spectra recorded at a photon energy of 12.0 eV. Without pyrolysis (lower trace) a peak due to the phthalide precursor at $m/z=134$ is visible as well as a smaller

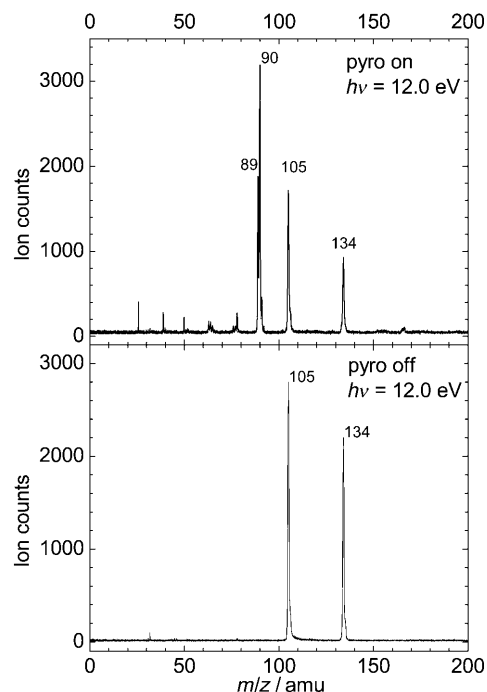


Figure 1. Mass spectra recorded at $h\nu = 12.0$ eV with pyrolysis off (lower trace) and on (upper trace). The mass 89 signal at high temperatures is due to C_7H_5 .

peak at $m/z=105$, which is due to dissociative photoionization via the loss of HCO. When the pyrolysis is turned on (upper trace), the precursor signal decreases and a peak at $m/z=90$ appears, corresponding to C_7H_6 . In addition, a peak is revealed at $m/z=89$, which grows in intensity with increasing pyrolysis temperature. The calculated bond dissociation energy of the allenic C–H bond is 340 kJ mol^{-1} and is the by far lowest in fulvenallene.^[2] The selective loss of this H-atom at high temperatures is thus not surprising. Small fragment peaks at lower masses are also present at high temperatures.

We subsequently recorded TPE-spectra of both species using photoelectron-photoion coincidence spectroscopy.^[8] This method permits recording a mass-selected photoelectron spectrum for each species, and is well-suited for the investigation of reactive intermediates.^[9] Both spectra in Figure 2 are dominated by one large peak at 8.22 eV (C_7H_6) and 8.19 eV (C_7H_5). Additional scans below 8 eV did not reveal any further signal. The dissociative ionization of fulvenallene only sets in above 11 eV and does not perturb the mass-selected TPES of C_7H_5 . Ionization energies of five different C_7H_5 isomers were computed by density functional theory (DFT) using the B3LYP exchange correlation functional and the 6-311++G** basis.^[10] The fulvenallenyl I_E (Scheme 1) was computed to be 8.17 eV

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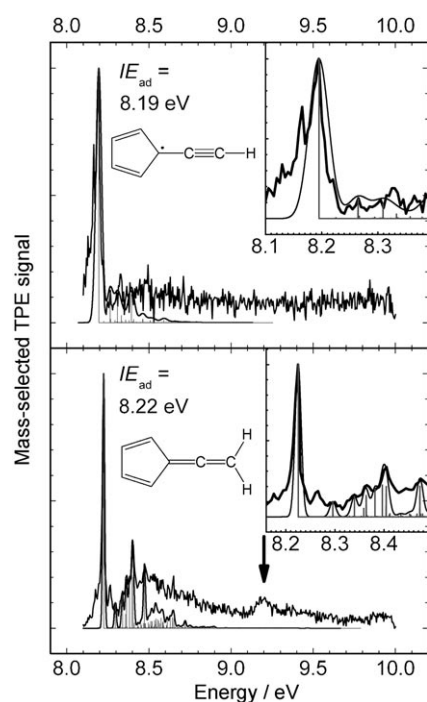


Figure 2. Mass-selected threshold photoelectron spectra of fulvenallene (lower trace) and fulvenallenyl (upper trace). A simulated spectrum based on a Franck-Condon fit (grey sticks) is given for comparison. The arrow in the lower trace indicates a band that can be assigned to an excited state of $C_7H_6^+$.

and the ionic ground state was found to have 1A_1 symmetry. IE_s between 6.44 eV and 7.49 eV were obtained for the other isomers.

To further confirm the correct assignment of the ions, the spectra were simulated by a Franck-Condon (FC) fitting procedure. Initially the geometries, vibrational frequencies and force constants of the neutral and ionic ground state of both species were computed by DFT. FC factors were calculated using the *fcfit* program (version 2.8.8).^[11] This program can be employed to simulate both absorption and emission processes, although it has been used before mainly for the simulation of dispersed emission spectra. The geometry of the ion was then varied until the best fit to the band intensities was obtained. The stick spectra were subsequently convoluted with a Gaussian function. The simulated spectra are given as thin lines in Figure 2. Note that contributions from autoionization, which can perturb the intensities, are not considered in the fit. A microwave spectrum of fulvenallene is available in the literature,^[12] but the derived geometry is very close to the *ab initio* one. The latter one was therefore employed in the fit. In fulvenallene, activity in C–C and C=C modes is evident in the spectrum (lower trace). Since the HOMO of the molecule is centered on the five-membered ring, ionization will lead to an increase in the length of the double bonds and a decrease in that of the single bonds in the ring. The experimental results thus match the expectations. The additional peak around 9.2 eV marked by an arrow can be assigned to the 2B_1 excited electronic state previously observed at 9.14 eV.^[13] On the other hand, only little vibrational activity is seen in the TPES of C_7H_5

(upper trace). The FC fit indicates the fundamentals of several modes of the five-membered ring to be active with low intensity only. In both molecules the ionic geometries optimized in the FC fit are close to the *ab initio* ones which are close to those computed by other groups.^[2,14] The bond lengths and angles are given in the Supporting Information. Note that it is not our aim to extract highly accurate geometries from the data, but rather to confirm the assignment of the spectra to the fulvenallene and fulvenallenyl isomers. Considering the closeness of the geometries derived from the fit with the computed ones this has been achieved. The ionization energies are summarized in Table 1. As visible, the agreement between experimental and calculated IE_s is remarkably good, considering that simple DFT was applied. The experimental values are assumed to be accurate within ± 10 meV (fulvenallene) and ± 20 meV (fulvenallenyl) as estimated from the half width at half maximum of the major band.

Table 1. Experimental and computed adiabatic ionization energies.

Species	Ionic State	IE_{ad} (exp) [eV]	IE_{ad} (calc) [eV]
C_7H_5	1A_1	8.19	8.17
C_7H_6	2A_2	8.22	7.93

Conventional photoelectron spectra of fulvenallene have been recorded before. The ionization energies of 8.22 ± 0.02 eV^[7] (IE_{ad}) and 8.29 eV^[13] (IE_{vert}) are close to the value determined here. However, both earlier spectra differ significantly in appearance and show several intense peaks rather than one. Our new data have two advantages over the earlier ones. 1) the photoelectron spectra are ion mass-selected and 2) the TPES can be fitted with a geometry close to that calculated for fulvenallene. The undetected presence of a side product like C_7H_5 in the earlier experiments might be a possible reason for this difference.

Experimental Section

The experiments were carried out at the VUV beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute, Villigen/CH. A bending magnet provides synchrotron radiation which is collimated and diffracted by a plane grating (600 grooves mm^{-1}) with a resolving power of 10^4 . A rare gas filter operated with a Kr/Ar/Ne mixture at a pressure of 10 mbar suppresses the higher harmonic radiation. A detailed description of the beamline^[15] and the experimental setup^[16] can be found elsewhere. In brief, experiments were carried out in a free jet apparatus equipped with a time-of-flight mass spectrometer and a velocity map imaging photoelectron spectrometer. Ions and electrons were collected in coincidence. This allows for recording ion mass-selected photoelectron spectra. Threshold electrons were selected with an energy resolution of 5 meV and the contribution of background electrons was subtracted as outlined in the literature.^[17] Fulvenallene and fulvenallenyl were generated by flash pyrolysis of phthalide, commercially obtained from Sigma-Aldrich, expanded in Ar through a 100 μm orifice into an electrically heated SiC tube.^[6]

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Keywords: combustion · gas-phase reactions · photoelectron spectroscopy · radicals · transient species

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