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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The chemical dynamics to synthesize the 2,4-pentadiynyl-1 radical, HCCCCCH$_2$(X^{2}B$_1$), via the neutral−neutral reaction of dicarbon with methylacetylene, was examined in a crossed molecular beams experiment at a collision energy of 37.6 kJ mol^{-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 $m/z = 51-48$. Our findings suggest 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 methyldiacetylene, CH$_3$−C≡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 kJ mol^{-1}. The 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 matrixes,[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 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 semiempirical MINDO/3 studies.[6] Mebel and co-workers 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 25 C$_5$H$_3$ isomers investigated, the 2,4-pentadiynyl-1 radical was found to be the most stable one.[5]

However, except for ESR and microwave spectroscopy, photodissociation, and 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, because of 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 in the formation of complex hydrocarbons in combustion systems. These studies also have close links to the chemical processing of the circumstellar envelopes of dying carbon such as that 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 underlying reaction dynamics of the formation of 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}Σ$_g^+$/a^{3}Π$_u$), with methylacetylene, CH$_3$CCH(X^{1}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 ref 8 in detail). Briefly, the main chamber can be evacuated by magnetically suspended turbo molecular pumps to the low 10^{-8} Torr region. The machine is equipped with a cold shield located between the chopper wheel and the interaction region (primary source) and

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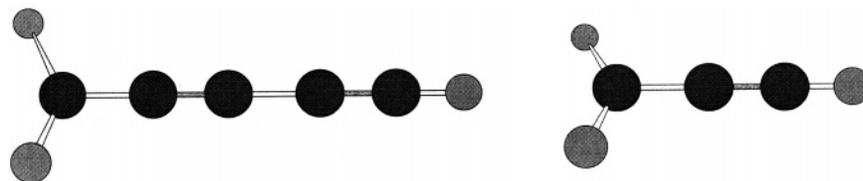
Figure 1. Structures of the 2,4-pentadiynyl-1 (left) and propargyl radicals (right).

downstream the skimmer (secondary source) to reduce the background from straight-through molecules into the detector. This shield is connected to a 10 K cold head and reduces the vacuum in the main chamber to 4×10^{-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[9] (10 mJ/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 ± 25 ms^{-1} and a speed ratio, S, of 3.9 ± 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;[8] the energy separation between both states is only 8.6 kJ mol^{-1}. This segment of the dicarbon beam crossed a pulsed methylacetylene beam perpendicularly (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 ± 0.8 kJ mol^{-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 d3-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 kJ mol^{-1};[10] the signal from the reaction of atomic carbon with methylacetylene only shows up at m/z values of 51 (C$_4$H$_3^+$) 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 secondary reactant beams to allow taking angular resolved TOF spectra. By taking and integrating the TOF spectra at distinct laboratory angles in 2.5° steps, we obtain the laboratory angular distribution, that is, the integrated signal intensity of an ion of distinct m/z versus the laboratory angle. For each angle, we accumulated up to 4×10^5 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, which is described in detail in refs 12 and 13. Briefly, this procedure initially assumes an angular distribution, $T(\theta)$, and a translational energy distribution, $P(E_T)$, in the center-of-mass reference frame (CM). TOF spectra and the laboratory angular distribution were then calculated from these $T(\theta)$ and $P(E_T)$ taking into account the beam spreads and the apparatus functions. Best fits of the TOF and laboratory angular distributions were achieved by refining the $T(\theta)$ parameters and the points of the $P(E_T)$.

3. Results

Reactive scattering signal was observed at $m/z = 63$ (C$_5$H$_3^+$), 62 (C$_5$H$_2^+$), 61 (C$_5$H$^+$), and 60 (C$_5^+$). Time-of-flight spectra for several scattering angles are shown in Figure 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 a signal at $m/z = 62-60$; note that the signal at $m/z = 62$ is stronger by a factor of 2 compared to that at $m/z = 63$. 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 are open to form C$_5$H$_3$ isomer(s) ($m/z = 63$) plus atomic hydrogen; the synthesis of any C$_5$H$_2$ 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 $m/z = 52$ (C$_4$H$_4^+$), suggesting that the pathway to form any C$_4$H$_4$ isomers plus atomic carbon is blocked. Time-of-flight spectra taken between $m/z = 51$ (C$_4$H$_3^+$) and 48 (C$_4^+$) could be fit with two channels, that is, a contribution from the reaction of dicarbon with methylacetylene (dissociative ionization of C$_5$H$_3$ 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 l-buten-3-yn-2-yl radical (i-C$_4$H$_3$(X^{2}A′)) giving rise to its parent at C$_4$H$_3^+$ ($m/z = 51$) and the C$_4$H$_2^+$ ($m/z = 50$), C$_4$H$^+$ ($m/z = 49$), and C$_4^+$ ($m/z = 48$) fragmentation patterns.[11] On the basis of 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 C$_5$H$_3$ isomer(s) under single collision conditions.

We can now integrate the TOF spectra to derive the laboratory angular distribution (LAB) of the C$_5$H$_3$ product(s) at the most intense m/z value of 62 (C$_5$H$_2^+$) (Figure 3). Here, the LAB distribution of the C$_5$H$_3$ isomer(s) at $m/z = 62$ peaks at the center of mass angle of $34.0° \pm 0.5°$. The overall shape depicts a slightly backward-scattered distribution extending about 40° in the scattering plane defined by both beams. This finding implies that a relatively small fraction of the total available energy is released into translational degrees of freedom of the products. On the basis of the center-of-mass translational energy distribution, $P(E_T)$ (Figure 4), we can extract information on the maximum translation energy of the reaction products in the center-of-mass frame. Here, 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 kJ mol^{-1}. Because the maximum energy released 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 C$_5$H$_3$ isomer plus atomic hydrogen to be 182 ± 10 kJ mol^{-1}. As can be seen from the $P(E_T)$ (Figure 4), the flux peaks away from zero translational energy. This proposes that at least one reaction channel to form the C$_5$H$_3$ isomer(s) has a tight exit transition state (repulsive carbon−hydrogen bond rupture involving a significant electron rearrangement). Finally, the translational energy distribution

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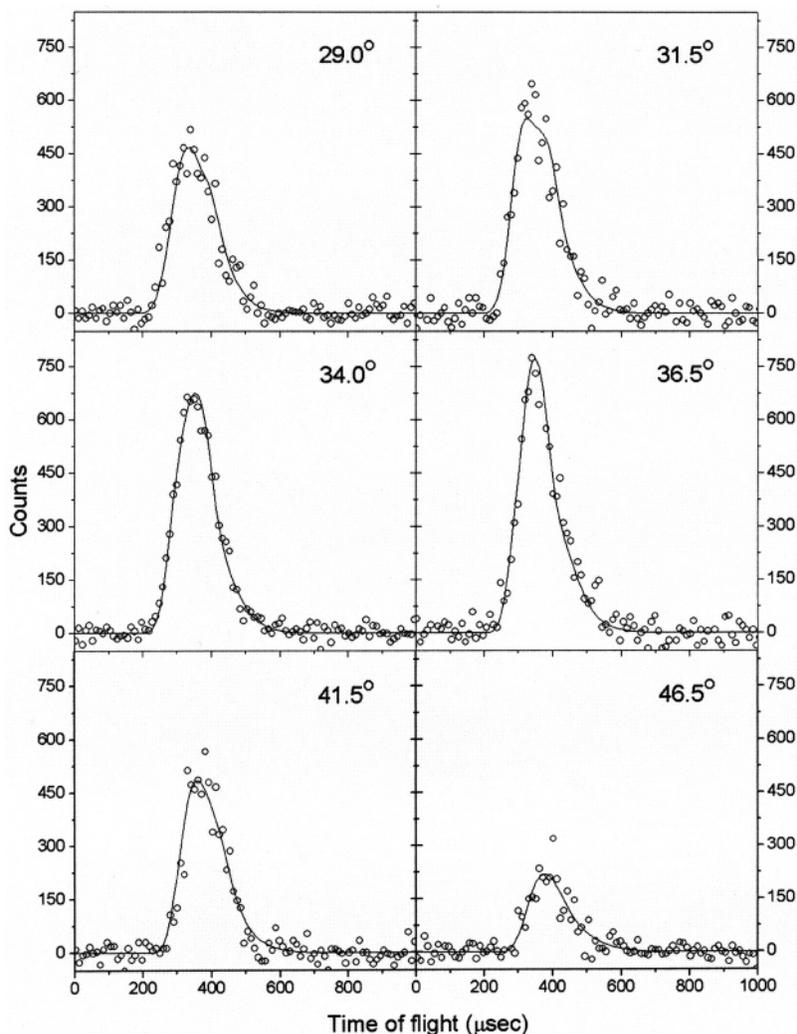
Figure 2. Time-of-flight data at $m/z = 62$ of distinct laboratory angles of the reaction of dicarbon with methylacetylene at a collision energy of 37.6 kJ mol^{-1}. The circles indicate the experimental data, and the solid lines indicate the calculated fit.

allows us to determine the amount of energy released into the translational degrees of the products to be 66 ± 5 kJ mol^{-1}, that is, a fraction of about $30 \pm 2\%$. This number suggests that the reaction proceeds in an indirect fashion via complex formation.[14] Also, an inspection of the center-of-mass angular distribution, $T(\theta)$, shows intensity over the complete angular range from $0°$ to $180°$; this implies indirect scattering dynamics and the involvement of at least one initial C_5H_4 collision complex in the entrance channel of the reaction. Also, the $T(\theta)$ depicts a distinct backward-scattering and a pronounced sideways-peaking between $85°$ and $120°$ is noticeable.

4. Discussion

The high-energy cutoff of the center-of-mass translational energy distribution of 182 ± 10 kJ mol^{-1} correlates nicely with the formation of the 2,4-pentadiynyl-1 radical, HCCCCCH$_2$, in its $^2B_1$ electronic ground state. The computed reaction energy of 193 ± 5 kJ mol^{-1} lies in excellent agreement with our experimental data.[15] What could be the underlying reaction dynamics to form the 2,4-pentadiynyl-1 radical from the methylacetylene and dicarbon reactants? For this we first compare the structure of the methylacetylene reactant with the radical reaction product and then propose a viable reaction intermediate (recall that the title reaction was found to be indirect), which correlates the reactants with the reaction product. Most importantly, the 2,4-pentadiynyl-1 radical (HCCCCCH$_2$) carries no

methyl group; to connect this radical to the methylacetylene reactant via a distinct intermediate, it is likely that in the reverse reaction a hydrogen atom adds to the radical center at the CH$_2$ group of the 2,4-pentadiynyl-1 radical. This would form a methyldiacetylene intermediate, CH$_3$−C≡C−C≡C−H. The next step is to associate the methyldiacetylene intermediate with the dicarbon and the methylacetylene reactants. Formally, the carbon chain of the methylacetylene molecule is expanded via "*insertion*" of a C$_2$ unit as compared to the methyldiacetylene intermediate. Because the dicarbon molecule cannot "*insert*" in one step into a carbon−carbon triple bond, we suggest that the dicarbon molecule adds to the carbon−carbon triple bond of the methylacetylene molecule to form initially cyclic C$_5$H$_4$ collision complex(es). A side-on addition would yield a four-membered cyclic intermediate, whereas an end-on addition would result in the formation of a three-membered ring collision complex. We have demonstrated previously that the initial collision complexes formed in the reaction of dicarbon molecules with unsaturated hydrocarbons can isomerize, yielding ultimately acyclic intermediates.[16] Here, we propose that the cyclic intermediates formed in the reaction of methylacetylene with dicarbon rearrange to yield finally the methyldiacetylene intermediate, CH$_3$−C≡C−C≡C−H, which then emits a hydrogen atom. 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.[8] Upon
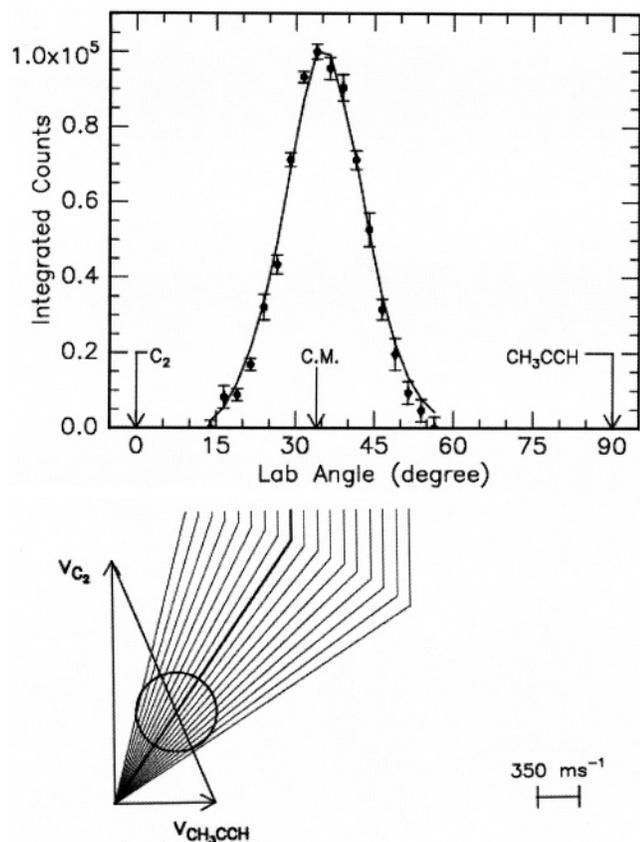
Figure 3. Lower: Newton diagram for the reaction of dicarbon with methylacetylene at a collision energy of 37.6 kJ mol^{-1}. The circle stands for the maximum center-of-mass recoil velocity of the 2,4-pentadiynyl-1 radical product. Upper: Laboratory angular distribution of the 2,4-pentadiynyl-1 radical at $m/z = 62$. Circles and error bars indicate experimental data, and the solid line indicates the calculated distribution.

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 methyldiacetylene 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 CD_3CCH to verify explicitly if the hydrogen atom is released from the methyl group or from the acetylenic carbon atom. Here, the decomposition of d3-methyldiacetylene, $CD_3-C\equiv C-C\equiv C-H$ ($m/z = 67$) could form $CD_2-C\equiv C-C\equiv C-H$ (D atom loss; $m/z = 65$) or $CD_3-C\equiv C-C\equiv C$ ($m/z = 66$; H atom loss). Experimentally, we only observed a 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 methyldiacetylene molecule but not from the acetylenic section of the decomposing reaction intermediates. On the singlet surface, $CH_3-C\equiv C-C\equiv C-H$ is expected to lose a hydrogen atom through a loose exit transition state. However, the experimentally observed off-zero peaking of the center-of-mass translational energy distribution might indicate, similar to the dicarbon plus acetylene system, the involvement of a triplet methyldiacetylene complex; the latter could decompose via a tight exit transition state. So far, we cannot quantify to what extent the singlet and triplet surfaces are involved in the reaction. Note that the reaction energy to form a second C_5H_3 isomer, HCCCHCCH, is energetically very close to $H_2CCCCCH$;[15] the difference being only about 1 kJ mol^{-1}. However, the synthesis of this isomer requires two successive hydrogen shifts from the methyldiacetylene inter-
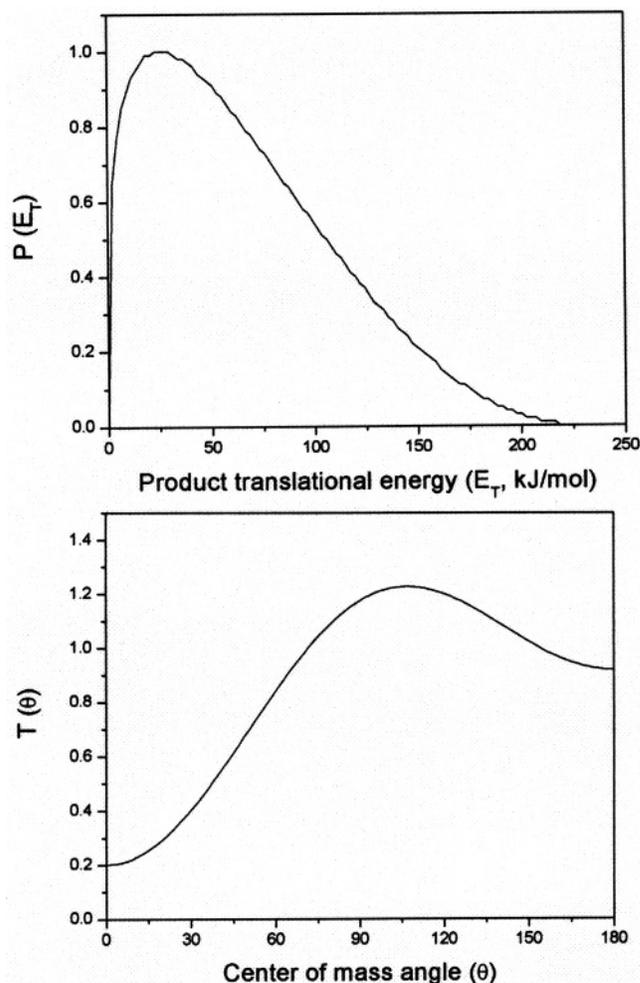
Figure 4. Center-of-mass translational energy flux distribution (top) and center-of-mass angular distribution (bottom) for the reaction of dicarbon with methylacetylene to form C_5H_3 radical(s) and atomic hydrogen at a collision energy of 37.6 kJ mol^{-1}.
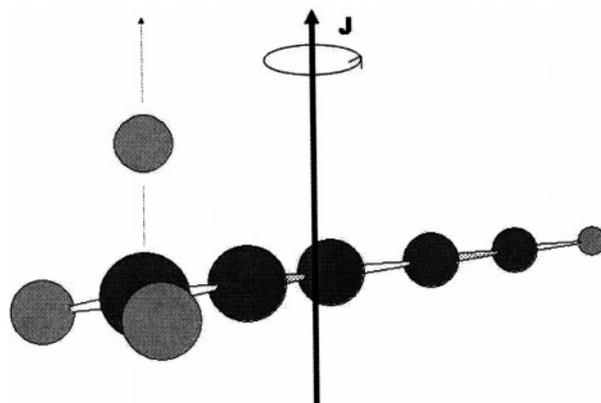
Figure 5. Schematic representation of the atomic hydrogen loss from the fragmenting methyldiacetylene intermediate. **J** represents the total angular momentum vector.

mediate followed by a successive hydrogen atom loss. Therefore, this process is expected to be less likely and a less important reaction pathway at most.[14]

We would like to comment briefly on the experimentally found sideways-peaking of the center-of-mass angular distribution between 85° and 120°. This behavior strongly resembles what has been observed for the reaction $F + C_6D_6 \rightarrow C_6D_5F + D$ in a crossed beam study by Lee and co-workers at a collision

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energy of 10.7 kJ mol^{-1};[17] these geometrical constraints were also found in the CN/C$_6$H$_6$,[18] CN/C$_2$H$_4$,[19] and F/C$_2$D$_4$[20] systems.[21] Therefore, our finding implies that that the light hydrogen atom is emitted favorably in a direction nearly perpendicular to the rotating plane of the H$_3$CCCCCH intermediate (Figure 5).

The present crossed beams study verifies the formation of the 2,4-pentadiynyl-1 radical (HCCCCCH$_2$; X^{2}B$_1$) 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 beam reactions of dicarbon with allene, a structural isomer of methylacetylene, are scheduled.

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