

A crossed molecular beam study on the synthesis of the interstellar 2,4-pentadiynylidyne radical (HCCCC)

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Crossed molecular beam experiments are performed to elucidate the synthesis of the 2,4-penta-diynylidyne [HCCCC($X^2\Pi$)] radical under single collision conditions—a crucial reaction intermediate to form polycyclic aromatic hydrocarbons and carbonaceous nanostructures in the interstellar medium and in combustion flames. The experiments demonstrate that the chemical dynamics of ground state carbon reacting with diacetylene [HCCCCH($X^1\Sigma_g^+$)] are indirect and proceed via addition of the electrophilic carbon atom to the π electron density of the diacetylene molecule yielding ultimately the carbenelike HCCCCCH($X^3\Sigma_g^-$) molecule. This intermediate fragments via hydrogen atom emission to yield the 2,4-pentadiynylidyne [HCCCC($X^2\Pi$)] radical. The chemical dynamics elucidated also allows us to predict that reaction of carbon atoms with polyynes of the generic formula $H(C\equiv C)_nH$ leads to the formation of hydrogen-terminated carbon clusters of the generic form HC_{2n+1} in extreme environments. The acetylene-related reactivity and electronic structure of the diacetylene molecule also allow us to project that reactions of the diacetylene molecule with cyano and ethynyl radicals result in a stepwise extension of the carbon skeleton forming cyanodiacetylene (HCCCCN) and triacetylene (HCCCCCH) plus atomic hydrogen. These predictions open the door to extensive laboratory studies involving hitherto poorly understood reactions of the diacetylene molecule under single collision conditions. © 2008 American Institute of Physics. [DOI: 10.1063/1.2987366]

I. INTRODUCTION

During the past decades, hydrogen-terminated carbon clusters of the generic formula C_nH ($n=2-7$) have received considerable attention due to their significance in astrochemistry,¹ in the chemical processing of hydrocarbon-rich atmospheres of planets and their moons,² and in combustion systems³ as hydrogen-deficient reaction intermediates leading ultimately to the formation of polycyclic aromatic hydrocarbon molecules and soot particles (Fig. 1).⁴ These singly hydrogenated, long chain carbon clusters are ubiquitous in the interstellar medium and have been detected not only in cold molecular clouds such as TMC-1 (Ref. 5) and in star-forming regions such as L1527,⁶ but also toward high-temperature domains (a few thousand Kelvin) such as carbon-rich protoplanetary nebulae (CRL 618) (Ref. 7) and around the circumstellar envelope of the carbon star IRC +10216.⁸

Whereas the synthesis of the lower members of this series such as the $C_{\infty v}$ symmetric 2-propyn-1-ylidyne [$C_3H(X^2\Pi)$] and 1,3-butadiynyl [$C_4H(X^2\Sigma^+)$] radicals can be rationalized in terms of bimolecular neutral-neutral reactions of ground state carbon atoms⁹ and dicarbon molecules¹⁰ with acetylene [$C_2H_2(X^1\Sigma_g^+)$], the formation of the next higher member of this series, i.e., 2,4-pentadiynylidyne [HCCCC($X^2\Pi$)], has not been understood to date. How can this molecule be “made” in the laboratory and also in interstellar space? To guide a directed synthesis, it is helpful

to evaluate first the properties of the 2,4-pentadiynylidyne radical. The first systematic study on the electronic states of C_nH ($n=2-7$) radicals was conducted by Woon.¹¹ For the odd- n series, these calculations indicate $^2\Pi$ electronic ground states, whereas for the even- n series, the electronic ground state switches from $^2\Sigma^+$ ($n=2,4$) to $^2\Pi$ ($n=6$). For the 2,4-pentadiynylidyne radical [HCCCC], the $^2\Pi$ electronic ground state was confirmed experimentally by McCarthy *et al.*¹² by investigating the hyperfine structure of its rotational spectrum. Crawford *et al.*¹³ carried out methodical studies on the structure and energetics of the 2,4-pentadiynylidyne molecule and its higher-energy isomers. The authors identified three low-lying isomers ranging in stability within about 100 kJ mol⁻¹ (Fig. 2): The most stable $C_{\infty v}$ symmetric linear C_5H isomer [HCCCC($X^2\Pi$)] (1), the C_{2v} symmetric cyclic HC_2C_3 isomer of medium stability [+21–25 kJ mol⁻¹ with respect to (1)], holding a 2B_2 ground state (2), and a second cyclic structure of C_s symmetry, C_2C_3H , with a $^2A'$ electronic ground state ranging 100–113 kJ mol⁻¹ above (1). The structure of these radicals has been confirmed recently by Haubrich *et al.*¹⁴ and Apponi *et al.*¹⁵ Subsequent computations by Mebel *et al.*¹⁶ and Sun *et al.*¹⁷ not only verified the stability sequence of (1)–(3), but also provided enthalpies of formation of the linear C_5H isomer [HCCCC($X^2\Pi$)] to be 923 and 931 kJ mol⁻¹, respectively. Based on these energetics, a reaction of ground state carbon atoms [$C(^3P)$] with diacetylene [$C_4H_2(X^1\Sigma_g^+)$] should synthesize the linear C_5H isomer [HCCCC($X^2\Pi$)] plus atomic hydrogen. Here, we test this hypothesis and conduct a directed synthesis of this

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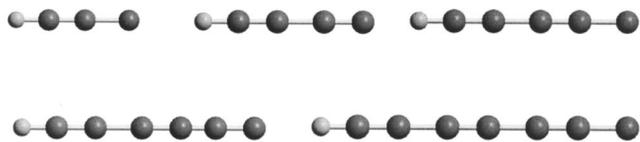


FIG. 1. Structures of hydrogen-terminated linear C_nH molecules ($n=3-7$).

linear C_5H isomer in the gas phase utilizing the crossed molecular beam approach. The application of the crossed molecular beam approach has one stringent prerequisite: It must be possible to generate a supersonic beam of carbon atoms and of diacetylene of sufficient intensity to identify the reaction product. In our laboratory, we have recently succeeded in generating an intense pulsed beam of diacetylene and incorporated this source for the very first time into a crossed beam machine. The aim to tackle the diacetylene system is also to gain an intimate insight into the chemical dynamics and reactions of this highly reactive molecule, which are still unexplored. Our studies will not only shed light on pathways to form the linear C_5H isomer [$HCCCC(X^2\Pi)$] in the interstellar medium, but also aspire to rationalize generalized concepts on how organic, hydrogen-terminated carbon clusters of the generic formula C_nH can be made under gas phase single collision conditions in extreme environments.

II. EXPERIMENTAL

The crossed molecular beam experiments were conducted under single collision conditions so that a particle of the primary beam (ground state carbon atom) is made to collide only with a single molecule (diacetylene molecule) of a second beam.¹⁸ Here, pulsed beams of ground state carbon atoms, $C(^3P_j)$, were generated in the primary source chamber via laser ablation of graphite at 266 nm.¹⁹ The ablated species were seeded in helium carrier gas (99.9999%; 3040 torr) released by a Proch-Trickl pulsed valve. After passing a skimmer, a four-slot chopper wheel selected a part of the carbon beam at a peak velocity of $2050 \pm 20 \text{ ms}^{-1}$. Note that the coablated dicarbon molecules were minimized to about 1% compared to the carbon number density by adjusting the laser energy, focus, and delay times. Tricarbon molecules do not react with closed shell unsaturated hydrocarbons under the present experimental conditions due to inherent entrance barriers.²⁰ No clusters higher than tricarbon are present in the primary beam. The atomic carbon beam crossed a pulsed diacetylene beam (+99.9%; $v_p = 580 \pm 20 \text{ ms}^{-1}$) entrained at seeding fractions of 5% in argon carrier gas perpendicularly at a collision energy of

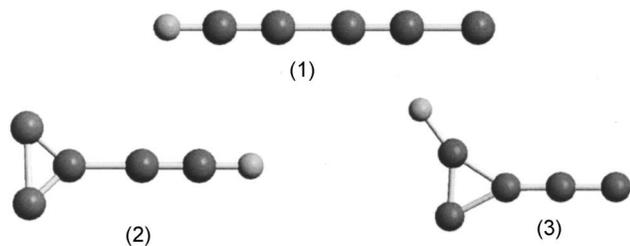


FIG. 2. Structures of the three energetically lowest C_5H isomers.

$22.1 \pm 0.4 \text{ kJ mol}^{-1}$ in the interaction region of the scattering chamber. The reactively scattered species were monitored using a quadrupole mass spectrometric detector in the time-of-flight (TOF) mode after electron-impact ionization of the molecules at 80 eV. The detector can be rotated within the plane defined by the primary and the secondary reactant beams to take angular resolved TOF spectra. By integrating the TOF spectra at distinct laboratory angles, we obtained the laboratory angular distribution (LAB), i.e., the integrated signal intensity of an ion at a well defined m/z value versus the laboratory angle. To obtain meaningful information on the chemical dynamics, TOF and LAB data were fitted using a forward-convolution routine.²¹ This approach initially presumes the angular flux distribution $T(\theta)$ and the translational energy flux distribution $P(E_T)$ in the center-of-mass (c.m.) system assuming mutual independence. TOF spectra and the laboratory angular distributions are then calculated from these $T(\theta)$ and $P(E_T)$ convoluted over the apparatus functions to obtain simulations of the experimental data. The essential output of this process is the generation of a product flux contour map, $I(\theta, u) = P(u) \times T(\theta)$. This function reports the intensity of the reactively scattered products (I) as a function of the c.m. scattering angle (θ) and product velocity (u) and is called the reactive *differential cross section*. This map can be seen as the *image* of the chemical reaction and contains *all* the information on the scattering process.

III. RESULTS AND DISCUSSION

In the crossed molecular beam study, reaction products were probed at ions of mass-to-charge (m/z) ratios of 61 and 60. These m/z values are consistent with ions of the formulas C_5H^+ and C_5^+ , respectively. The TOF spectra of both ions were superimposable. This finding alone implies that C_5^+ originates from dissociative ionization of the C_5H parent molecule in the electron-impact ionizer and that molecules of the generic formula C_5H are the only reaction products in this mass range. It should be stressed that neither radiative association to C_5H_2 nor higher masses were observed. This suggests that dicarbon and tricarbon molecules, which are still presenting the primary beam, do not contribute to reactive scattering signal at $m/z=61$. Also, under single collision conditions, the C_5H_2 molecule is unstable. Due to the stronger signal at $m/z=61$ compared to $m/z=60$, TOF data and the corresponding laboratory angular distribution were extracted from the C_5H^+ ions. These data are shown in Figs. 3 and 4. As evident, the LAB distribution is relatively narrow and spread over only 45° within the scattering plane defined by the carbon atom and the diacetylene beams. Further, the LAB distribution peaks close to the corresponding c.m. of the system of $(49.7 \pm 0.5)^\circ$.

Quantitative information on the chemical dynamics are extracted by transforming the data from the laboratory coordinate system to the c.m. system. The solid lines placed over the experimental data in Figs. 3 and 4 are the calculated fits utilizing the best-fit c.m. functions as compiled in the product flux contour map of the heavy reaction product(s), i.e., molecules of the generic formula C_5H . The shape of the best-fit c.m. angular distribution, $T(\theta)$, is forward-backward

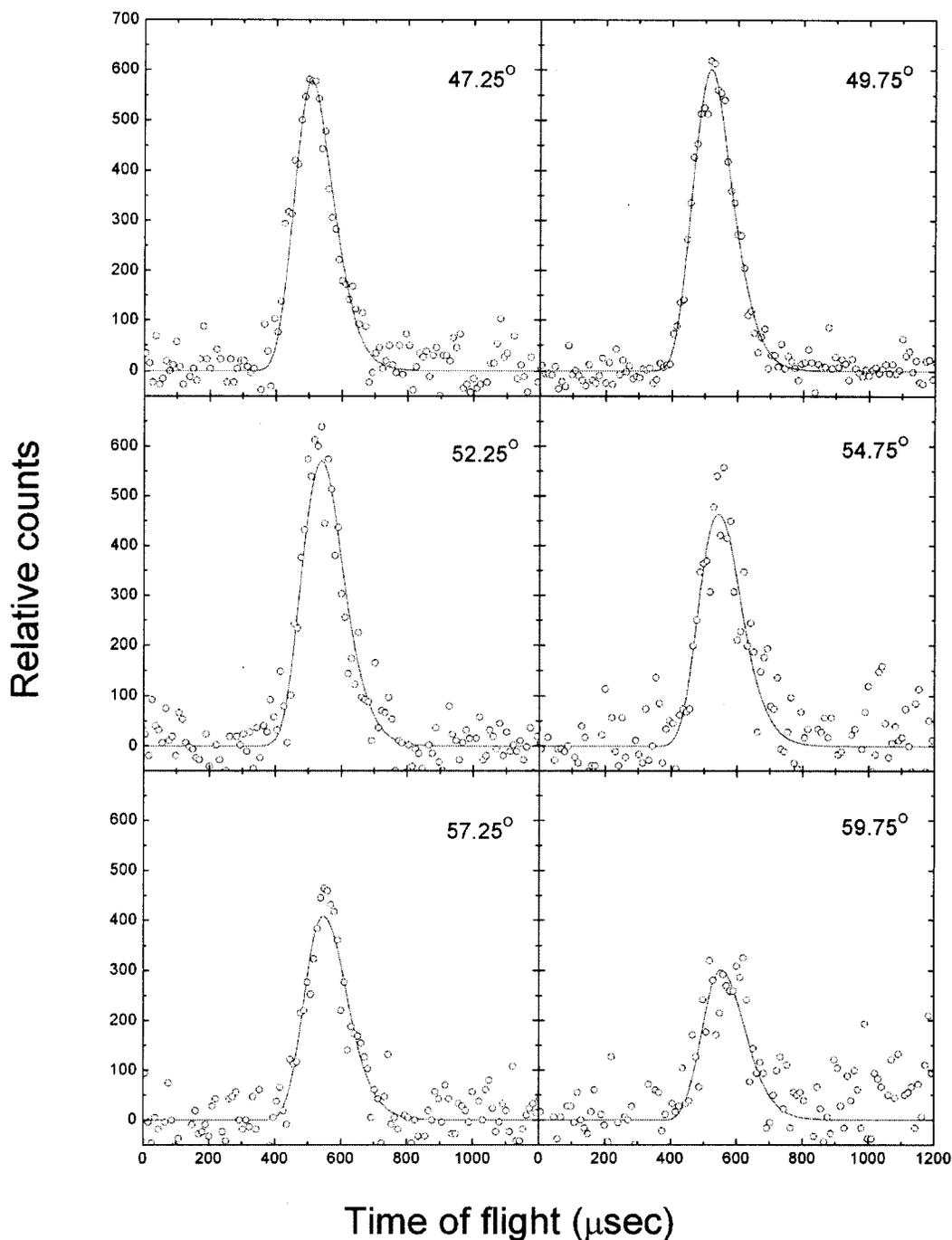


FIG. 3. TOF spectrum recorded at mass-to-charge ratio (m/z) of 61 (C_5H^+). The open circles represent the experimental data and the solid lines represent the fits. The quadrupole mass filter was set at a constant $m/z=61$ and operated them in the TOF mode to record the arrival time of the ionized products of $m/z=61$.

symmetric, but with a small minimum at 90° as evident from the flux contour map (Fig. 5). The flux of the C_5H reaction product stretches over the complete angular range from 0° to 180° ; this is indicative of a chemical reaction involving a bound reaction intermediate of the generic formula C_5H_2 . The forward-backward symmetry further indicates that the lifetime of the reaction intermediate, which decomposes to C_5H isomer(s) plus atomic hydrogen, is longer than its rotational period.²² Alternatively, if the intermediate is symmetric, so that the rotation can interconvert both hydrogen atoms,⁹ this can be also reflected in a forward-backward symmetric flux contour plot; in this case, no information on

the lifetime of the reaction intermediate can be obtained. In addition to the angular part of the flux contour map, it should be stressed that the best-fit product translational energy distribution, $P(E_T)$, depicts a maximum of about 10 kJ mol^{-1} ; within the error limits of the experiment, the $P(E_T)$ is expressed with a high energy cutoff of $60 \pm 8 \text{ kJ mol}^{-1}$. Here, the translational energy release helps us to extract which C_5H isomer is formed. Due to energy conservation and in the limit that all available energy channels into the translational degrees of freedom of the products, the high-energy cutoff, E_{max} , presents the sum of the collision energy and the absolute of the reaction energy. Therefore, a subtraction of the

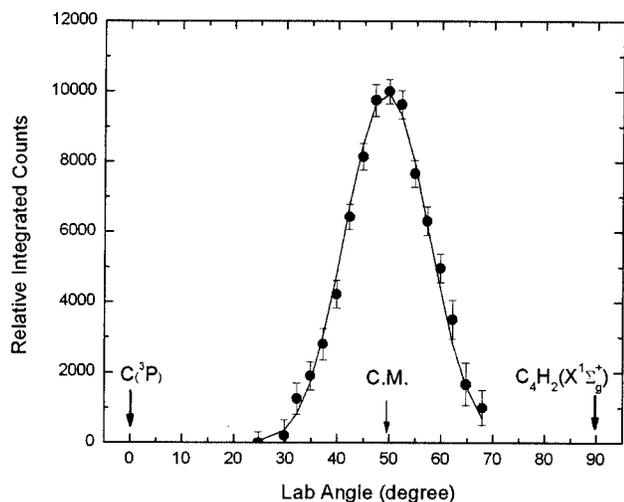


FIG. 4. Laboratory angular distributions recorded at mass-to-charge ratio (m/z) of 61 (C_5H^+). The solid circles represent the experimental data and the solid lines represent the fits utilizing the best-fit c.m. functions.

collision energy from $E_{\max} = 60 \pm 10 \text{ kJ mol}^{-1}$ calculates the reaction to be exoergic by $38 \pm 8 \text{ kJ mol}^{-1}$. Considering the energetics of the C_5H isomers (Fig. 1), these data are consistent with the formation of the linear 2,4-pentadiynylidyne [$HCCCCC(X^2\Pi)$] molecule (1) formed in the reaction of carbon atoms with diacetylene via decomposition of a C_5H_2 reaction intermediate (Fig. 6). Based on the energetics alone, we cannot exclude the formation of smaller amounts of the thermodynamically less stable isomer (2). However, we have to stress that no fit of the experimental data could be achieved by solely including the energetics of the cyclic structure (2). However, considering the stability of the third isomer (3), we can conclude that the reaction to form (3) is too endoergic ($+65 \pm 10 \text{ kJ mol}^{-1}$); therefore, this channel is well above the collision energy of $22.1 \pm 0.4 \text{ kJ mol}^{-1}$ to be opened.

To extract the chemical dynamics leading to the formation of the linear 2,4-pentadiynylidyne [$HCCCCC(X^2\Pi)$] radical (1), we are merging our experimental findings with electronic structure calculations on the C_5H_2 (intermediates) and C_5H (products) potential energy surfaces.^{13,16,17} A comparison of the structures of the diacetylene reactant and the linear 2,4-pentadiynylidyne [$HCCCCC(X^2\Pi)$] molecule

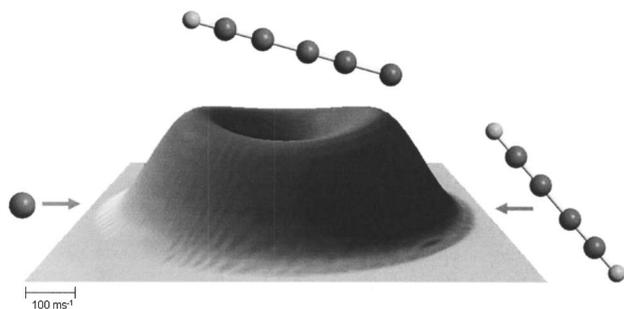


FIG. 5. c.m. velocity contour flux map for the reaction of ground state carbon atoms (left; 0°) with diacetylene (right; 180°) forming atomic hydrogen plus the 2,4-pentadiynylidyne radical. The grey colors connect data points with an identical flux. The units of axis are given in ms^{-1} (see legend).

portrays that formally, the carbon chain is extended by one carbon atom at the expense of a hydrogen atom (Figs. 1, 2, and 6). Here, a reversed reaction of an addition of atomic hydrogen to linear 2,4-pentadiynylidyne [$HCCCCC(X^2\Pi)$] at the terminal carbon atom is expected to form a linear $HCCCCCH$ reaction intermediate (i4). As a matter of fact, recent experimental and theoretical studies elucidated that this molecule holds a $D_{\infty h}$ point group and a $X^3\Sigma_g^-$ ground state; it must be considered as a triplet carbene with its carbene function located at the central carbon atom; two ethynyl groups are connected to the carbenelike atom.²³ It should be noted that the decomposition of $HCCCCCH(X^3\Sigma_g^-)$ to form $HCCCCC(X^2\Pi)$ plus atomic hydrogen involves a significant reorganization of the electron density from a carbene function at the central carbon atom in i4 to the unpaired electron in the π orbital at the terminal carbon atom of $HCCCCC(X^2\Pi)$. This reorganization of electron density is often connected with a tight exit transition state connecting the fragmenting intermediate to the final product. As a matter of fact, the existence of a tight exit transition state has been verified experimentally via the best-fit product translational energy distribution, $P(E_T)$, depicting a maximum of about 10 kJ mol^{-1} and also computationally predicting an exit transition state located 22 kJ mol^{-1} above the separated products.¹⁷ Note that this intermediate, which is stabilized by 416 kJ mol^{-1} with respect to the separate reactants,¹⁷ can only be excited to B-like rotations due to its linearity; these rotations interconvert the chemically equivalent hydrogen atoms in the $HCCCCCH(X^3\Sigma_g^-)$ molecule. Consequently, there exists an equal probability of a hydrogen atom to be released into θ and $\pi - \theta$; this *always* translates into a forward-backward symmetric flux contour map as extracted experimentally (Fig. 5). Also, it is important to outline that the total angular momentum is conserved. Since the emitted hydrogen atom is light compared to the $HCCCCC(X^2\Pi)$ radical, 80%–85% of the initial angular momentum is channeled into rotational excitation of products. This is documented by the moderate polarization of the angular part of the flux contour map.

Having identified the linear $HCCCCCH(X^3\Sigma_g^-)$ molecule as the decomposing complex, the next step in our investigation is to elucidate the formation routes of i4 from the atomic carbon and diacetylene reactants. Based on the calculations, on the chemical dynamics, and on the kinetics of the reactions of atomic carbon with acetylene^{9,17,24,25} and methylacetylene,²⁶ we can suggest that the carbon atom as an electrophilic reactant adds without barrier to (i) the C1 atom forming an open chain intermediate i1, (ii) to the C1 and C2 carbon atoms simultaneously yielding a cyclic intermediate i2, or (iii) to C2 yielding intermediate i3. These intermediates were computed to reside in potential energy wells of 185, 226, and 185 kJ mol^{-1} , respectively, compared to the reactants.¹⁷ The acyclic structures i1 and i3 isomerize instantaneously to the cyclic intermediate i2, which in turn ring opens to the linear $HCCCCCH(X^3\Sigma_g^-)$ molecule (i3). Note that a hydrogen shift connecting i1 directly to i4 was found not to compete with the ring closure pathway.²²

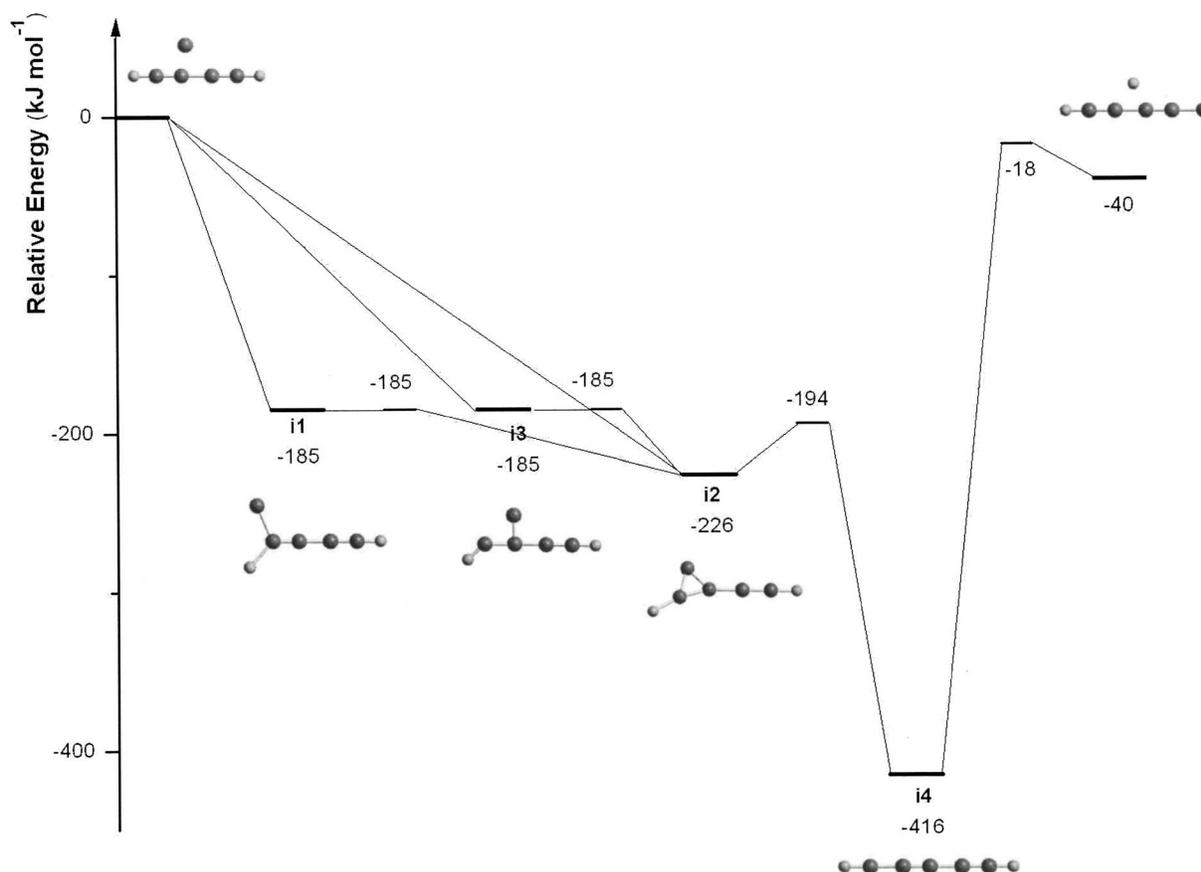


FIG. 6. Reaction mechanism of ground state carbon atoms with diacetylene molecules under single collision conditions. Relative energies are given with respect to the separated reactants in kJ mol^{-1} and were taken from Ref. 17. The accuracy of the energies is $\pm 5 \text{ kJ mol}^{-1}$.

IV. SUMMARY

We have demonstrated experimentally that the 2,4-pentadiynylidyne [$\text{HCCCCC}(X^2\Pi)$] radical can be formed in an exoergic gas phase reaction between atomic carbon and diacetylene under single collision conditions. The chemical dynamics are indirect and proceed via addition of the electrophilic carbon atom to the π electron density of the diacetylene molecule yielding after isomerization a $\text{HCCCCCH}(X^3\Sigma_g^-)$ intermediate. The latter fragments via hydrogen atom emission via a tight exit transition state to yield the 2,4-pentadiynylidyne [$\text{HCCCCC}(X^2\Pi)$] radical. Since the reaction has no entrance barrier, is exoergic, and all transition states involved reside below the energy of the separated reactants, we have verified that bimolecular collisions of atomic carbon with diacetylene can synthesize the 2,4-pentadiynylidyne [$\text{HCCCCC}(X^2\Pi)$] radical in the interstellar medium and also in combustion flames. It should be outlined that the 2,4-pentadiynylidyne radical was also the product of the crossed beam reaction of ground state tricarbon molecules with acetylene molecules.²⁵ However, this reaction was found to have an entrance barrier and endoergic. Due to these findings, in cold molecular clouds holding averaged translational temperatures of 10 K, the 2,4-pentadiynylidyne radical should be synthesized via the barrierless and exoergic reaction of ground state carbon atoms with diacetylene, but not via bimolecular collisions of tricarbon molecules with acetylene; however, in high temperature

combustion flames and close to the atmospheres of carbon stars, the elevated temperatures might also trigger the formation of this radical via bimolecular reactions of tricarbon molecules with acetylene. In our present studies, we have also identified three C_5H_2 intermediates, among them the $\text{HCCCCCH}(X^3\Sigma_g^-)$ isomer as the thermodynamically most stable structure. Although under single collision conditions as present in our experiments and in the interstellar medium this intermediate cannot be stabilized by a third body reaction, dense media such as atmospheres of planets and their satellites as well as combustion systems can supply a third body encounter to stabilize the reaction intermediate if the collision time is shorter than the lifetime of the $\text{HCCCCCH}(X^3\Sigma_g^-)$ molecule. This can lead to a stabilization and—due to the open shell character of the intermediate—also to reactions of this molecule.²⁷ The chemical dynamics elucidated here also leads us to the prediction that reaction of carbon atoms with polyynes of the generic formula $\text{H}(\text{C}\equiv\text{C})_n\text{H}$ will lead to the formation of hydrogen-terminated carbon clusters of the form HC_{2n+1} in extreme environments. The acetylene-related reactivity and electronic structure of the diacetylene molecule also allow us to forecast that reactions of this molecule with cyano and ethynyl radicals lead to a stepwise extension of the carbon skeleton forming cyano-diacetylene (HCCCCCN) and triacetylene (HCCCCCCH) plus atomic hydrogen. These predictions shall open the door to extensive laboratory studies involving reactions of the di-

acetylene molecule under single collision conditions, which are not only relevant to interstellar chemistry, but also to the chemical processing of the atmosphere of Saturn's moon Titan, which is often dubbed as a natural time capsule to understand the origin and evolution of our solar system.

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