Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
International Journal of Mass Spectrometry 261 (2007) 100–107
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Mass spectra of the 2,4-pentadiynylidyne (C_5H; $X^2\Pi$) and 2,4-pentadiynyl-1 (n-C_5H_3; X^2B_1) radicals

Xibin Gu, Ying Guo, Ralf I. Kaiser*

Department of Chemistry, University of Hawai'i at Manoa, Honolulu, HI 96822, USA

Received 11 June 2006; received in revised form 28 July 2006; accepted 28 July 2006
Available online 7 September 2006

Abstract

We employed the crossed molecular beams method to synthesize the 2,4-pentadiynylidyne, C_5H ($X^2\Pi$), and the 2,4-pentadiynyl-1, n-$C_5H_3(X^2B_1)$, radicals *in situ* under single collision conditions via the reactions of tricarbon molecules with acetylene and ethylene, respectively. Time-of-flight spectra of the radicals were recorded at the center-of-mass angles at various mass-to-charge ratios from $m/z = 63$ ($C_5H_3^+$) to $m/z = 36$ (C_3^+). Integrating these time-of-flight spectra and normalizing them to the most intense peak, intensity ratios of $I(m/z=61){:}I(m/z=60){:}I(m/z=49){:}I(m/z=48){:}I(m/z=37){:}I(m/z=36) = 0.49 \pm 0.04{:}0.27 \pm 0.03{:}1{:}0.15 \pm 0.02{:}0.32 \pm 0.03{:}0.11 \pm 0.04$ can be extracted for the 2,4-pentadiynylidyne radical. In case of the 2,4-pentadiynyl-1 molecule, we find intensity ratios of $I(m/z=63){:}I(m/z=62){:}I(m/z=61){:}I(m/z=60){:}I(m/z=51){:}I(m/z=50){:}I(m/z=49){:}I(m/z=48){:}I(m/z=39){:}I(m/z=38){:}I(m/z=37){:}I(m/z=36) = 0.39 \pm 0.04{:}0.50 \pm 0.05{:}0.32 \pm 0.03{:}0.10 \pm 0.03{:}0.03 \pm 0.01{:}1.0{:}0.24 \pm 0.02{:}0.02 \pm 0.01{:}0.24 \pm 0.03{:}0.65 \pm 0.05{:}0.57 \pm 0.05{:}0.36 \pm 0.03$ at an electron impact energy of 70 eV. The absolute ionization cross sections of the 2,4-pentadiynylidyne and 2,4-pentadiynyl radicals were estimated to be $8.6 \pm 1.7 \times 10^{-16}$ cm^2 and $9.7 \pm 1.9 \times 10^{-16}$ cm^2, respectively. Our data can be employed in future space missions to detect the C_5H and C_5H_3 radicals – crucial reaction intermediates in the formation of polycyclic aromatic hydrocarbon molecules – in the atmospheres of hydrocarbon rich planets (Jupiter, Saturn, Uranus, Neptune, Pluto) and their moons (Titan) and also in combustion flames via mass spectrometry coupled with matrix interval arithmetic.

Keywords: Electron impact ionization; Fragmentation pattern; Mass spectrum; Free radical

1. Introduction

During the last years, the 2,4-pentadiynylidyne ($C_5H(X^2\Pi)$) and of the 2,4-pentadiynyl-1 (C_5H_3 (X^2B_1)) radicals have received considerable attention in the astrochemistry [1–7] and in the combustion chemistry communities [8–10] due to their prospective roles as precursors to polycyclic aromatic hydrocarbons (PAHs) [11] and fullerenes [12–14]. The 2,4-pentadiynyl-1 radical (C_5H_3; X^2B_1), for instance, could either react with a methyl radical (CH_3, X^2A_2''; (reaction (1))) [15] or with the C_5H_5 isomers 1-methylbutatrienyl [$H_2CCCCCH_3$; X^2A''] [16], 4-methylbutatrienyl [$HCCCCH(CH_3)$; X^2A''] [16], 1-vinylpropargyl [$HCCCH(C_2H_3)$; X^2A''] [17,18], or 3-vinylpropargyl [$H_2CCC(C_2H_3)$; X^2A''] [17,18], (reaction (2)) to access the C_6H_6 and $C_{10}H_8$ potential energy surfaces (PES) potentially leading to benzene and naphthalene/azulene in combustion flames and in planetary atmospheres via successive isomerization steps. These molecules are thought to build up even more complex polycyclic aromatic hydrocarbons (PAHs) yielding ultimately soot particles [19–23]:

$$C_5H_3 + CH_3 \rightarrow C_6H_6 \tag{1}$$

$$C_5H_3 + C_5H_5 \rightarrow C_{10}H_8 \tag{2}$$

Due to their importance in combustion processes, detailed information on the mass spectra and on the fragmentation patterns of both radicals will help to follow the concentration of the 2,4-pentadiynylidyne and of the 2,4-pentadiynyl-1 radicals in combustion flames in real time and to determine absolute radical concentrations not only via spectroscopy such as Fourier transform microwave spectroscopy [24], but also via mass spectrometry coupled to an electron impact ionizer on line and *in situ*. Very recently, a combination of quadrupole mass spectrometry (QMS) with matrix interval arithmetic (MIA) has been shown to be capable of extracting the chemical composition of complex

---

* Corresponding author. Tel.: +1 808 9565730; fax: +1 808 9565908.
E-mail address: kaiser@gold.chem.hawaii.edu (R.I. Kaiser).

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2006.07.023

gas mixtures even in the presence of highly reactive radicals and closed shell molecules [25]. To expand this approach to radicals, the fragmentation patterns of these molecules such as of the linear C_5H and C_5H_3 species are imperative. For instance, ion counts at $m/z = 63$ from $C_5H_3^+$ – the parent ion of the C_5H_3 radical – can also originate from dissociative ionization and fragmentation of more complex hydrocarbons such as benzene (C_6H_6). Therefore, the actual ion current recorded at $m/z = 63$ depicts the sum of the ion currents of all molecules contributing to this mass-to-charge ratio. Note that selective photoionization utilizing a tunable ultraviolet photon source – a soft ionization technique which effectively eliminates the fragmentation of the radical cation to smaller fragments – coupled to a mass spectrometric device is feasible to reveal the time dependent concentrations of radials in combustion flames [26]. However, since this technique requires a tunable vacuum ultraviolet light source – either a synchrotron or four wave mixing schemes – this method can hardy be utilized to identify radicals in the framework of, for instance, an *in situ* exploration of hydrocarbon-rich atmospheres of planets and their moons via space crafts. In this paper, we derive the first mass spectra of the 2,4-pentadiynylidyne ($C_5H(X^2\Pi)$) and 2,4-pentadiynyl-1 radicals (n-$C_5H_3(X^2B_1)$) which are generated *in situ* under single collision conditions in crossed molecular beams experiment via the reaction of tricarbon molecules with acetylene and ethylene, respectively [27,28]. In contrast to bulk experiments, where reactants are mixed, the key benefit of a crossed beams method is the capability to form both reactants, here tricarbon (C_3) molecules and the hydrocarbon beam, in separate supersonic beams. The reactants of each beam are made to collide only with the molecules of the other beam, and the products formed fly undisturbed towards the mass spectrometric detector. These features provide an unmatched method to *synthesize* unstable radicals like $C_5H(X^2\Pi)$ and $C_5H_3(X^2B_1)$.

2. Experimental setup

We synthesized the 2,4-pentadiynylidyne ($C_5H(X^2\Pi)$) and 2,4-pentadiynyl-1 radicals (n-C_5H_3 (X^2B_1)) in crossed molecular beams reactions of the tricarbon molecule, $C_3(X^1\Sigma_g{}^+)$, with acetylene, $C_2H_2(X^1\Sigma_g{}^+)$, and ethylene, $C_2H_4(X^1A_g)$, *in situ*. Briefly, the main chamber of the crossed beams machine is evacuated to the low 10^{-8} Torr region [29]. Two source chambers are located inside the vessel. A pulsed supersonic beam of tricarbon molecules, $C_3(X^1\Sigma_g{}^+)$, was generated via laser ablation of graphite at 266 nm [30]. Here, the 30 Hz, 25 mJ output of a Spectra Physics GCR-270-30 Nd:YAG laser is focused onto a rotating carbon rod and the ablated species were seeded into helium carrier gas released by a Proch-Trickl pulsed valve operating at 60 Hz and 80 μs pulses with 4 atm backing pressure. A four slot chopper wheel located between the skimmer and a cold shield selects segments of the seeded beam with peak velocities of $3880 \pm 100\,\mathrm{ms}^{-1}$ (acetylene experiment) and $3197 \pm 100\,\mathrm{ms}^{-1}$ (ethylene experiment) and speed ratios S of 1.5 ± 0.1 and 1.9 ± 0.1, respectively. The operation conditions were optimized so that the ablation beam contains mainly tricarbon 80% and only to a less extent dicarbon (5%) and atomic carbon (15%). The pulsed tricarbon and the pulsed hydrocarbon beams (550 Torr backing pressure; acetylene: $v_p = 902 \pm 5\,\mathrm{ms}^{-1}$; $S = 15.7 \pm 0.1$; ethylene: $v_p = 890 \pm 5\,\mathrm{ms}^{-1}$; $S = 15.7 \pm 0.1$) pass through skimmers and cross at 90° in the interaction region of the scattering chamber. The time-of-flight spectra of the parent and of the fragmentation patterns of the newly formed C_5H and C_5H_3 radicals were recorded in the plane of both beams using a rotatable quadrupole mass spectrometer with an electron impact ionizer at the center-of-mass angle of the reaction. The Brink-type electron impact ionizer [31] is surrounded by a liquid nitrogen shield and is located in the third region of a triply differentially pumped ultra high vacuum chamber (10^{-11} Torr); the quadrupole mass filter and the Daly-type scintillation particle detector [32] are connected to the second region. Recall that the fragmentation patterns of a molecule strongly depend on the kinetic energy of the electron. Here, we recorded these patterns at 70 eV electron energy, i.e., the *standardized* electron energy utilized to setup the NIST mass spectral database.

3. Results

The data analysis procedure is similar to the one utilized previously in our laboratory to extract the mass spectrum of the linear butadiynyl radical, $C_4H(X^2\Sigma^+)$ [33], and of the 1-butene-3-yne-2-yl radical, i-$C_4H_3(X^2A')$ [34]. Most importantly, we have to consider that the ablation beam does not contain solely the desired tricarbon molecule, but also carbon atoms and dicarbon molecules, $C_2(X^1\Sigma_g{}^+/a^3\Pi_u)$ [30]. Tricarbon molecules were found to react with acetylene and ethylene to the 2,4-pentadiynylidyne radical ($C_5H(X^2\Pi)$) and to the 2,4-pentadiynyl-1 radical (n-$C_5H_3(X^2B_1)$) through tricarbon versus atomic hydrogen exchange pathways (reactions (3) and (6), respectively) [35]. Considering the acetylene system, bimolecular collisions of dicarbon, $C_2(X^1\Sigma_g{}^+/a^3\Pi_u)$, with acetylene yielded the butadiynyl radical, $C_4H(X^2\Sigma^+)$, plus atomic hydrogen (reaction (4)) [33]. The situation of the carbon atoms is more complicated. At the present velocity of the ablation beam, the latter contains carbon atoms both in their electronic ground (^3P) and first electronically excites states (^1D) [36]. The reaction of $C(^3P)$ with acetylene was found to yield the cyclic and linear C_3H isomers (reaction (5a)) as well as tricarbon plus molecular hydrogen (reaction (5b)) [37]. On the other hand, $C(^1D)$ was suggested to react only to the cyclic C_3H isomer plus atomic hydrogen (reaction (5c)) [36]. In a similar way, the carbon, dicarbon, and tricarbon species can react with ethylene via multiple pathways as summarized in reactions (6)–(8). These considerations suggest that we have to find a technique to distinguish if the reactive scattering signal actually comes from the reaction of tricarbon molecules or from dicarbon molecules/carbon atoms with acetylene and ethylene.

Considering the acetylene reaction, the mass of the C_5H radical of 61 amu dictates that signal of the parent ion at $m/z = 61$ and of the fragmentation pattern at 60 (C_5^+) originates solely from the C_5H molecule. However, ions at lower mass-to-charge ratios such as of 49 (C_4H^+), 48 (C_4^+), and 37 (C_3H^+) could originate from dissociative ionization of the C_5H parent ($m/z = 49$,