Mass spectrum of the 1-butene-3-yne-2-yl radical (i-C₄H₃; X²A')

Ying Guo, Xibin Gu, Ralf I. Kaiser

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

Received 11 October 2005; received in revised form 16 November 2005; accepted 16 November 2005

Available online 27 December 2005

Abstract

The crossed molecular beams method has been applied to produce the 1-butene-3-yne-2-yl radical, i-C₄H₃(X²A') under single collision conditions via the reaction of dicarbon molecules with ethylene. We recorded time-of-flight spectra of the radical at the center-of-mass angle (28.0°) of the parent ion (m/z=51; C₄H₃⁺) and of the fragments at m/z=50 (C₃H⁺), m/z=49 (C₂H⁺), m/z=48 (C⁺), m/z=39 (C₃H₃⁺), m/z=38 (C₂H₂⁺), m/z=37 (C⁺), and m/z=36 (C₂⁺). This yielded relative intensity ratios of 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) = 0.47±0.01:0.01:0.01:0.01:0.01:0.01:0.01:0.01. Note that the intensity of the ¹³C isotopic peak of the 1-butene-3-yne-2-yl radical at m/z=51 (¹³C₃H₃⁺) is about 0.04±0.01 relative to m/z=51. Employing linear scaling methods, the absolute electron impact ionization cross section of the 1-butene-3-yne-2-yl radical was computed to be 7.8±1.6 × 10⁻²⁰ cm². These data can be employed to monitor the 1-butene-3-yne-2-yl radical in oxygen-poor combustion flames and in the framework of prospective explorations of planetary atmospheres (Jupiter, Saturn, Uranus, Neptune, Pluto) and of their moons (Titan, Triton, Oberon) in situ via matrix interval arithmetic assisted mass spectrometry.

© 2005 Elsevier B.V. All rights reserved.

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

1. Introduction

Free hydrocarbon radicals are central reactive intermediates in astrochemistry [1], planetary atmospheres [2,3], and in combustion flames [4–6]. Resonantly stabilized free radicals (RSFR) such as the C₂H₂ symmetric propargyl (C₂H₂) or the 1-butene-3-yne-2-yl (i-C₄H₃; H₂CCCH₂; Cᵥ point group) radicals are of particular importance. Both open shell species are believed to play a crucial role in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot in the combustion of fuels [7–34]. In RSFRs, the unpaired electron is delocalized and spread out over two or more sites in the molecule. This results in a number of resonant electronic structures of comparable importance. Due to the delocalization, resonantly stabilized free hydrocarbon radicals are more stable than ordinary radicals, have lower enthalpies of formation, and normally form weaker bonds with stable molecules (including molecular oxygen) [35–37]. These weakly bound addition complexes are not easily stabilized by collisions at high temperature. Consequently, RSFRs are relatively unreactive and can reach high concentration in flames. These high concentrations and the relatively fast rates of the radical–radical reactions make them important intermediates to form complex hydrocarbons in flames. Therefore, both in terrestrial settings like combustion flames [38] and extraterrestrial environments such as the interstellar medium [39] and planetary atmospheres [40–42], these radicals and the 1-C₄H₃ isomer in particular have been suggested as precursors to complex polycyclic aromatic hydrocarbons and possibly fullerenes like C₆₀ [43]. Nevertheless, despite the importance of the i-C₄H₃ radical in combustion processes and in the chemical processing of hydrocarbon rich planetary atmospheres, the mass spectrum of this molecule is still obscure [44]. However, a detailed knowledge of the fragmentation pattern will help to follow combustion flames in real time and to determine absolute radical concentrations not only via spectroscopic techniques (Fourier transform microwave spectroscopy [45]; laser induced fluorescence [46]), but also via mass spectrometry coupled to an electron impact ionizer. Very recently, a powerful combination of quadrupole mass spectrometry (QMS) with matrix interval arithmetic (MIA) has been shown to be capable of extracting the chemical composition...
of complex gas mixtures on line and in situ even in the presence of thermally labile molecules [47]. To extend this method to radicals, the fragmentation patterns of these molecules such as of the i-C₂H₁ radical are crucial. For example, signal at m/z = 51 from C₄H₅⁺ – the parent ion of the i-C₂H₃ radical – can be contaminated from the fragmentation of more complex hydrocarbons such as butatriene (C₆H₆) and benzene (C₆H₆). Therefore, the ion current recorded at m/z = 51 presents actually the sum of the ion currents of all molecules contributing to this mass-to-charge ratio. We would like to stress that in principle, 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 radicals in combustion flames [48]. However, since this technique requires a tunable vacuum ultraviolet light source – either a synchrotron or four wave mixing schemes – this method can hardly be utilized to identify radicals in the framework of in situ investigation of hydrocarbon-rich atmospheres of planets and their moons via space crafts.

In this paper, we present the first mass spectrum of the 1-butene-3-yn-2-yl radical, i-C₂H₃(X²Σ⁺), which is prepared in situ under single collision conditions in a crossed molecular beams experiment [49]. 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 dicarbon molecules and ethylene, in separate supersonic beams. The reagents of each beam are made to collide only with the molecules of the other beam, and the products formed are undisturbed towards the mass spectrometric detector. These features provide an unparalleled method to scrutinize the outcome of a single collision event and also to synthesize unstable radicals such as i-C₂H₃(X²Σ⁺) excluding higher order collisions.

2. Experimental setup

We generated the 1-butene-3-yn-2-yl radical (i-C₂H₃; X²Σ⁺) in a crossed molecular beams reaction of the dicarbon molecule, C₂X²Σ⁺(a¹Σ⁺), with ethylene, C₂H₄, in situ. Briefly, the main chamber of the crossed beams machine is pumped to the low 10⁻⁶ Torr region. Two source chambers – each pumped by a 20001 s⁻¹ and a 4301 s⁻¹ maglev pump – are located inside the vessel (Fig. 1). A pulsed supersonic beam of dicarbon molecules, C₂X²Σ⁺(a¹Σ⁺), was generated via laser ablation of graphite at 266 nm [50]. Here, the 30 Hz, 10 mJ output of a Spectra Physics with a peak velocity of 1969 m s⁻¹ and a speed ratio S of 5.5 ± 0.1. The pulsed dicarbon and the pulsed ethylene beam pass through skimmers and cross at 90° to the reaction region of the scattering chamber. The time-of-flight spectra of the parent and of the fragmentation patterns of the newly formed i-C₂H₃ radical were recorded in the plane of both beams using a rotating quadrupole mass spectrometer with an electron-impact ionizer at the center-of-mass angle of the reaction of 28.0°. The Brink-type electron impact ionizer [51] 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) (Fig. 1); the quadrupole mass filter and the Daly-type scintillation particle detector [52] are connected to the second region. Note 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 experimental strategy is similar to the one utilized previously in our laboratory to extract the mass spectrum of the linear butadiynyl radical, C₄H(X²Σ⁺) [53]. Firstly, we have to account for the fact that the ablation beam does not contain solely the dicarbon molecule but also carbon atoms, C(3 P j ), and the tricarbon molecule, C₃(X¹Σ⁺) [50]. The presence of the tricarbon molecules does not obstruct the reactive scattering signal since the reaction with ethylene was found to occur only at collision energies higher than 41 ± 1 kJ mol⁻¹ [54]. In the present experiment, the collision energies were determined to be 30.2 kJ mol⁻¹ (dicarbon-ethylene) and 36.8 kJ mol⁻¹ (tricarbon-ethylene). However, we have to point out that bimolecular collisions of ground state carbon atoms with ethylene are very rapid within gas kinetics and were found to form the propargyl radical plus atomic hydrogen via reaction (1) in a strongly exoergic reaction [55]. On the other
hand, reactions of dicarbon with ethylene synthesize solely the 1-butene-3-yne-2-yl radical, i-C₃H₄ (reaction (2)) [56]:

\[ C(3P_j) + C₂H₄ \rightarrow C(3P_j)C₂H₄ + H \]  

(1)

\[ C₂X(3Σ⁺)/σ^+ → C₂H₂ + i-C₃H₄ \rightarrow i-C₃H₄ + H. \]  

(2)

Secondly, we have to find a method to distinguish if the reactive scattering signal actually comes from the reaction of carbon atoms or from dicarbon molecules with ethylene. Considering the mass of the i-C₃H₄ radical of 51 amu, we expect that signal at m/z = 51 and of the fragmentation patterns at 50 (C₂H₃⁺), 49 (C₃H₄⁺), and 48 (C₄⁺) comes solely from the i-C₃H₄ radical. Conversely, ions at lower mass-to-charge ratios of 39 (C₂H₃⁺), 38 (C₂H₄⁺), and 37 (C₃H⁺) originate either from the fragmentation of the i-C₃H₄ radical in the electron impact ionizer or from the propargyl radical (reaction (1)) and its fragmentation patterns. Note that signal at m/z = 36 (C₂⁺) has contributions from reactions (1) and (2) as well as from inelastically scattered tricarbon molecules from the ethylene beam. It is imperative to distinguish these pathways. Here, we performed a transformation of the coordinate system from the laboratory system to the center-of-mass reference frame. The latter is convenient to get the relationship between both coordinate systems and incorporates the dynamics of the reactions (1) and (2).

In the present experiment, a beam of the dicarbon with a lab velocity V_{C₂} crosses a supersonic beam of ethylene with a lab velocity V_{C₂H₄} at 90° (Fig. 2). These velocities are represented as vectors. The vector connecting the tips of the dicarbon and ethylene vectors defines the relative velocity vector g. Note that in the laboratory system, the center of mass frame moves with the velocity V_{CM}. With respect to the dicarbon beam, this vector holds a fixed center-of-mass angle, θ_{CM}, of 28.0° and 46.5° for the reactions of ethylene with dicarbon and atomic carbon, respectively. The center-of-mass velocity vector starts at the crossing point of the reactant beams and terminates at the center-of-mass of the system which is actually located on the relative velocity vector g. Since we have two reactions – those of ethylene with dicarbon and atomic carbon – concurrently, we also have to label two center of masses, CM_{C₂H₄} and CM_{C₃H₃}, which are both located on the relative velocity vector g (Fig. 2). These center-of-masses play a key role to distinguish if the signal at lower mass-to-charge-ratios actually originates from reaction (1) and (2) alone or a combination of both pathways.

To set apart both options, we can investigate the energetics of reactions (1) and (2) in depth. The total, maximum available energy, E_{available}, of each reaction, which can be released in translational energy of the reaction products, is simply the sum of the collision energy, E_{c}, plus the absolute of the exothermicity of the reaction, ΔH_{r}^{0}, i.e., 215 ± 8 and 160 ± 5 kJ mol⁻¹ for reactions (1) and (2), respectively. Energy and momentum conservation dictates how the available energy will be partitioned among the reaction products; this enables us to compute the maximum recoil velocities of the heavy reaction products of H₂CCCH (reaction (1)) and i-C₃H₄ (reaction (2)) in the center-of-mass system (u_{CM}) and in the laboratory system (u_{lab}):

\[ u_{CM} = \sqrt{\frac{2m_iE_{available}}{m_{CM}(m_{CM} + m_i)}} \]  

(3)

\[ u_{lab} = \sqrt{\frac{2m_iE_{available}}{m_{CM}(m_{CM} + m_i)}} \]  

(4)

 Principally, these product molecules can scatter in a sphere which is centered at the center-of-mass of the reaction; this sphere holds a radius of a velocity vector. If we project these spheres into the two-dimensional velocity vector diagram (Fig. 2) around the center-of-mass of the reaction yields two circles with radii of u_{CM} (dashed circle) and u_{lab} (solid circle). A thorough examination of these recoil circles, the so called Newton Circles, presents essential guidance for the crossed beams experiment and for the elucidation of the mass spectrum of the 1-butene-3-yne-2-yl radical. Let us track a line from the crossing point of the supersonic dicarbon and the ethylene beams along the center of mass of the velocity vector of the dicarbon plus ethylene reaction – placed 28.0° relative to the dicarbon vector – to the center-of-mass of the reaction. This vector crosses first the Newton circle of the propargyl radical reaction product (reaction (1)) and then the Newton circle of the...
Fig. 3. Time-of-flight spectra of the 1-butene-3-yn-2-yl radical and its fragmentation pattern at various mass-to-charge ratios. The circles represent the experimental data, the lines the fits derived from the dynamics of the carbon-ethylene (dash-dot line), dicarbon-ethylene (dashed line) and tricarbon-ethylene (dot line) systems. Data were taken with a mass resolution of 1 amu.

\( i-C_4H_3 \) radical (reaction (2)). This suggests that TOF spectra recorded at \( m/z \) values of 39 and lower will have contributions from two channels, i.e., from the propargyl radical and its fragmentation patterns and also from the fragments of the \( i-C_4H_3 \) radical. Most important, the center-of-mass velocity vector crosses also the Newton Circle of inelastically scattered tricarbon molecules; therefore, signal at \( m/z = 36 \) has also a third component coming from inelastically scattered tricarbon molecules (Figs. 2 and 3). Selected time-of-flight spectra recorded at the center-of-mass angle of 28.0° are shown in Fig. 3. Here, the time-of-flight spectra taken at \( m/z = 51-48 \) are – after scaling – superimposable and could be fit with identical center-of-mass functions derived from reaction (2) [53]. This supports the deduction from Fig. 2 that ions at these
masses come from the C_4H_3^+ parent and from its fragment
down to C^+*. It is evident that the time-of-flight spectra at
m/z = 39–37 have two contributions: a slower part from reaction
(1) and a faster part from reaction (2). Consequently, the latter
presents the contribution of the fragmentation pattern of the
C_4H_3^+ parent to m/z = 39–37. Finally, signal at m/z = 36 must
be fit with three channels, i.e., from reactions (1) and (2) as
well as inelastically scattered tricarbon molecules (Fig. 2). By
integrating these time-of-flight spectra and normalizing them
to the most intense peak, this yielded relative intensity ratios
of (m/z = 51)/(m/z = 50)/(m/z = 49)/(m/z = 48)/(m/z = 39):
(m/z = 38)/(m/z = 37)/(m/z = 36) = 0.47 ± 0.01:0.94 ± 0.01:1.00:
0.07 ± 0.02:0.31 ± 0.01:0.23 ± 0.02:0.24 ± 0.01:0.12 ± 0.01 at
70 eV electron impact energy. Upper limits at mass-to-charge
ratios between 27 and m/z = 24 and m/z = 14–12 were
derived to be 0.02 ± 0.01. Note that the intensity of the
^{13}C isotopic peak of the 1-butene-3-yn-2-yl radical at m/z = 52
(^{13}C_2C_2H_3^+) is about 0.04 ± 0.01 relative to m/z = 51. In
addition, the absolute ionization cross section of the butadiynyl
radical has been determined to be 7.8 ± 1.6 x 10^{-18} cm^2.

4. Conclusions

The crossed molecular beams method was exploited to form
the 1-butene-3-yn-2-yl radical, i-C_4H_3(X=\tilde{A}) under single
collision conditions via the reaction of dicarbon molecules with
ethylen. Time-of-flight spectra of the radical were recorded at
the center-of-mass angle of 28.0° at mass-to-charge ratios of
m/z = 51 (C_4H_3^+; parent ion) and of the fragments at m/z = 50–48
and m/z = 39–36. Integrating these time-of-flight spectra and
normalizing them to the most intense peak, intensity ratios
of (m/z = 51)/(m/z = 50)/(m/z = 49)/(m/z = 48)/(m/z = 39):
(m/z = 38)/(m/z = 37)/(m/z = 36) = 0.47 ± 0.01:0.94 ± 0.01:1.00:
0.07 ± 0.02:0.31 ± 0.01:0.23 ± 0.02:0.24 ± 0.01:0.12 ± 0.01 at
70 eV electron impact energy can be extracted. Upper limits at
mass-to-charge ratios between 27 and m/z = 24 and m/z = 14–12
were derived to be 0.02 ± 0.01. Note that the intensity of the
^{13}C isotopic peak of the 1-butene-3-yn-2-yl radical at m/z = 52
(^{13}C_2C_2H_3^+) is about 0.04 ± 0.01 relative to m/z = 51. In
addition, the absolute ionization cross section of the butadiynyl
radical has been determined to be 7.8 ± 1.6 x 10^{-18} cm^2.

Acknowledgements

This work was supported by the National Science Foundation
(CHE-0234461; YG, RIK) and by the US Department of Energy:
Basic Energy Sciences (DE-FG02-03ER15411; XG, RIK).

References

To Planetary Systems, Astronomical Society of the Pacific, San Fran-