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Formation of the 1,3,5-Hexatriynyl Radical ($C_6H(X^2\Pi)$) via the Crossed Beams Reaction of Dicarbon ($C_2(X^1\Sigma_g^+/a^3\Pi_u)$), with Diacetylene ($C_4H_2(X^1\Sigma_g^+)$)

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Crossed molecular beams experiments were conducted to investigate the chemical dynamics of the reaction of dicarbon molecules, $C_2(X^1\Sigma_g^+/a^3\Pi_u)$, with diacetylene, $C_4H_2(X^1\Sigma_g^+)$ at two collision energies of 12.1 and 32.8 kJmol^{-1}. The dynamics were found to be indirect, involved C_6H_2 intermediates, and were dictated by an initial addition of the dicarbon molecule to the carbon−carbon triple bond of diacetylene. The initial collision complexes could isomerize. On the singlet surface, the resulting linear triacetylene molecule ($C_6H_2(X^1\Sigma_g^+)$) decomposed without an exit barrier to form the linear 1,3,5-hexatriynyl radical ($C_6H(X^2\Pi)$). On the triplet surface, the dynamics suggested at least a tight exit transition state involved in the fragmentation of a triplet C_6H_2 intermediate to yield the 1,3,5-hexatriynyl radical ($C_6H(X^2\Pi)$) plus atomic hydrogen. On the basis of the experimental data, we recommend an experimentally determined enthalpy of formation of the 1,3,5-hexatriynyl radical of 1014 ± 27 kJmol^{-1} at 0 K. Our experimental results and the derived reaction mechanisms gain full support from electronic structure calculations on the singlet and triplet C_6H_2 potential-energy surfaces. The identification of the 1,3,5-hexatriynyl radical under single collision conditions implies that the neutral−neutral reaction of dicarbon with diacetylene can lead to the formation of 1,3,5-hexatriynyl radicals in the interstellar medium and possibly in the hydrocarbon-rich atmospheres of planets and their moons such as Saturn's satellite Titan.

1. Introduction

The linear 1,3,5-hexatriynyl radical ($C_6H(X^2\Pi)$) presents the third member in a series of polyacetylenic radicals of the generic formula $H-(C\equiv C)_n -$ among them the ethynyl radical (HC_2 ($X^2\Sigma^+$), $n = 1$) and the 1,3-butadiynyl radical ($HC_4(X^2\Sigma^+)$, $n = 2$). These linear hydrocarbon radicals have received considerable interest due to their importance in the astrochemical evolution of the interstellar medium,[1−10] in the chemical processing of hydrocarbon-rich atmospheres of planets and their moons such as Saturn's satellite Titan,[11,12] and in oxygen-poor combustion flames. Here, these open-shell species serve as hydrogen-deficient precursors that lead ultimately to the formation of polycyclic aromatic hydrocarbons (PAHs) and carbonaceous grain particles (soot, interstellar grains).[13−15] The 1,3,5-hexatriynyl radical presents an interesting case. As a matter of fact, this species was first detected in 1986 in extraterrestrial environments toward the cold molecular cloud TMC-1[16] and in the circumstellar envelope of the dying carbon star IRC+10216.[17,18] Two years later, Gottlieb and co-workers recorded its millimeter-wave rotational spectrum of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ ladders between 146.5 and 199.6 GHz in the terrestrial laboratory.[19] A subsequent theoretical study by Pauzat and Ellinger verified that the $^2\Pi$ state presented the electronic ground state;[20] the lowest excited $^2\Sigma^+$ state was found to be about 20−25 kJmol^{-1} higher in energy. These theoretical investigations also triggered matrix studies and the assignment of electronic transitions[21] and the carbon−carbon stretching mode at 1953 cm^{-1}.[22] A subsequent theoretical study by Liu et al. confirmed this analysis.[23] Woon et al. and Schaefer et al. conducted the first systematic studies on the electronic states of important polyacetylenic transient species. Quite interestingly, the electronic ground-state was found to switch from a $^2\Sigma^+$ state for ethynyl and 1,3-butadiynyl to a $^2\Pi$ state for the 1,3,5-hexatriynyl radical.[24]

However, despite the importance of the 1,3,5-hexatriynyl radical (HCCCCCC) in the chemical evolution of extraterrestrial environments and of combustion flames, the synthetic routes to form this highly hydrogen-deficient molecule have not been resolved to date. Could there be any directed synthesis to this species? Recall that the related 1,3-butadiynyl radical (HCCCC) was formed in the bimolecular reaction of the dicarbon molecule with acetylene as elucidated in crossed molecular beams experiments (eq 1).[25,26] Here, the dicarbon molecule added to the acetylenic bond and − after various isomerization steps − *formally* inserted into the carbon−carbon triple bond of the acetylene unit.

$$C_2(X^1\Sigma_g^+/a^3\Pi_u) + C_2H_2(X^1\Sigma_g^+) \rightarrow C_4H(X^2\Sigma^+) + H(^2S_{1/2}) \qquad (1)$$

Because the acetylenic group is also present in the diacetylene molecule, we conducted crossed molecular beams studies and combined these investigations with electronic structure calculations to see if the neutral−neutral reaction of dicarbon with the next higher member of the polyacetylenes series − diacetylene − yields the 1,3,5-hexatriynyl radical (HCCCCCC) under single-collision conditions via a related reaction mechanism (eq 2). Because dicarbon and diacetylene are also important transient species in the atmosphere of Saturn's moon Titan,[27] our studies can also shed light to what extent the 1,3,5-hexatriynyl radical

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TABLE 1: Peak Velocities (v_p) and Speed Ratios (S) of the Intersecting Segments of the Supersonic Beams Together with the Corresponding Collision Energies (E_c) and Center-of-Mass Angles (Θ_{CM})

beam	v_p, ms^{-1}	S	E_c, kJmol^{-1}	Θ_{CM}
$C_4H_2(X^1\Sigma_g^+)$/Ar	600 ± 20	8.0 ± 0.5		
$C_2(X^1\Sigma_g^+/a^3\Pi_u)$/He	1920 ± 20	4.0 ± 0.3	32.8 ± 0.6	32.8 ± 1.0
$C_2(X^1\Sigma_g^+/a^3\Pi_u)$/Ne	1070 ± 20	5.5 ± 0.3	12.1 ± 0.5	48.4 ± 1.0

can be formed via bimolecular neutral−neutral reactions in the hydrocarbon-rich atmosphere of this moon.[28−31]

$$C_2(X^1\Sigma_g^+/a^3\Pi_u) + C_4H_2(X^1\Sigma_g^+) \rightarrow C_6H(X^2\,\Pi) + H(^2S_{1/2}) \qquad (2)$$

2. Experimental Setup and Data Processing. Our experiments were conducted under single collision conditions in a crossed molecular beams machine.[32−35] Pulsed dicarbon beams were produced in the primary source by laser ablation of graphite at 266 nm by focusing about 5 mJ per pulse on the rotating carbon rod.[36] The ablated species were seeded in neat carrier gas (helium or neon, Gaspro, 99.9999%, 3040 torr, Table 1) released by a Proch−Trickl pulsed valve operated at pulse widths of 80 μs and −400 V. After passing a skimmer, a four-slot chopper wheel mounted after the ablation zone selected a part out of the seeded dicarbon beam, which then crossed a pulsed diacetylene beam (C_4H_2, 99.5% purity) at seeding fractions of 5% in argon. To optimize the intensity of each supersonic beam, which strongly depends on the distance between the pulsed valve and the skimmer, on line and in situ, each pulsed valve was placed on a ultra-high vacuum compatible micro-positioning translation stage with three stepper motors. This allows monitoring the beam intensity versus the position of the pulsed valve in each source chamber.

Diacetylene itself was synthesized according to an adapted literature procedure. Nine grams of 1,4-dichloro-2-butyne ($ClCH_2CCCH_2Cl$) was dissolved in 15 mL ethyl alcohol (C_2H_5OH) and warmed up to 353 K. Aqueous sodium hydroxide (NaOH, 60%) solution was added dropwise under stirring. White diacetylene vapor evolved and was carried away in a stream of helium carrier gas. The diacetylene gas was bubbled through a 13% aqueous sodium hydroxide solution, dried over calcium chloride, and frozen in a liquid nitrogen trap (77 K). Gas mixtures of 5% diacetylene in argon (99.9999%, Gaspro) were prepared at 293 K and at a pressure of 2280 Torr. These mixtures were stable for months. The purity of the diacetylene was checked via mass spectrometry and was found to be 99.5%+. Without the calcium chloride, higher yields but lower purities of only 99% were achieved.

At all velocities, the ablation beams contain dicarbon in its $X^1\Sigma_g^+$ electronic ground-state as well as in its first electronically excited $a^3\Pi_u$ state.[26] Although the primary beam contains carbon atoms and tricarbon molecules as well, these species do not interfere with the ion counts of the dicarbon − diacetylene system at mass-to-charge ratios (m/z) of 73 (C_6H^+) and 72 (C_6^+). Test experiments showed that tricarbon reacts with diacetylene only at collision energies larger than about 80 kJmol^{-1}. Reactive scattering signal from the reaction of atomic carbon with diacetylene only yields ion counts at m/z values of 61 (C_5H^+) and lower.[37] The reactively scattered species were monitored using a triply differentially pumped quadrupole mass spectrometric detector (QMS) in the time-of-flight (TOF) mode after electron-impact ionization of the neutral molecules at 80 eV electron energy. Our detector can be rotated within the plane defined by the primary and the secondary reactant beams to allow recording angular resolved TOF spectra. By taking and integrating the TOF spectra, we obtain the laboratory angular distribution (LABORATORY), which portrays the integrated signal intensity of an ion of distinct m/z versus the laboratory angle. At each angle, we accumulated up to 7.5 × 10^5 TOF spectra; this resulted in data accumulation times of up to 8 h per angle accounting for the repetition rate of the ablation laser of 30 Hz. Each time, up to 5.0 × 10^4 TOFs were accumulated per sweep. To gain information on the chemical dynamics, the laboratory data (TOF and LABORATORY distributions) were transformed into the CM frame and fit using a forward-convolution routine.[38,39] This procedure initially assumes an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the CM 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. Electronic Structure Calculations. Molecular structures and vibrational frequencies of the reactants and products of the $C_2 + C_4H_2$ reactions and various C_6H_2 intermediates and transition states in the lowest singlet and triplet electronic states have been calculated at the hybrid density functional B3LYP/6-311G** level of theory[40,41] employing the *GAUSSIAN 98* program package.[42] Single-point relative energies of various species were then refined using the coupled clusters CCSD(T) method[43] as implemented in the *MOLPRO 2006* program package[44] with extrapolation to the complete basis set (CBS) limit. To achieve this, we computed CCSD(T) total energies for each stationary point with Dunning's correlation-consistent cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets[45] and projected them to CCSD(T)/CBS total energies by fitting $E_{tot}(x) = E_{tot}(\infty) + Be^{-Cx}$ where x is the cardinal number of the basis set (2, 3, 4, and 5, respectively) and $E_{tot}(\infty)$ is the CCSD(T)/CBS total energy.[46] CCSD(T)/CBS calculations using this extrapolation scheme are normally able to provide accuracy of ± 5 kJmol^{-1} for the energetics.

4. Results

In our crossed beams experiments, we probed signal at mass-to-charge ratios of $m/z = 73$ (C_6H^+) and 72 (C_6^+). The TOF spectra at $m/z = 73$ (C_6H^+) (Figure 1) and 72 (C_6^+) were superimposable after scaling. This finding alone suggests that the molecular hydrogen elimination channel is closed and that signal at $m/z = 72$ originated from a dissociative ionization of the C_6H parent radical in the ionizer of the detector by the 80 eV electrons. Therefore, the only reactive channel from dicarbon reactions observed in the present mass range is the formation of a product of the gross formula C_6H together with the light hydrogen atom. The corresponding LABORATORY distributions recorded at $m/z = 73$ are depicted in Figure 2. At both collision energies, the distributions are relatively narrow and are spread about 30° in the scattering plane defined by both beams. Also, both graphs are nearly symmetric with respect to the CM angles independent of the collision energy. Both LABORATORY distributions peak close to the CM angles (Figure 2, Table 1).

Having discussed the laboratory data, we are turning our attention to the CM angular ($T(\theta)$) and translational energy distributions ($P(E_T)$) (Figure 3). Most importantly, the laboratory data could be fit at both collision energies with a single channel of the mass combination 73 amu (C_6H) and 1 amu (H). It has to be stressed that, at the collision energies of 12.1 and 32.8 kJmol^{-1}, the derived CM angular distributions are essentially

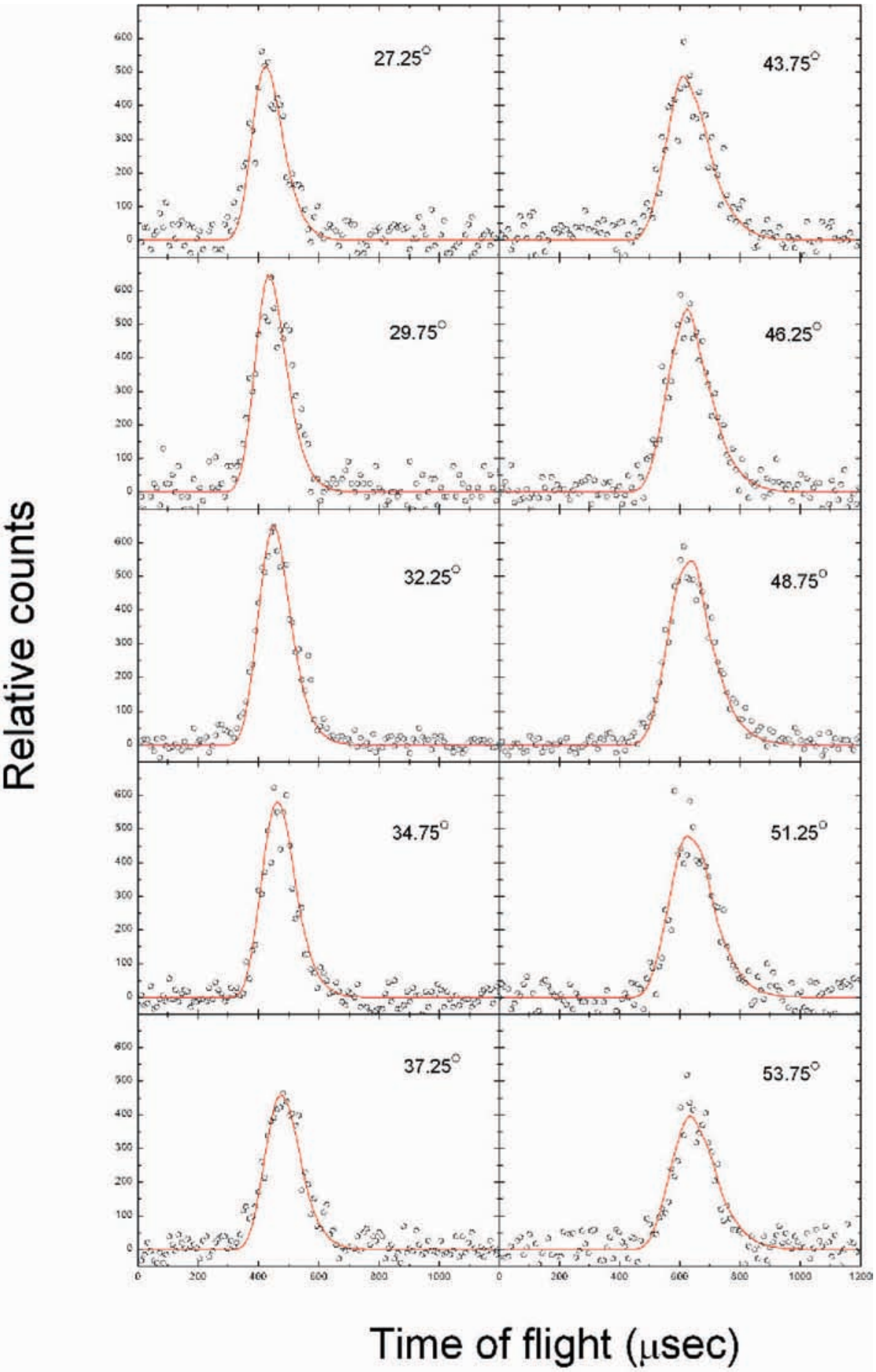

Figure 1. Selected time-of-flight data for *m*/*z* = 73 (C_6H^+) recorded at two collision energies of 12.1 and 32.8 kJmol^{-1} (left and right column, respectively) at various laboratory angles for the reaction of dicarbon molecules with diacetylene. The circles indicate the experimental data, the solid lines the calculated fits.

identical. In both cases, the CM angular distributions, which are forward−backward symmetric with respect to 90° and only weakly polarized, were obtained. Within the error limits, these were either isotropic or depicted shallow minima at 90°. These findings alone indicate that the dicarbon−diacetylene system involves indirect scattering dynamics via the formation of bound C_6H_2 reaction intermediate(s).[47] Also, the inherent forward−backward symmetry of the $T(\theta)$s suggests that the lifetime of the intermediate(s) is longer than its (their) rotational period[48] or that the intermediate is symmetric.[49] In the latter case, a rotational axis would interconvert both hydrogen atoms; this leads to an emission of atomic hydrogen with equal probability into θ° and $\pi-\theta$° and results into a forward−backward symmetric CM angular distribution. It should be noted that the mild polarization is the effect of the poor coupling between the initial and final orbital angular momentum due to the light mass of the departing hydrogen atom.[47] Angular momentum conservation dictates that most of the initial orbital angular momentum channels into the rotational excitation of the polyatomic C_6H product.

The CM translational energy distribution provides additional information to understand the chemical dynamics of the dicarbon−diacetylene system. First, both $P(E_T)$s depict relative broad distribution maxima starting close to zero translational

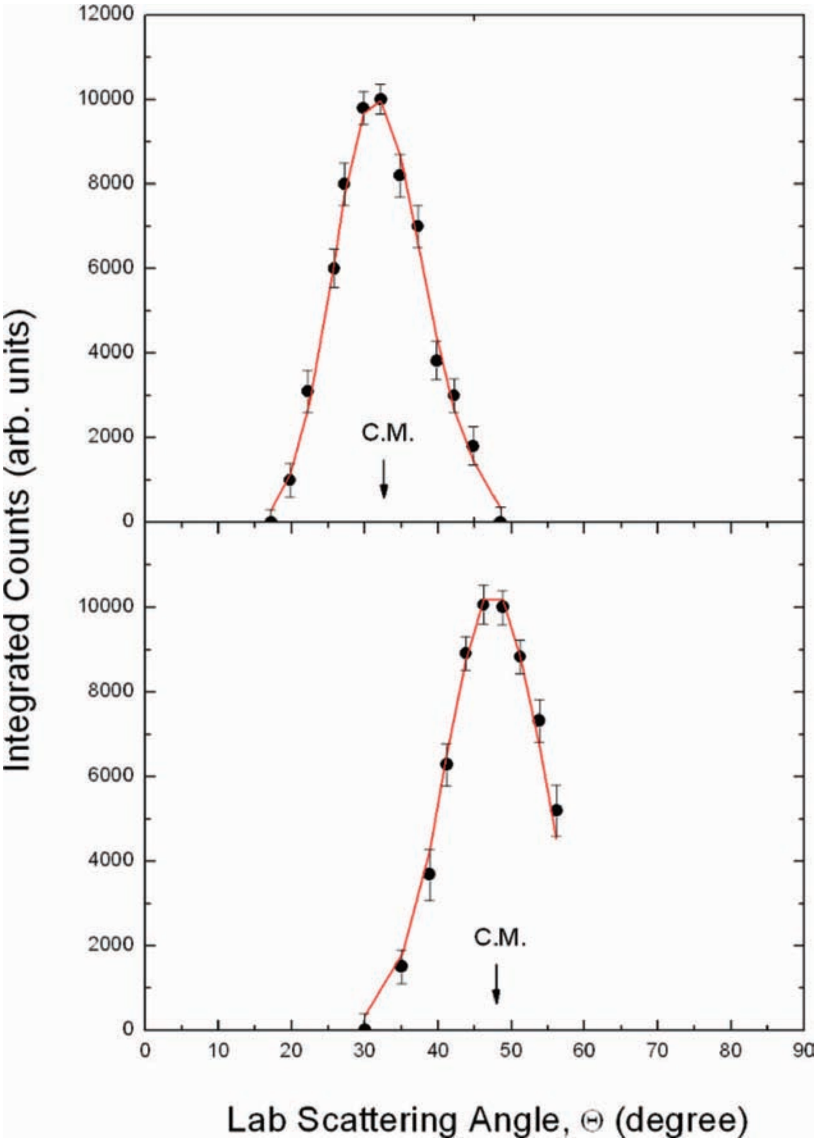

Figure 2. Laboratory angular distribution of the C_6H radical recorded at $m/z = 73$ (C_6H^+) for two collision energies of 12.1 and 32.8 kJmol^{-1} (top and bottom, respectively). Circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions.

energy up to about 18 kJmol^{-1}. This suggests that at least one channel involves an exit barrier of this order of magnitude. Also, as the collision energy rises, and the maximum translational energy, E_{max}, shifts from 70 to 90 kJmol^{-1} for the best fit functions. Our error analysis indicates that the tails of the $P(E_T)$s can be either extended or cut by up to about 15 to 20 kJmol^{-1} without significantly changing the results of the fit. Because the maximum translational energy presents the sum of the collision energy and the absolute of the exoergicity of the reaction, the magnitude of E_{max} can be used to extract the reaction exoergicity. Averaging over both collision energies, we determine that the formation of C_6H and the hydrogen atom is exoergic by 58 ± 20 kJmol^{-1}. Recall that the dicarbon reactants are in the singlet and also in the first excited triplet state; the enthalpy of formation of $C_2(a^3\Pi_u, \nu = 0)$ is lower by 7.3 kJmol^{-1} compared to $C_2(X^1\Sigma_g^+, \nu = 0)$. Therefore, the reaction to form C_6H plus atomic hydrogen on the singlet surface is exoergic by about 51 ± 20 kJmol^{-1}; we would like to note that this value presumes that dicarbon molecules in the excited triplet state contribute significantly to the scattering signal. Also, it should be mentioned that there is a possible role of rovibrational excitation of the dicarbon reactant that has not been accounted so far. The energy content of the dicarbon vibrational states might be quite sizable. For instance, the first vibrational level of dicarbon in both electronic states has an energy content of about 19−22 kJ mol^{-1}. Therefore, the unknown vibrational energy content of dicarbon might alter the value of the enthalpy of reaction and increase the uncertainty. This could shift the reaction energies to lower values than mentioned above. From these CM translational energy distributions, we can also compute the fraction of the energy channeling into the translational modes of the products, that is $\langle E_T\rangle/E_{max}$ with $\langle E_T\rangle$ being the averaged translational energy of the products. This suggests fractions of about 26 ± 6% almost independent of the collision energy. This order of magnitude indicates indirect scattering dynamics.[50]

5. Discussion

We are combining now our experimental results with the computations in an attempt to derive the underlying reaction mechanism. On the basis of the CM translational energy distributions, the formation of the C_6H isomer plus atomic hydrogen was found to be exoergic by about 51 ± 20 kJmol^{-1}

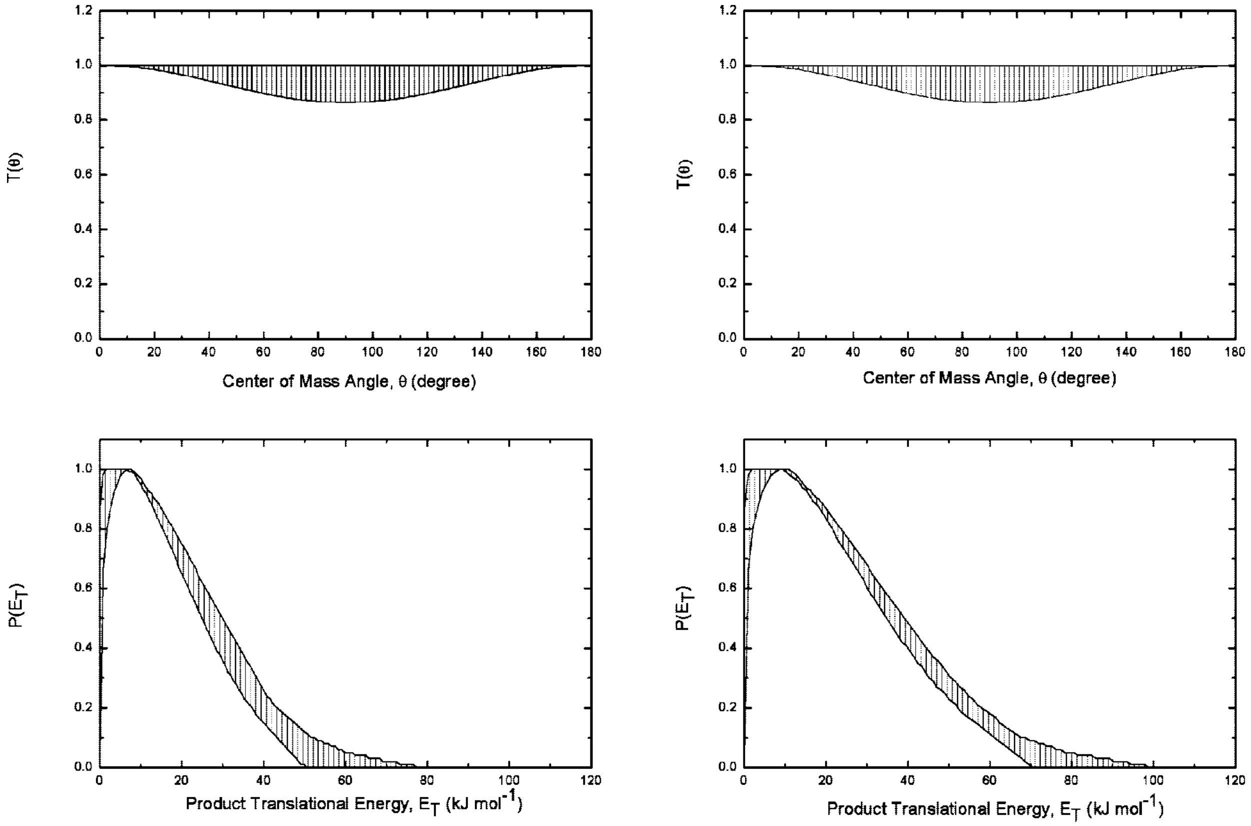

Figure 3. Center-of-mass angular (top) and translational energy flux distributions (bottom) for the C_6H radical plus atomic hydrogen loss channel of the reaction of dicarbon molecules with diacetylene at two collision energies of 12.1 and 32.8 kJmol^{-1} (left and right column, respectively). Hatched areas indicate the acceptable upper and lower ranges within the experimental error limits of the laboratory angular distribution and the beam velocities.

on the singlet surface, keeping in mind potential higher error limits as discussed above. We can compare this experimental data with the theoretically predicted value. Our present theoretical study to form the 1,3,5-hexatriynyl radical plus atomic hydrogen on the singlet surface suggests an exoergicity of about 44 ± 5 kJmol^{-1} (Figure 4). This data agrees very well with the experimental value. Also, on the basis of a combined experimental and theoretical study of the carbon−hydrogen bond strength of the triacetylene molecule of 531 ± 7 kJmol^{-1},[51] the enthalpy of formation of the 1,3,5-hexatriynyl radical could be determined to be 1006 ± 27 kJmol^{-1}. The present CCSD(T)/CBS calculation gives the C−H bond strength in C_6H_2 as 546 kJmol^{-1} that corresponds to a slightly higher value of 1021 ± 5 kJmol^{-1} for the enthalpy of formation of C_6H. Taking these data, this translates into a reaction energy of −55 ± 27 kJmol^{-1} at 0 K to form the 1,3,5-hexatriynyl radical plus atomic hydrogen. Therefore, the experimental and predicted reaction energies agree within the error limits and suggest indeed the synthesis of the linear 1,3,5-hexatriynyl radical. We recommend an enthalpy of formation of the 1,3,5-hexatriynyl radical of 1014 ± 27 kJmol^{-1} at 0 K. Recall that the first electronically excited state was found to be about 20−25 kJmol^{-1} higher in energy.[20] Therefore, on the basis of the energetics alone, we cannot exclude that some 1,3,5-hexatriynyl radicals are formed in the first electronically excited $^2\Sigma^+$ state.

Having identified the 1,3,5-hexatriynyl radical as the reaction product, we are turning our attention now to the dynamics of its formation. Considering the reversed barrierless recombination of the 1,3,5-hexatriynyl radical with atomic hydrogen (Figure 4), the electronic structure calculations suggest the formation of a linear triacetylene molecule (H−C≡C−C≡C−C≡C−H) on the singlet surface; this structure is bound by about 589 kJmol^{-1} with respect to the separated reactants. The unimolecular decomposition of the $D_{\infty h}$ symmetric singlet triacetylene molecule has no exit barrier and hence is expected to be a simple bond rupture process via a loose exit transition state; this in turn should be reflected in a CM translational energy distribution peaking at or close to zero translational energy. Also, this molecule represents a symmetric structure that can only be excited to B-like rotations. Consequently, the hydrogen atom can be emitted with equal probability into $\theta°$ and $\pi-\theta°$; this results always in a forward−backward symmetric CM angular distribution. When we compare the structure of the decomposing triacetylene intermediate with those of the reactants, we realize that the triacetylene molecule (H−C≡C−C≡C−C≡C−H) is formally extended by one acetylene unit compared to the diacetylene reactant (H−C≡C−C≡C−H). In the related gas-phase reaction of singlet dicarbon with acetylene (H−C≡C−H), which forms a diacetylene (H−C≡C−C≡C−H) intermediate, the reaction proceeded barrierless via an initial addition of dicarbon to the carbon−carbon triple bond followed by isomerization(s) of the initial adduct to ultimately yield the linear diacetylene intermediate (H−C≡C−C≡C−H).[25,26] The electronic structure calculations indicate that dicarbon adds without entrance barrier to the carbon−carbon triple bond either end on or side on, yielding two cyclic C_6H_2 intermediates s1 and s2, respectively. We did not locate any reaction pathway for an insertion of the dicarbon unit into the carbon−hydrogen bond of the diacetylene molecule. Both structures can isomerize easily through a barrier located 62.1 kJmol^{-1} above s1. As suggested from the experimental data, the intermediates rearrange yielding ultimately the linear triacetylene intermediate s3. The latter

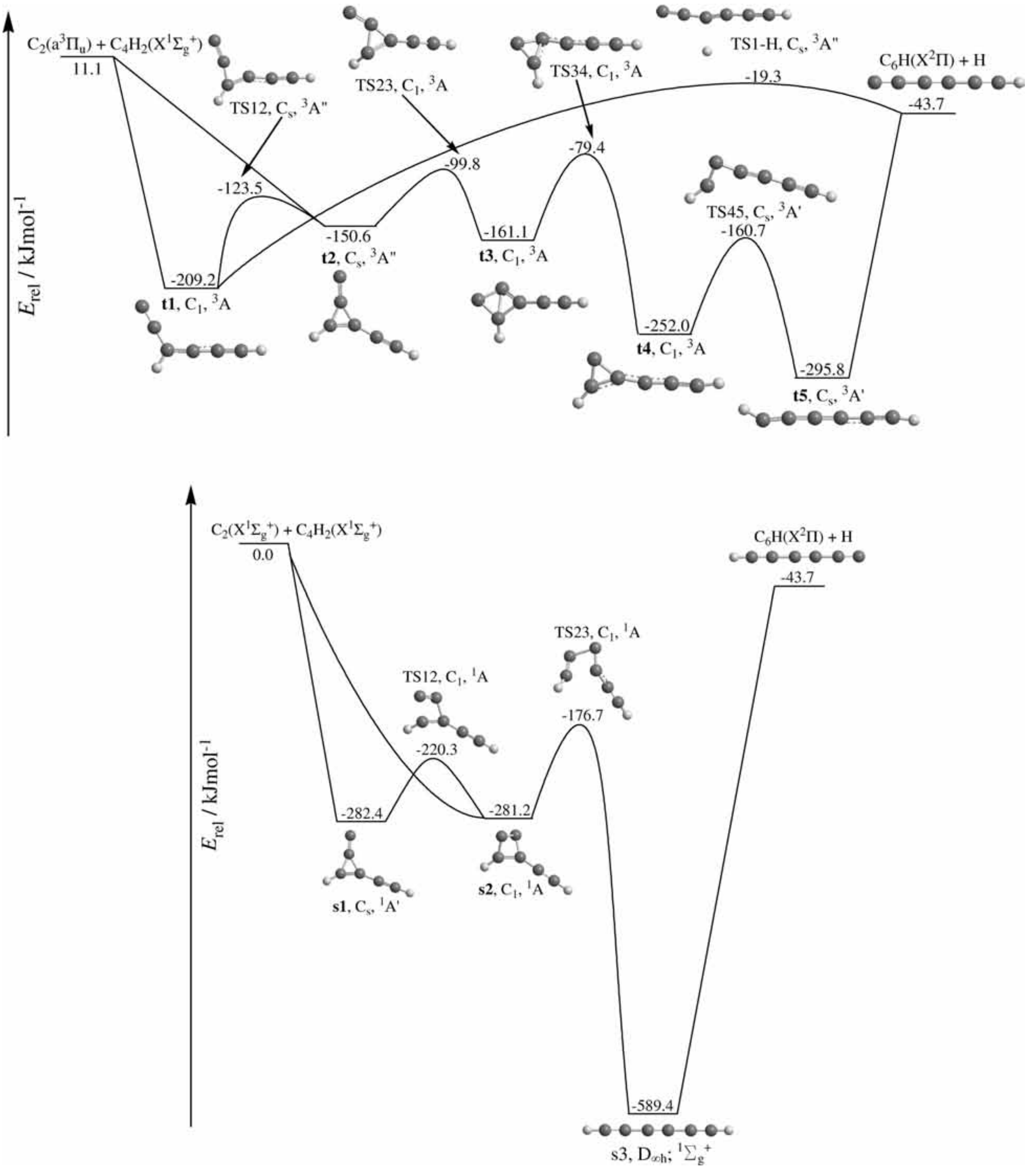

Figure 4. (a) Calculated triplet C_6H_2 potential-energy surface. Point groups and electronic wave functions are also indicated. Uncertainties of the computed energies are 5 kJmol^{-1}. (b) Calculated singlet C_6H_2 potential-energy surface. Point groups and electronic wave functions are also indicated. Uncertainties of the computed energies are 5 kJmol^{-1}.

decomposed without exit barrier to form the 1,3,5-hexatriynyl radical plus atomic hydrogen. It should be noted that the triacetylene molecule was observed in fuel-rich hydrocarbon flames.[52] However, this reaction mechanism alone cannot explain the broad plateau of the CM translational energy distribution (Figure 3). Recall that a reaction on the singlet surface alone is expected to provide a translational energy distribution peaking at or close to zero translational energy. This plateau-like feature is similar to those patterns observed in the related reactions of dicarbon with acetylene (C_2H_2)[25,26] and of dicarbon with ethylene (C_2H_4).[53] Combined with electronic structure calculations, this was interpreted in terms of the involvement of two distinct reaction channels from singlet dicarbon ($X^1\Sigma_g$) and triplet dicarbon ($a^3\Pi_u$). In those previous studies, the corresponding singlet C_4H_2 and singlet C_4H_4 intermediates were found to decompose without exit barrier and showed simple carbon−hydrogen bond rupture processes. This channel alone would result in a $P(E_T)$ peaking at or very close to zero translational energy. However, on the triplet manifolds, the C_4H_2 and C_4H_4 intermediates lost their hydrogen atoms via tight exit transition states; these patterns would be reflected in $P(E_T)$s peaking away from zero translational energy. An involvement of the singlet *and* triplet surfaces is suggested to lead to a combination of both features and hence to broad plateau-like distribution maxima.

This pattern has been derived for the dicarbon−diacetylene system as well (Figure 3). Our electronic structure calculations confirm the tight nature of the exit transition state on the triplet surface. Here, the dicarbon molecule was found to add either to one or to two carbon atoms of the diacetylene molecule forming intermediates t1 and t2, respectively. The collision complex t2 could isomerize via two intermediates t3 and t4 to form triplet triacetylene (t5). Because the experimental data suggest an exit barrier on the triplet surface, intermediate t1 is likely identified as the decomposing intermediate; the latter decomposed via a tight exit transition state located 24.4 kJmol^{-1} above the separated products. A barrierless fragmentation of t5 alone cannot account form the derived translational energy distributions. Therefore, we can suggest that, on the triplet surface, the reaction also proceeds via complex formation; however, it involves the decomposition of a triplet C_6H_2 intermediate via a tight exit transition state.

6. Conclusions

We have studied the crossed molecular beams reaction of dicarbon molecules, $C_2(X^1\Sigma_g{}^+/a^3\Pi_u)$, with diacetylene, $C_4H_2(X^1\Sigma_g{}^+)$, under single collision conditions. On the basis of the CM translation energy distribution and a comparison of the experimental reaction energy with the computed one, the formation of the 1,3,5-hexatriynyl radical plus atomic hydrogen was elucidated. On the singlet and triplet surfaces, the underlying chemical dynamics were found to be indirect, involved C_6H_2 intermediates, and were dictated by an initial addition of the dicarbon molecule to the carbon−carbon triple bond of diacetylene. The initial collision complex could isomerize. On the singlet surface, the resulting linear triacetylene molecule ($C_6H_2(X^1\Sigma_g{}^+)$) decomposed without exit barrier to form the linear 1,3,5-hexatriynyl radical. On the triplet surface, the dynamics indicated a tight exit transition state involved in the fragmentation of a triplet C_6H_2 intermediate to yield the 1,3,5-hexatriynyl radical ($C_6H(X^2\Pi)$) plus atomic hydrogen. The explicit identification of the 1,3,5-hexatriynyl radical under single-collision conditions suggests that the neutral−neutral reaction of dicarbon with diacetylene can lead to the formation of 1,3,5-hexatriynyl radicals in the interstellar medium and in the hydrocarbon-rich atmospheres of planets and their moons such as Saturn's satellite Titan, where both singlet dicarbon and diacetylene reactants are supposed to exist. Note that the reaction of the related ethynyl and 1,3-butadiynyl radicals with acetylene lead to the formation of diacetylene (reaction (3))[54] and triacetylene (reaction (4))[55] respectively under single collision conditions. Therefore, it is interesting to investigate in future studies to what extent the reaction of the 1,3,5-hexatriynyl radical ($C_6H(X^2\Pi)$) with acetylene can form tetraacetylene (HCCCCCCCCH) in Titan's atmosphere (reaction(5)).

$$C_2H(X^2\Sigma^+) + C_2H_2(X^1\Sigma_g^+) \rightarrow C_4H_2(X^1\Sigma_g^+) + H(^2S_{1/2}) \qquad (3)$$

$$C_4H(X^2\Sigma^+) + C_2H_2(X^1\Sigma_g^+) \rightarrow C_6H_2(X^1\Sigma_g^+) + H(^2S_{1/2}) \qquad (4)$$

$$C_6H(X^2\,\Pi) + C_2H_2(X^1\Sigma_g^+) \rightarrow C_8H_2(X^1\Sigma_g^+) + H(^2S_{1/2}) \qquad (5)$$

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