



# The threshold photoelectron spectrum of cyanovinylacetylene leads to an upward revision of the ionization energy



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## ABSTRACT

Cyanovinylacetylene  $C_5H_3N$  was investigated by threshold photoelectron spectroscopy. The ionization energy (IE) was determined to be 10.04 eV. This value constitutes an upward revision of the earlier value of 9.33 eV. For both stereoisomers (trans and cis) computations predict very similar IEs and spectra. At 11.08 eV and 11.17 eV excited cationic states are observed. For the precursor 3-bromopyridine an IE of 9.34 eV was obtained. The appearance energy  $AE_{0K}$  (3-bromopyridine, 3-pyridyl<sup>+</sup>) was determined to be 11.71 eV and a bond dissociation energy of the C–Br bond in the 3-bromopyridine cation of 229 kJ mol<sup>-1</sup> was derived.

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## 1. Introduction

The threshold photoelectron (TPE) spectrum of cyanovinylacetylene, (1-cyanobut-1-ene-3-yne,  $C_5H_3N$ ) yielding an accurate ionization energy (IE) and resolution of the vibrational structure in the cation is presented in this paper. Cyanovinylacetylene has been reported to be an important intermediate in the pyrolysis of pyridine [1–3]. Nitrogen in coal is bound in a high percentage in pyridinic and pyrrolic structures and decomposes in combustion to unwanted  $NO_x$ , which can poison catalysts and presents a health threat [4]. Reliable data on potential combustion intermediates are therefore crucial for understanding combustion processes. Accurate ionization energies (IEs) and TPE spectra are required to identify molecules in flames on-line by photoionization mass spectrometry (PIMS) [5–7] or in photoelectron photoion coincidence (PEPICO) experiments, which have been established in recent years [8–11]. Pyridine itself can be seen as a model system for nitrogen-containing fuel sources. The primary decomposition step of pyridine under pyrolytic conditions is the loss of an H atom leading to one of three isomeric pyridyl radicals  $C_5H_4N$ . A second H-atom loss yields a  $C_5H_3N$  isomer. Different products for this step have been considered. Computations predict cyanovinylacetylene to be the thermodynamically favored product both for 2- and 3-pyridyl decomposition, even though this pathway

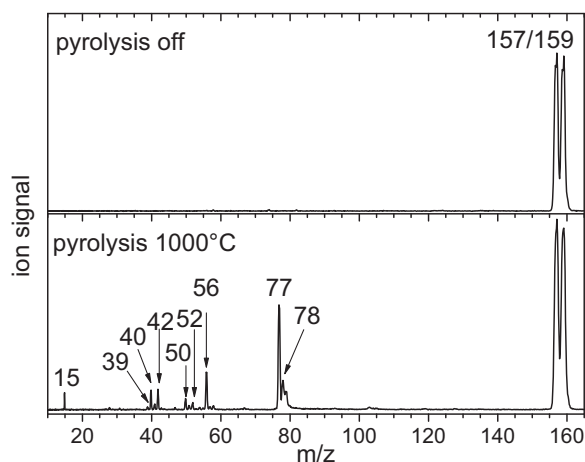
necessitates a ring opening [12]. Being  $\sigma$ -radicals, pyridyl radicals are very reactive and have short lifetimes. They have been isolated in matrices and detected in ESR [13] and IR [14] experiments, but gas phase experiments remain challenging. Recently, Zhang et al. succeeded in producing 2-pyridyl in the gas phase by photolysis of 2-chloropyridine and 2-bromopyridine, but only at a low yield [15]. Cyanovinylacetylene, by contrast, has been observed directly in gas phase experiments multiple times [1–3,15]. Its microwave spectrum has been recorded, because carbon chains with cyano groups like cyanovinylacetylene are potentially interesting for astrochemistry [16]. The ionization energy of cyanovinylacetylene was determined to be  $9.33 \pm 0.10$  eV by PIMS [2,3], which is in agreement with DFT computations that also yielded an IE of 9.33 eV [2]. However, ionization energies can be determined to a much greater accuracy by threshold photoelectron spectroscopy (TPES). In this study, 3-bromopyridine was used as a precursor in flash pyrolysis to initiate the formation of the 3-pyridyl radical. Further decomposition products like cyanovinylacetylene were then investigated by mass-selected TPES employing the imaging photoelectron photoion coincidence (iPEPICO) setup at the VUV X04DB beamline of the Swiss Light Source storage ring.

## 2. Experiment and computations

The iPEPICO (imaging photoelectron photoion coincidence) setup of the X04DB VUV beamline at the Swiss Light Source storage ring was employed for recording the mass-selected threshold photoelectron spectrum of cyanovinylacetylene. Details on the experiment can be found in the literature [17,18]. Hence, only a

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**Figure 1.** Mass spectra of 3-bromopyridine recorded at 10.5 eV at room temperature (upper panel) and at a reactor temperature of 1000 °C (lower panel) show rich chemistry.

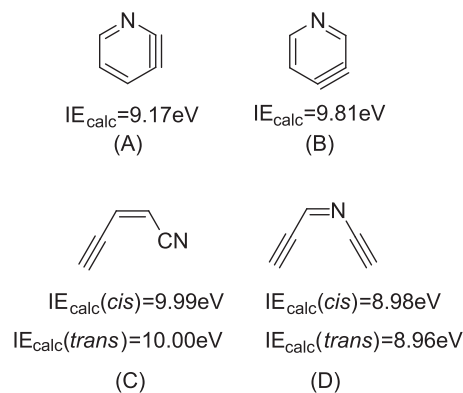
brief overview is given here. Vacuum ultraviolet (VUV) synchrotron radiation is provided by a bending magnet and dispersed by a  $1501\text{ mm}^{-1}$  grating monochromator yielding a photon energy resolution of  $E/\Delta E \geq 10^3$ . Higher harmonic radiation was suppressed by a differentially pumped rare-gas filter (mixture of Ar/Ne/Kr). The VUV radiation ionizes the sample in the experimental chamber, where ions and electrons are extracted by a  $120\text{ V cm}^{-1}$  electrical field. Cations were detected with a Wiley–McLaren time-of-flight mass spectrometer (Jordan C-726) and the electrons were velocity map imaged on a delay line anode (Roentdek DLD40). A multiple start/multiple stop coincidence scheme was employed to correlate electrons and ions from the same event [19] and threshold photoelectrons were selected with a resolution of 5 meV. Hot electron contributions were considered as described in the literature [20]. The precursor 3-bromopyridine was heated to 50 °C, seeded in 1.0 bar of argon and pyrolyzed in an electrically heated SiC tube. A description of the pyrolysis source can be found elsewhere [21]. For recording the TPE spectrum of cyanovinylacetylene, a pyrolysis power of 65 W corresponding to about 1000 °C was used and the spectrum was recorded in 15 meV steps with an acquisition time of 240 s per data point.

Quantum chemical computations were performed utilizing the GAUSSIAN09 program package [22]. Ionization energies were computed with the CBS-QB3 composite method [23,24], which uses B3LYP/6-311G(2d,d,p) (CBSB7) geometries and vibrational frequencies. Franck–Condon simulations at 0 K based on these computations were performed using the program FCFit v2.8 [25].

### 3. Results and discussion

For the precursor 3-bromopyridine itself we determined an IE of  $9.34 \pm 0.02\text{ eV}$  from a TPE-spectrum (see Figure S1 in the supplementary data for further information). Pyrolyzing 3-bromopyridine necessitates a very high temperature compared to previous experiments in which halogenated hydrocarbons were used to generate radicals upon pyrolysis [26–29]. Mass spectra at 10.5 eV, which are depicted in Figure 1, show that even at a pyrolysis temperature of about 1000 °C a strong precursor signal at  $m/z = 157/159$  is observed.

However, several fragment peaks are distinctly present in the mass spectrum at 1000 °C. The peaks in the lower  $m/z$  region at  $m/z = 15, 39, 40, 42, 50, 52,$  and 56 can be assigned to methyl [30,31], propargyl [29], allene [32] and propyne [33], propene [34], diacetylene [35], vinylacetylene [35], and isobutene [36] by comparing the



**Figure 2.** Chemical structures of isomers of the composition  $\text{C}_5\text{H}_3\text{N}$  ( $m/z = 77$ ): 2,3-pyridyne (A), 3,4-pyridyne (B), *cis*- and *trans*-cyanovinylacetylene (C), and *cis*- and *trans*-N-2-propynylidene-ethynamine (D). The ionization energies were computed on the CBS-QB3 level.

recorded TPE spectrum with the ones reported in the literature. These smaller fragments originate either from pyrolysis induced fragmentation of the precursor or from bimolecular reactions inside the pyrolysis tube, which are likely to occur under the experimental conditions [37]. The strongest peak in the mass spectrum, besides the precursor doublet, is  $m/z = 77$ . The weakest bond in 3-bromopyridine is the C–Br bond, which is expected to be cleaved first upon pyrolysis leading to the 3-pyridyl radical corresponding to  $m/z = 78$ . Previous studies have shown that this highly reactive  $\sigma$ -radical subsequently loses a hydrogen atom and a species of the composition  $\text{C}_5\text{H}_3\text{N}$  is formed [1–3,15]. Liu et al. computed the decomposition energetics of the pyridyl isomers [12]. Four different constitutions for  $\text{C}_5\text{H}_3\text{N}$  were considered as depicted in Figure 2: 2,3-didehydropyridine (A), 3,4-didehydropyridine (B), cyanovinylacetylene (C), and N-2-propynylidene-ethynamine (D). For (C) and (D), there exists a *cis* and a *trans* stereoisomer, respectively.

The activation barrier for the formation of the cyanovinylacetylene, which is defined by the H loss after the ring opening, was found to be  $295\text{ kJ mol}^{-1}$ , which is the lowest for any of the product molecules in Figure 2 according to the computations on QCISD(T)/cc-pVDZ level of theory. The formation of the didehydropyridines (A) and (B) requires 66 and  $44\text{ kJ mol}^{-1}$ , respectively, more energy. The barrier on the pathway to isomer (D) is  $173\text{ kJ mol}^{-1}$  higher in energy compared to the transition state leading to (C). The energy difference between the *cis* and *trans* isomers of (C) and (D) was neglected by Liu et al. [12]. Note that our CBS-QB3 computations predict it to be around  $2.2\text{ kJ mol}^{-1}$ , which justifies the assumption of Liu.

The upper panel of Figure 3 shows the mass-selected TPE spectrum for the  $m/z = 77$  peak observed in the pyrolysis of 3-bromopyridine.

The mass-selected TPE spectrum features a sharp peak at 10.04 eV, which is followed by less intense bands at 10.20, 10.30, 10.55, 11.08, and 11.17 eV. The ionization energy of the observed isomer can thus be assigned to  $10.04 \pm 0.02\text{ eV}$ . Quantum chemistry was employed to compare the computed IEs for the isomers A–D with the experiment. For (C) and (D) the *trans* and *cis* isomers were considered, respectively. The cyanovinylacetylene isomers yielded the best match on CBS-QB3 level of theory with a computed ionization energy of 9.99 eV for *cis*-cyanovinylacetylene and 10.00 eV for *trans*-cyanovinylacetylene. The computed ionization energies for the other isomers are 9.17 eV (A), 9.81 eV (B), 8.98 eV (*cis*-D), and 8.96 eV (*trans*-D). Franck–Condon simulations for both stereoisomers of (C) were performed, which are shown in the lower two panels of Figure 3. Both match the experimental spectrum well. Although the simulation of *trans*-cyanovinylacetylene yields

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