Formation of the 2,4-pentadiynyl-1 radical (H$_2$CCCCCH, X$^2$B$_1$) in the Crossed Beams Reaction of Dicarbon Molecules with Methylacetylene

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ABSTRACT

The chemical dynamics to synthesize the 2,4-pentadiynyl-1 radical, HCCCH₂(X²B₁), via the neutral–neutral reaction of dicarbon with methylacetylene, were examined in a crossed molecular beams experiment at a collision energy of 37.6 kJmol⁻¹. The laboratory angular distribution and time-of-flight spectra of the 2,4-pentadiynyl-1 radical and its fragmentation patterns were recorded at m/z = 63 – 60 and m/z = 51 – 48. A forward-convolution fitting of our data reveals that the reaction dynamics are indirect and dictated by an initial attack of the dicarbon molecule to the π electron density of the methylacetylene molecule to form cyclic collision complexes. The latter ultimately rearranged via ring opening to methyl-diacetylene, CH₃-C≡C≡C-H. This structure decomposed via atomic hydrogen emission to the 2,4-pentadiynyl-1 radical; here, the hydrogen atom was found to be emitted almost parallel to the total angular momentum as suggested by the experimentally observed sideways scattering. The overall reaction was strongly exoergic by 182 ± 10 kJmol⁻¹. The explicit identification of the resonance-stabilized free 2,4-pentadiynyl-1 radical represents a solid background for the title reaction to be included into more refined reaction networks modeling the chemistry of circumstellar envelopes and also of sooting combustion flames.
1. Introduction

The 2,4-pentadiynyl-1 radical (Figure 1) represents an important transition species in combustion flames as a prototype representative of resonance-stabilized free radicals (RSFRs).\(^1\) Compared to the propargyl radical, HCCCH\(_2\)(X\(^2\)B\(_1\)) (Figure 1), the 2,4-pentadiynyl-1 radical is expanded by one carbon-carbon triple bond to give rise to a linear heavy carbon atom backbone. This molecule has a \(^2\)B\(_1\) electronic ground state and belongs to the C\(_{2v}\) point group. Identified tentatively via electron spin resonance (ESR) spectroscopy in cryogenic matrices,\(^2\) the existence of a nearly prolate 2,4-pentadiynyl-1 radical was confirmed via microwave spectroscopy in pulsed discharge supersonic molecular beams via four of its rotational transitions between 8 and 22 GHz.\(^3\) Recent molecular beam studies of the photodissociation of benzene (C\(_6\)H\(_6\)) at 193 nm and 248 nm suggested the existence of a C\(_5\)H\(_3\) plus CH\(_3\) channel; however the exact nature of the structural isomers could not be elucidated.\(^4\) A latest computational investigation of the unimolecular dissociation of benzene\(^5\) superseded early semi-empirical MINDO/3 studies.\(^6\) Mebel and coworker actually suggested that the 2,4-pentadiynyl-1 radical could be formed from benzene and its fulvene isomer through pathways involving an initial 1,2 hydrogen shift in the benzene ring followed by ring opening, a series of hydrogen shifts in the open shell structures, and a final methyl group loss. Among the twenty five C\(_5\)H\(_3\) isomers investigated, the 2,4-pentadiynyl-1 radical was found to be the most stable one.\(^5\)

However, except the ESR and microwave spectroscopy and photodissociation as well as theoretical studies, little is known about the reaction dynamics and formation routes of this significant reaction intermediate in extreme environments. Here, resonance-stabilized free radicals are believed to play an important role in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot particles in the combustion of aromatic fuels. Owing to the electron delocalization, RSFRs are more stable than ordinary radicals and – due to the partial delocalization of the unpaired electron - relatively unreactive. Therefore, RSFRs can reach a high concentration in flames. These high concentrations and the relatively fast rates of the RSFR plus RSFR reactions make them important intermediates to form complex hydrocarbons in combustion systems. These studies have also close links to the chemical processing of the circumstellar envelopes of dying carbon such as of IRC+ 10216.\(^7\) Therefore, it is necessary to investigate the formation routes of RSFRs to include these mechanisms into interstellar and combustion chemistry networks. This paper is the first in a series to unravel the formation and the underlying reaction dynamics to form various
C$_5$H$_3$ isomers under single collision conditions via unimolecular decomposition of singlet and triplet C$_5$H$_4$ intermediates utilizing the crossed molecular beams approach. Here, we present the chemical dynamics of the reactions of the dicarbon molecule, C$_2$(X$^1\Sigma_g^+/a^3\Pi_u$), with methylacetylene, CH$_3$CCH(X$^1\text{A}_1$), to form the 2,4-pentadiynyl-1 radical on the C$_5$H$_4$ potential energy surface via a dicarbon versus atomic hydrogen exchange pathway.

2. Experimental Setup and Data Processing

The experiments were carried out under single collision conditions in a crossed molecular beams machine at The University of Hawaii described in Reference 8 in detail. Briefly, the main chamber can be evacuated by magnetically suspended turbo molecular pumps to the low 10$^{-8}$ torr region. To reduce the background from straight-through molecules into the detector, the machine is equipped with a cold shield located between the chopper wheel and the interaction region (primary source) and downstream the skimmer (secondary source). This shield is connected to a 10 K cold head and reduces the vacuum in the main chamber to 4 $\times$ 10$^{-9}$ torr. Both source chambers are placed inside the main chamber so that the reactant beams cross perpendicularly. Pulsed dicarbon beams were produced in the primary source by laser ablation of graphite at 266 nm (10 mJ per pulse at 30 Hz). The ablated species were seeded in neat carrier gas (helium, 99.9999 %, 3040 torr) released by a Proch-Trickl pulsed valve. After passing a skimmer, a four-slot chopper wheel mounted after the ablation zone selected a part out of the seeded dicarbon beam at a peak velocity $v_p$ of 2075 $\pm$ 25 ms$^{-1}$ and a speed ratio $S$ of 3.9 $\pm$ 0.2; note that at this velocity, the beam contains dicarbon in its $X^1\Sigma_g^+$ electronic ground state as well as in its first electronically excited $a^3\Pi_u$ state; the energy separation between both states is only 8.6 kJmol$^{-1}$. This segment of the dicarbon beam crossed a pulsed methylacetylene beam (CH$_3$CCH; 99.6 %; 520 torr; $v_p = 840 \pm 5$ ms$^{-1}$; $S = 11.2 \pm 0.2$) released by a second pulsed valve under a well-defined collision energy of 37.6 $\pm$ 0.8 kJmol$^{-1}$ in the interaction region. Note that the ablation beam also contains carbon atoms as well as tricarbon molecules. To identify the position of the atomic hydrogen loss, we also carried out experiments with partially deuterated d$_3$-methylacetylene (CD$_3$CCH). Note that although the primary beam contains carbon atoms and tricarbon molecules, these species were found not to interfere with the reactive scattering signal of the dicarbon–methylacetylene reaction at mass-to-charge ratios (m/z) of 63 (C$_5$H$_3$+) and 62 (C$_5$H$_2$+). Here, tricarbon reacts with methylacetylene only at collision energies larger than about 50 kJmol$^{-1}$.10
signal from the reaction of atomic carbon with methylacetylene only shows up at m/z values of 51 (C₄H₅⁺) and lower.¹¹

The reactively scattered species are monitored using a quadrupole mass spectrometric detector (QMS) in the time-of-flight (TOF) mode after electron-impact ionization of the neutral molecules. Our detector can be rotated within the plane defined by the primary and the secondary reactant beams to allow taking angular resolved TOF spectra. By taking and integrating the TOF spectra at distinct laboratory angles in 2.5º steps, we obtain the laboratory angular distribution, i.e. the integrated signal intensity of an ion of distinct m/e versus the laboratory angle. For each angle, we accumulated up to 4 × 10⁵ TOF spectra. Information on the chemical dynamics were obtained by fitting these TOF spectra of the reactively scattered products and the product angular distribution in the laboratory frame (LAB) using a forward-convolution routine. This procedure initially assumes an angular distribution T(θ) and a translational energy distribution P(Eₜ) in the center-of-mass reference frame (CM). TOF spectra and the laboratory angular distribution were then calculated from these T(θ) and P(Eₜ). Best fits of the TOF and laboratory angular distributions were achieved by refining the T(θ) parameters and the points of the P(Eₜ). The final outcome is the generation of a product flux contour map which reports the differential cross section, I(θ,u), of the product as the intensity as a function of angle θ and product center-of-mass velocity u. This map serves as an image of the reaction and contains all the information of the reactive scattering process.

3. Results

Reactive scattering signal was observed at m/z = 63 (C₅H₃⁺), 62 (C₅H₂⁺), 61 (C₅H⁺), and 60 (C₅⁺). Time-of-flight spectra (TOF) for several scattering angles are shown in Fig. 2. TOF spectra recorded at all mass-to-charge-ratios between 63 and 60 reveal identical patterns suggesting that m/z = 63 fragments to yield signal at m/z = 62 – 60; note that signal at m/z = 62 is stronger by a factor of 2 compared to m/z = 63. The indistinguishable patterns of the lower mass-to-charge ratios further imply that in this range of masses only the dicarbon versus hydrogen exchange pathways is open to form C₅H₃ isomer(s) (m/z = 63) plus atomic hydrogen; the synthesis of any C₅H₂ isomers (m/z = 62) and molecular hydrogen can be excluded. We would like to stress that no higher masses were observed. For completeness, we also investigated the signal at lower mass-to-charge ratios. Here, no signal was found at m/z = 52 (C₄H₄⁺) suggesting that the pathway to form any C₄H₄ isomers plus atomic carbon is blocked. Time-of-flight
spectra taken between m/z = 51 (C₄H₃⁺) and 48 (C₄⁺) could be fit with two channels, i.e. a contribution from the reaction of dicarbon with methylacetylene (dissociative ionization of C₅H₃ in the electron impact ionizer) and from the involvement of the scattering signal of atomic carbon plus methylacetylene reaction leading to atomic hydrogen and the 1-buten-3-yn-2-yl radical (i-C₄H₃(X²A′)) giving rise to its parent at C₄H₃⁺ (m/z = 51) and the C₄H₂⁺ (m/z = 50), C₄H⁺ (m/z = 49), and C₄⁺ (m/z = 48) fragmentation patterns. Based on these considerations, the interpretation of the TOF data alone implies the existence of a dicarbon versus atomic hydrogen exchange pathway together with the formation of C₅H₃ isomer(s) under single collision conditions.

We can now integrate the TOF spectra to derive the laboratory angular distribution (LAB) of the C₅H₃ product(s) at the most intense m/z value of 62 (C₅H₂⁺) (Figure 3). Here, the LAB distribution of the C₅H₃ isomer(s) at m/z = 62 peaks at the center of mass angle of 34.0°. The overall shape depicts a backward-scattered distribution extending about 40° in the scattering plane defined by both beams. This finding implies a relatively small fraction of the total available energy is released into translational degrees of freedom of the products. Most important, the best fit of the LAB distribution and of the TOF spectra was achieved with one channel and a translational energy distribution extending up to 220 ± 10 kJmol⁻¹. Since the maximum energy releases presents simply the sum of the reaction exoergicity and the collision energy, we can subtract the latter to derive the experimentally determined reaction exoergicity forming the C₅H₃ isomer plus atomic hydrogen to be 182 ± 10 kJmol⁻¹. As can be seen from the flux contour map (Figure 4), the flux peaks away from zero velocity in the center of mass system; the broad peak corresponds to center-of-mass translational energies between 15 and 40 kJmol⁻¹. This proposes that at least one reaction channel to form the C₅H₃ isomer(s) has a tight exit transition state (repulsive carbon-hydrogen bond rupture involving a significant electron rearrangement). Finally, the translational energy part of the flux contour map allows us to determine the amount of the energy released into the translational degrees of the products to be 66 ± 5 kJmol⁻¹, i.e. a fraction of about 30 ± 2 %. This number suggests that the reaction proceeds in an indirect fashion via complex formation.
85° and 120° is clearly noticeable. This finding implies that the light hydrogen atom is emitted nearly perpendicularly to the rotating H---H2CCCCCH intermediate almost parallel to the total angular momentum vector (Figure 5).

4. Discussion

The high-energy cutoff of the center-of-mass translational energy distribution of 182 ± 10 kJmol⁻¹ correlates nicely with the formation of the 2,4-pentadiynyl-1 radical, HCCCCCH₂, in its ²B₁ electronic ground state. The computed reaction energy of 193 ± 5 kJmol⁻¹ lies in excellent agreement with our experimental data. Based on our crossed beams data, the following reaction dynamics can be proposed. The dicarbon molecule – recall that we have dicarbon in its X¹Σ⁺ electronic ground state as well as in its first electronically excited a³Π_u state – adds to the carbon – carbon triple bond of the methylacetylene molecule to form initial C₅H₄ collision complex(es). This pathway is suggested to be similar to the reaction of dicarbon with acetylene in which three- and four-membered ring structures can be formed initially. This ultimate fate of the cyclic intermediates is governed by ring opening processes to yield the methylidiacetylene molecule, CH₃-C≡C-C≡C-H. Upon formation of this intermediate, the five heavy atoms can rotate in a plane almost perpendicular to the total angular momentum vector around the C axis of the methylidiacetylene molecule. The asymmetric flux contour map indicates that this intermediate decomposes within less than a rotational period to form the 2,4-pentadiynyl-1 radical plus atomic hydrogen. Note that we also carried out an experiment utilizing CD₃CCH to verify explicitly if the hydrogen atom is released from the methyl group or from the acetylenic carbon atom. Here, the decomposition of d3-methylidiacetylene, CD₃-C≡C-C≡C-H (m/z = 67) could form CD₂-C≡C-C≡C-H (D atom loss; m/z = 65) or CD₃-C≡C-C≡C (m/z = 66; H atom loss). Experimentally, we only observed signal at m/z = 65, but not at m/z = 66. This verifies experimentally that the released hydrogen atom originates from the methyl group of the methylidiacetylene molecule, but not from the acetylenic section of the decomposing reaction intermediates. On the singlet surface, CH₃-C≡C-C≡C-H is expected to lose a hydrogen atom thru a lose exit transition state. However, the experimentally observed off-zero peaking of the center-of-mass angular distribution might indicate – similar to the dicarbon plus acetylene system the involvement of a triplet methylidiacetylene complex; the latter could decomposes via a tight exit transition state. So far, we cannot quantify to what extent the singlet and triplet surfaces are involved in the reaction.
Despite these open questions, the present crossed beams study verifies the formation of the 2,4-penta-diynyl-1 radical (HCCCCCH$_2$; $X^2B_1$) under single collision conditions via the neutral – neutral reaction of dicarbon with methylacetylene. The explicit identification of this reaction product represents a solid background for the title reaction to be included in reaction networks modeling combustion flames as well as outflow of dying carbon stars. Future experiments will investigate the collision energy dynamics of this important reaction and also combine the experimental data with extensive electronic structure calculations on the singlet and triplet C$_5$H$_4$ surfaces. Also, studies of the crossed beams reactions of dicarbon with allene, a structural isomer of methylacetylene, are scheduled.

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