A crossed molecular beam study on the formation of hexenediynyl radicals ($H_2CCCCCCH$; C_6H_3 (X^2A')) *via* reactions of tricarbon molecules, $C_3(X^1\Sigma_g^+)$, with allene (H_2CCCH_2; X^1A_1) and methylacetylene (CH_3CCH; X^1A_1)

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Crossed molecular beams experiments have been utilized to investigate the reaction dynamics between two closed shell species, *i.e.* the reactions of tricarbon molecules, $C_3(X^1\Sigma_g^+)$, with allene (H_2CCCH_2; X^1A_1), and with methylacetylene (CH_3CCH; X^1A_1). Our investigations indicated that both these reactions featured characteristic threshold energies of 40–50 kJ mol^{-1}. The reaction dynamics are indirect and suggested the reactions proceeded *via* an initial addition of the tricarbon molecule to the unsaturated hydrocarbon molecules forming initially cyclic reaction intermediates of the generic formula C_6H_4. The cyclic intermediates isomerize to yield eventually the acyclic isomers $CH_3CCCCCH$ (methylacetylene reaction) and $H_2CCCCCCH_2$ (allene reaction). Both structures decompose *via* atomic hydrogen elimination to form the 1-hexene-3,4-diynyl-2 radical (C_6H_3; $H_2CCCCCCH$). Future flame studies utilizing the Advanced Light Source should therefore investigate the existence of 1-hexene-3,4-diynyl-2 radicals in high temperature methylacetylene and allene flames. Since the corresponding C_3H_3, C_4H_3, and C_5H_3 radicals have been identified *via* their ionization potentials in combustion flames, the existence of the C_6H_3 isomer 1-hexene-3,4-diynyl-2 can be predicted as well.

1. Introduction

During the last decade, the investigation of the synthetic routes and chemical reactivity of resonantly stabilized free radicals (RSFRs) have received particular attention due to their role in the formation of polycyclic aromatic hydrocarbons (PAHs) in combustion flames.[1] These molecules are also believed to play a critical role in the formation of soot during the combustion of hydrocarbon fuels under oxygen-poor conditions.[2–4] In RSFRs, the unpaired electron is delocalized over at least two carbon atoms. This causes a number of resonant structures of similar importance.[5] 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.[4–8] Such weakly bound addition complexes are not easily stabilized by collisions at high temperature. Therefore, RSFRs can reach high concentration under combustion conditions making them important reaction intermediates to form complex, often polycyclic aromatic hydrocarbons in flames.[9]

Crossed molecular beam experiments[10–12] have played an important role in accessing the relevant regions of the potential energy surfaces (PESs) of RSFRs experimentally and in elucidating possible reaction pathways how resonantly stabilized free radicals might be formed in combustion flames.[13] This is of particular importance with respect to the formation routes to propargyl (C_3H_3) *via* reaction of atomic carbon with ethylene[14] and singlet methylene with acetylene,[15] the *n*- and *i*-C_4H_3 isomers (HCCHCCH and H_2CCCCH) through bimolecular reactions of dicarbon with ethylene and carbon with allene/methylacetylene,[16,17] and of the *n*- and *i*-C_5H_3 radicals involving bimolecular collisions of dicarbon molecules with allene and methylacetylene.[18] However, little data are available on the next member of this series, *i.e.* the hexenediynyl radical (C_6H_3), although Goeres *et al.*[19] as well as Frenklach *et al.* outlined its potential role to form PAHs in combustion systems.[20] Hausmann and coworkers' flame study remains the only experimental identification of an acyclic C_6H_3 radical to date. Here, the 1-hexene-3,4-diynyl-2 isomer, $H_2CCCCCCH$, was identified *via* scavenging of the radical product as a methylthioether in combustion flames.[21] But how can C_6H_3 radicals be 'made' in the laboratory under well-defined conditions? Based on the crossed beams studies of carbon atoms and dicarbon molecules with ethylene (C_2H_4) and methylacetylene/allene (C_3H_4) and the identification of the carbon/dicarbon *versus* atomic hydrogen exchange pathway to C_3H_3, C_4H_3, and C_5H_3 radicals, we may expect that the reaction of tricarbon molecules, $C_3(X^1\Sigma_g^+)$, with allene and methylacetylene could yield the next higher member in this series: C_6H_3. Previous experimental investigations of this reaction were limited to kinetic studies proposing very small

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rate constants in the range of 3–5 × 10^{-13} cm^3 s^{-1} at room temperature.[22] The authors interpreted the data in terms of an 'activation energy' in the entrance channel; reaction products could not be identified. In the present paper, we elucidate on the chemical dynamics of the reactions of the tricarbon molecule, $C_3(X^1\Sigma_g^+)$, with allene and methylacetylene to form C_6H_3 isomers on the singlet C_6H_4 potential energy surface *via* a tricarbon *versus* atomic hydrogen exchange pathway under single collision conditions.

2. Experimental

The experiments were conducted under single collision conditions in a crossed molecular beams machine at The University of Hawaii.[17,18] Briefly, the main chamber is evacuated by three turbo molecular pumps plus cryo cooling to about 4 × 10^{-9} Torr. Two source chambers are placed inside the main chamber so that the reactant beams cross perpendicularly. Pulsed tricarbon beams were produced in the primary source by laser ablation of graphite at 266 nm[23] (8–20 mJ per pulse; Table 1). The ablated species were seeded in neat carrier gas (helium, 99.9999%, Airgas) released by a Proch–Trickl pulsed valve. A four-slot chopper wheel mounted between the skimmer and the interaction region selected a segment out of the seeded beam.[24] This segment of the tricarbon beam crossed a pulsed methylacetylene or allene beam (CH_3CCH, 99.8%, Linde; H_2CCCH_2, 99.5%, Aldrich) released by a second pulsed valve under a well-defined collision energy in the interaction region of the scattering chamber. The experimental conditions (delay times, photodiode-laser and photodiode-pulsed valve; backing pressure, laser power, diameter of the laser focus) were optimized so that atomic carbon, dicarbon, and tricarbon only are present in the ablation beam.[23] No higher carbon clusters are present in the beam. To pin down the position of the hydrogen loss in the tricarbon–methylacetylene system, a crossed beams reaction was also carried out with partially deuterated methylacetylene (CD_3CCH, 99 + % D enrichment, CDN). The reactively scattered species are 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. The detector can be rotated within the plane defined by the primary and the secondary reactant beams to allow taking angular resolved TOF spectra. By integrating the TOF spectra at distinct laboratory angles, we obtain the laboratory angular distribution, *i.e.* the integrated signal intensity of an ion of distinct m/z *versus* the laboratory angle. 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.[25] 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 $P(E_T)$. Best fits of the TOF and laboratory angular distributions were achieved by refining the $T(\theta)$ parameters and the points of the $P(E_T)$. Since the reactions of tricarbon molecules with unsaturated hydrocarbons have characteristic threshold energies, E_o,[26] we also implemented the energy dependence of the cross section, σ, within the line-of-center model *via* eqn (1) with the translational energy E_T for $E_T \geq E_o$ in the fitting routine.[27]

$$\sigma \sim [1 - E_o/E_T] \quad (1)$$

Table 1 Peak velocities (v_p), speed ratios (S) and the center-of-mass angles (Θ_{CM}), together with the nominal collision energies (E_c) of the tricarbon—allene and tricarbon—methylacetylene systems

Beam	v_p/ms^{-1}	S	E_c/kJ mol^{-1}	Θ_{CM}
$CH_3CCH(X^1A_1)$	840 ± 5	9.0 ± 1.0	—	—
$C_3(X^1\Sigma_g^+)$/He	2669 ± 102	2.7 ± 0.3	74.2 ± 5.1	19.3 ± 0.7
$C_3(X^1\Sigma_g^+)$/He	3330 ± 125	1.9 ± 0.1	111.7 ± 8.1	15.7 ± 0.6
$CD_3CCH(X^1A_1)$	830 ± 5	8.8 ± 1.0	—	—
$C_3(X^1\Sigma_g^+)$/He	3330 ± 125	1.9 ± 0.1	115.4 ± 8.3	16.6 ± 0.6
$H_2CCCH_2(X^1A_1)$	840 ± 5	9.0 ± 1.0	—	—
$C_3(X^1\Sigma_g^+)$/He	2843 ± 101	3.1 ± 0.3	83.3 ± 5.5	18.2 ± 0.6
$C_3(X^1\Sigma_g^+)$/He	3504 ± 151	2.3 ± 0.1	123.0 ± 10.2	14.9 ± 0.7

3. Results

For both the tricarbon–allene and the tricarbon–methylacetylene systems, we observed reactive scattering signals at m/z = 75 ($C_6H_3^+$), 74 ($C_6H_2^+$), 73 (C_6H^+), and 72 (C_6^+). The TOF spectra recorded at all mass-to-charge ratios between 75 and 72 exhibited identical patterns. This finding indicates that the C_6H_3 neutral undergoes dissociative ionization in the electron impact ionizer. These indistinguishable patterns of the lower mass-to-charge ratios further necessitates that in this range of masses only the tricarbon *versus* atomic hydrogen exchange pathway is open to form C_6H_3 isomer(s) (m/z = 75) plus atomic hydrogen. We would like to mention that the signal at m/z = 74 is almost twice as strong as the ion counts at 75. Selected time-of-flight spectra (TOF) for various scattering angles recorded at the most intense ion at m/z = 74 are depicted in Fig. 1. Signals at mass-to-charge ratios lower than 72 were also examined. Here, time-of-flight spectra taken between m/z = 63 ($C_5H_3^+$) and 60 (C_5^+) had to be fit with two contributions from the reaction of tricarbon with methylacetylene/allene (dissociative ionization of C_6H_3 in the electron impact ionizer to fragments holding m/z = 63–60) and from the reaction of dicarbon with allene/methylacetylene leading to the formation of C_5H_3 isomers.[16,17] Finally, the carbon atoms in the beam can also react with allene/methylacetylene to form atomic hydrogen and the 1-buten-3-yn-2-yl radical (i-$C_4H_3(X^2A')$) giving rise to its parent at $C_4H_3^+$ and their fragments at, for instance, $C_4H_2^+$ (m/z = 50), C_4H^+ (m/z = 49), and C_4^+ (m/z = 48).[16,17] Based on these findings, the analysis of the TOF spectra involves the existence of a tricarbon *versus* atomic hydrogen exchange pathway leading in both the tricarbon–methylacetylene and tricarbon–allene reactions to the formation of C_6H_3 isomer(s). The TOF spectra can now be integrated to obtain the laboratory angular distributions (LAB) of the C_6H_3 product(s) at the most intense m/z value of 74 ($C_6H_2^+$) (Fig. 2). Note that for all the systems investigated, the LAB distributions are very narrow and extend only by about 20° in the scattering plane defined by both beams.

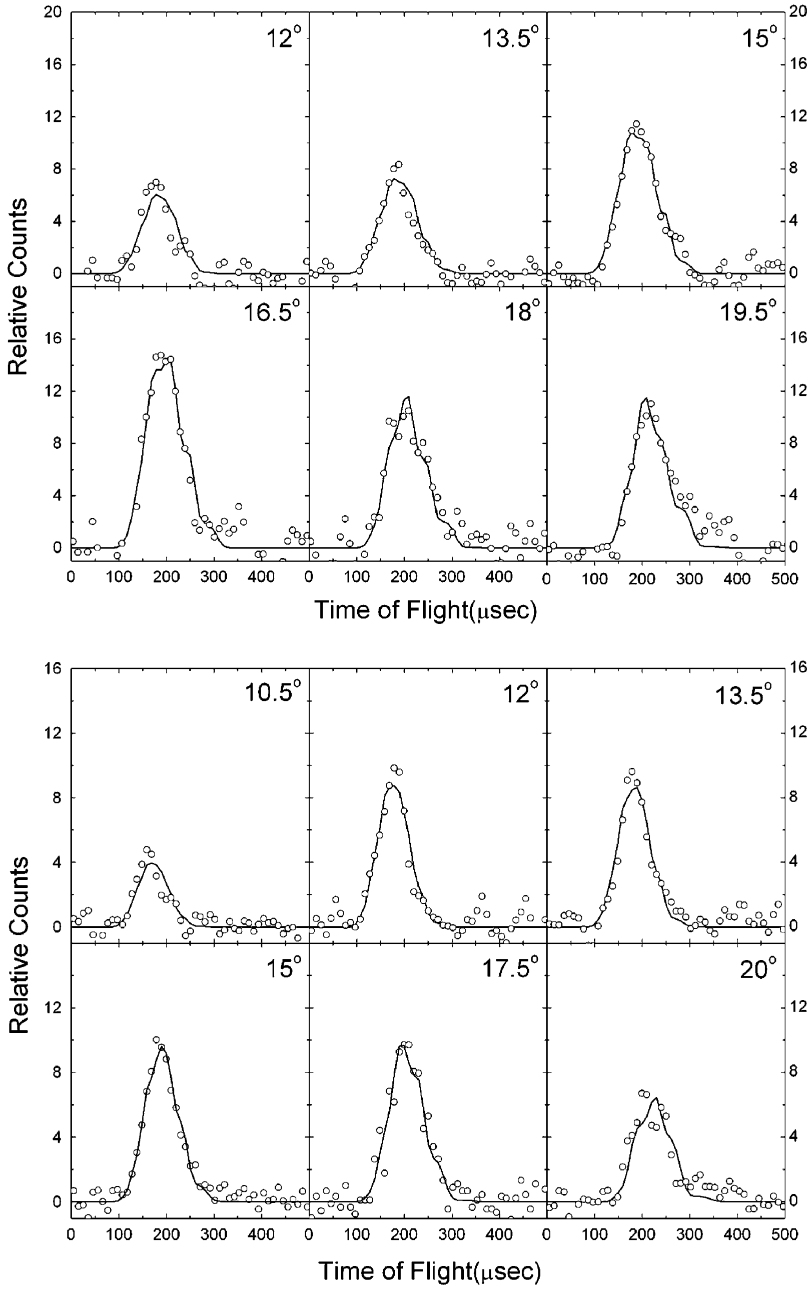


Fig. 1 Selected time-of-flight data for m/z = 74 ($C_6H_2^+$) recorded at collision energies of 111.7 (tricarbon–methylacetylene) and 123.0 kJ mol^{-1} (tricarbon–allene) at various laboratory angles. The circles indicate the experimental data, the solid lines the calculated fit.

In case of the tricarbon–methylacetylene system, we also carried out the reaction of tricarbon with partially deuterated methylacetylene, CD_3CCH, and recorded TOF spectra at a laboratory angle of 15°. The goal of this experiment was to elucidate the position of the hydrogen atom loss in the methylacetylene system, *i.e.* from the acetylenic and/or methyl group. In the case of CD_3CCH, a hydrogen and deuterium loss channel would lead to signals at m/z = 78 ($C_6D_3^+$) and m/z = 77 ($C_6D_2H^+$), respectively. Most importantly, the neutral C_6D_3 product cannot undergo dissociative ionization to m/z = 77, but to m/z = 76 ($C_6D_2^+$). Therefore, the signal at m/z = 78 and/or 77 would directly identify to what extent the reaction intermediate loses a hydrogen and/or deuterium atom. We recognize that based on statistical arguments, there is a three times higher chance of a deuterium atom emission *versus* the hydrogen loss pathway. Therefore, the signal was accumulated ten times longer at m/z = 78 than at m/z = 77. As a matter of fact, in our crossed beams experiment, we only observed a signal at m/z = 77 ($C_6D_2H^+$), but not at m/z = 78 ($C_6D_3^+$) (Fig. 3). Therefore, the deuterium atom is emitted from the D3-methyl group. This finding suggests further that in the case of the tricarbon–methylacetylene reaction, the atomic hydrogen loss originates from the methyl group.

We would like to address now the derived center-of-mass translational energy distributions, $P(E_T)$ (Fig. 4). First, we can obtain information on the maximum translation energy of the

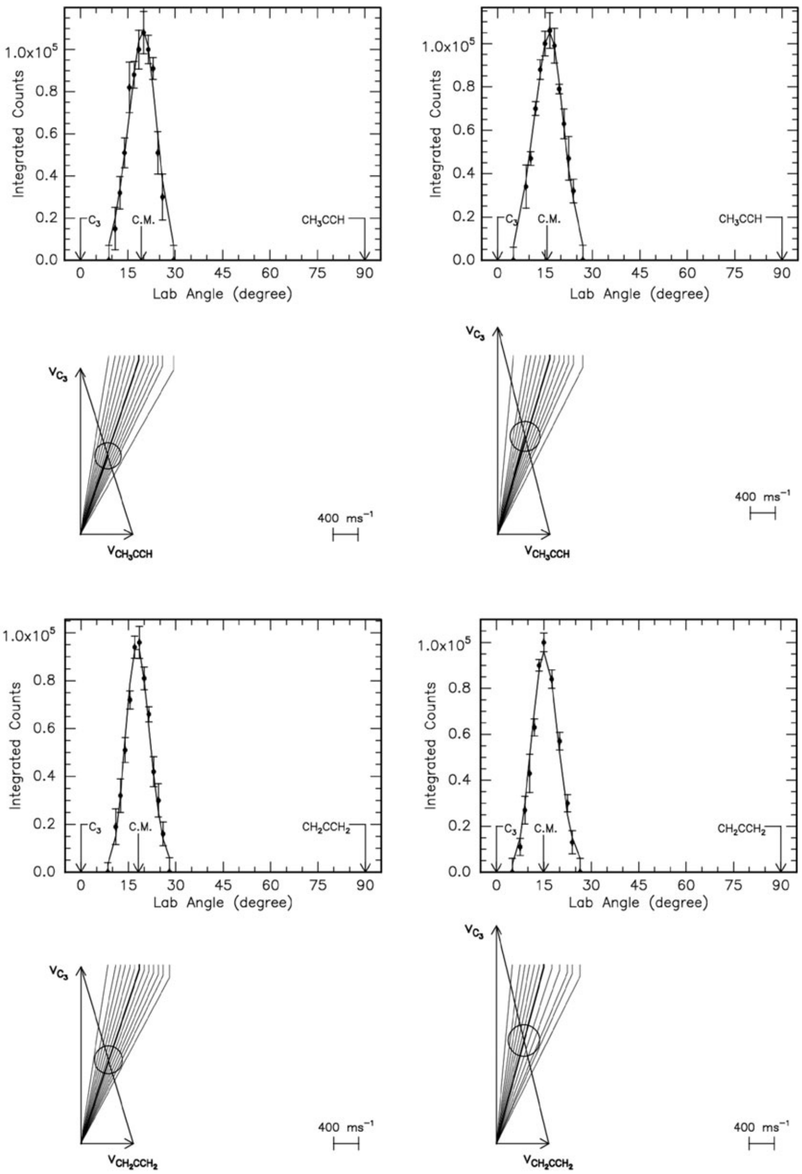


Fig. 2 Newton diagrams for the reaction of tricarbon molecules with methylacetylene (upper) and allene (lower) at collision energies of 74.2 (top left), 111.7 (top right), 83.3 (bottom left), and 123.0 kJ mol^{-1} (bottom right) together with the corresponding laboratory angular distribution of the C_6H_3 radical(s) recorded at $m/z = 74$. Circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions.

reaction products in the center-of-mass frame. For both the methylacetylene and allene reactants, best fits of the data were achieved with a single channel fit and translational energy distributions extending up to 123–143 kJ mol^{-1} (74.2 and 83.3 kJ mol^{-1} collision energy) and 166–180 kJ mol^{-1} (123.0 and 111.7 kJ mol^{-1} collision energy). As a mater of fact, we can utilize identical $P(E_T)$s to fit the allene and methylacetylene data at lower (Fig. 4a) and higher (Fig. 4b) collision energies. Recall that the maximum energy portrays the sum of the absolute of the reaction exoergicity and the collision energy. Therefore, by subtracting the latter, we can derive the experimentally determined reaction exoergicity to form the C_6H_3 isomer(s) plus atomic hydrogen to be in the range of 50–70 kJ mol^{-1}. Also, the $P(E_T)$s peaks away from zero translational energy between 20 and 90 kJ mol^{-1}. Generally speaking, as the collision energy increases in each system, the peak shifts to larger translational energies. It should be stressed that in order to get an acceptable fit of the data, it was important to include the energy-dependence of the reactive cross section *via* eqn (1). Here, we varied the entrance barrier between 10 and 100 kJ mol^{-1}. Best fits were extracted for entrance barriers between 40 and 50 kJ mol^{-1}.

The very narrow range of the reactive scattering signal as evident from the LAB distribution combined with the limited speed ratio of the tricarbon beam makes it difficult to extract quantitative information from the center-of-mass angular distributions, $T(\theta)$. Recall that to obtain a fast supersonic beam and a high speed ratio simultaneously, various techniques can be applied. These are, for instance, in the photodissociation of a precursor molecule such as hydrogen iodide

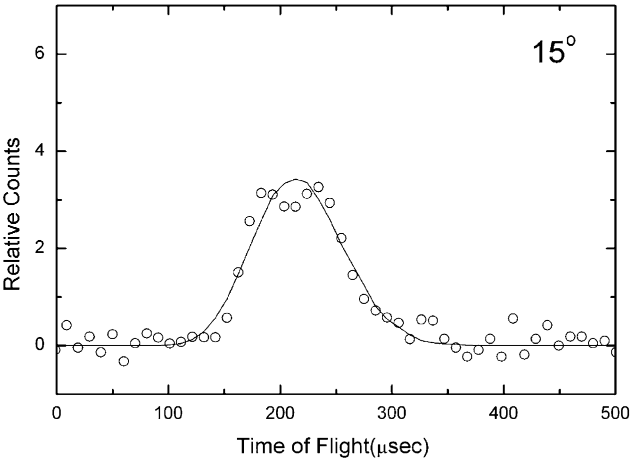


Fig. 3 Time-of-flight spectrum of m/z = 77 ($C_6D_2H^+$) recorded at collision energies of 115.4 kJ mol^{-1} (tricarbon–D3–methylacetylene). The circles indicate the experimental data, the solid lines the calculated fit obtained with identical center-of-mass functions as for the tricarbon–methylacetylene reaction.

to obtain a high-velocity and narrow velocity spread of a hydrogen atom beam. Secondly, pulsed, pyrolytic sources can give fast beams of organic radicals such as allyl and phenyl of up to 3300 ms^{-1} with speed ratios in the range of 8–10.[28] To obtain fast tricarbon beams, we have to utilize laser ablation of graphite and must select the early part of the ablation beam in which the tricarbon molecules are poorly helium-seeded. This results in only limited speed ratios (Table 1). Unfortunately, there is currently no alternative to produce high velocity (> 3300 ms^{-1}) tricarbon molecules except pulsed laser ablation. Based on the limited speed ratio, the fluctuations of the tricarbon beam velocity, and the narrow range of the reactive scattering signal, we cannot draw definite conclusions if the $T(\theta)$ is forward or backward scattered with respect to the tricarbon beam. We would like to stress that it is imperative to have intensity over the complete angular range from 0° to 180° to fit our data; this suggests that the reactions are indirect and involve C_6H_4 intermediate(s). However, we can vary the intensity ratios at the poles, $I(0°)/I(180°)$, from 2.5 to 0.5 without having a significant effect on the fit.

4. Discussion

To address the reaction dynamics involved, we would like to comment first on the energetics of the title reactions. Based on the center-of-mass translational energy distributions, the reactions of tricarbon with both allene and methylacetylene are found to be exoergic by 50 kJ mol^{-1} to 70 kJ mol^{-1}. We expect that the reaction of tricarbon with allene is more exoergic by 6 kJ mol^{-1} as compared to the tricarbon–methylacetylene reaction. However, this energy difference falls within the error limits of the data. We can compare now the experimentally derived energetics with those obtained for distinct C_6H_3 isomers (Fig. 5). To calculate relative energies of the C_6H_3 + H products with respect to the C_3 + C_3H_4 reactants, we used the G2M(RCC,MP2) computational scheme,[29] which approximates coupled cluster RCCSD(T) calculations[30] with the large 6-311 + G(3df,2p) basis set with geometries optimized at the hybrid density functional B3LYP/6-311G(d,p) level.[31,32] The GAUSSIAN 98[33] and MOLPRO 2002[34] program packages were employed for the calculations. The G2M(RCC,MP2)//B3LYP/6-311G(d,p) + ZPE[B3LYP/6-311G(d,p)] calculational approach is expected to provide accuracies of 5–10 kJ mol^{-1} for relative energies. Here, the formation of atomic hydrogen plus the C_{2v} symmetric 1-hexene-3,5-diynyl-2 radical (**p1**; $H_2CCCCCCH$; X^2A') was computed to be exoergic by 53 kJ mol^{-1} (Fig. 5); this number agrees nicely with the experimentally derived energetics. The latter are—compared to the computed data—slightly higher. This could be either the result of the limited speed ratio of our beam and/or the existence of vibrationally excited tricarbon molecules in the ablation beam.[35] Note that the quality of the fits is very sensitive to the low energy cut-off of the center-of-mass translational energy distributions; reaction energies of −35 kJ mol^{-1} (**p2**) and −10 kJ mol^{-1} (**p3**) (C_3 − CH_3CCH) and −41 kJ mol^{-1} and −16 kJ mol^{-1} (C_3 − H_2CCCH_2) cannot fit the data satisfactorily. In addition, from the energetic viewpoint, the fourth isomer **p4** cannot be formed at lower collision energies since the reaction endoergicity cannot be compensated by the collision energy (Table 1). Therefore we can conclude that the 1-hexene-3,5-diynyl-2 radical is likely to be

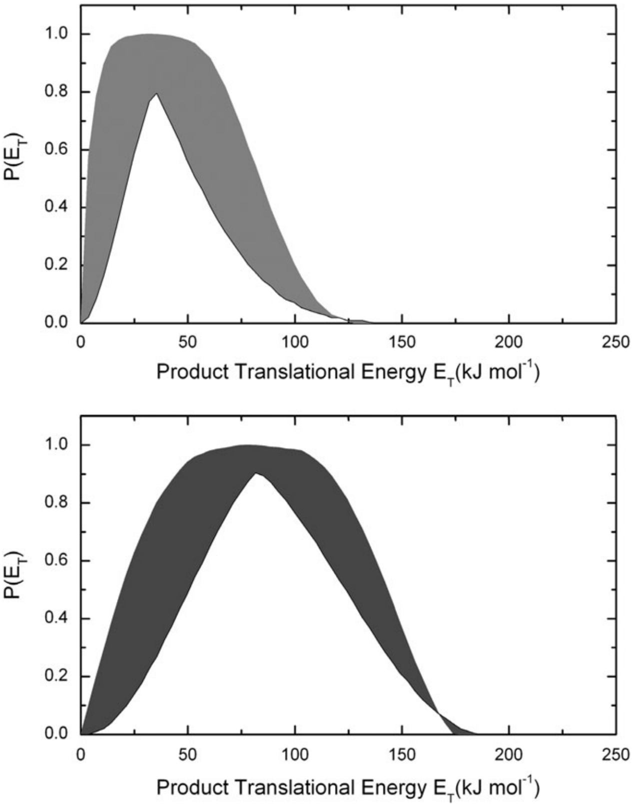
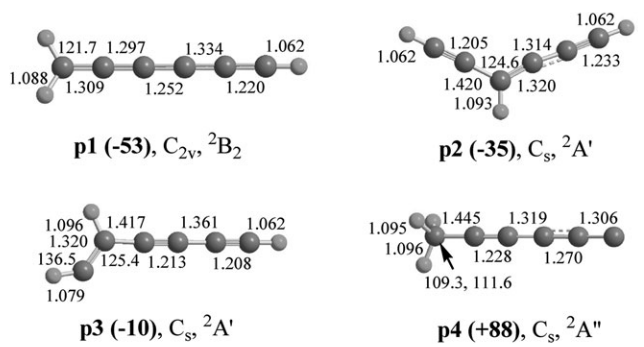


Fig. 4 Center-of-mass translational energy flux distributions for reaction of tricarbon with methylacetylene and allene to form C_6H_3 radical(s) and atomic hydrogen. At both lower (74.2 and 83.3 kJ mol^{-1}; upper) and higher (111.7 and 123.0 kJ mol^{-1}; lower) collision energies, data for the allene and methylacetylene reactants could be fit with essentially identical center-of-mass translational energy flux distributions.



p1 (-53), C_{2v}, $^2B_2$ **p2 (-35)**, C_s, $^2A'$

p3 (-10), C_s, $^2A'$ **p4 (+88)**, C_s, $^2A''$

Fig. 5 Structures of various doublet C_6H_3 isomers. The reaction energies are given in kJ mol^{-1} relative to the tricarbon and methylacetylene reactants. The energetics in the tricarbon–allene system are more exoergic by 6 kJ mol^{-1}. Bond distances are given in Å, bond angles in °. Point groups and the symmetry of the electronic ground state are also given.

the dominating reaction product; based on the $P(E_T)$s alone, minor amounts of **p2** and **p3** cannot be excluded.

We attempt now to resolve the underlying reaction dynamics to form the 1-hexene-3,5-diynyl-2 radical in reactions of tricarbon with allene and methylacetylene. Here, we first associate the structure of the methylacetylene and allene reactants with the reaction product (Fig. 5) and then suggest feasible reaction intermediates on the singlet surface. Note that even we could not extract quantitative information from the center-of-mass angular distributions, the data suggest that the reactions must be indirect *via* C_6H_4 reaction intermediates. The 1-hexene-3,5-diynyl-2 radical reaction product ($H_2CCCCCCH$) has no methyl group. To correlate this structure to the methylacetylene reactant *via* C_6H_4 reaction intermediate(s), it is likely that the reversed reaction of a hydrogen atom addition to the radical center at the CH_2 group of the $H_2CCCCCCH$ product forms a $CH_3CCCCCH$ intermediate. On the other hand, if the hydrogen atom adds to the acetylenic carbon atom at the terminal CH group, we would expect the formation of a $H_2CCCCCCH_2$ structure, *i.e.* hexapentaene. Further, we have to connect the $CH_3CCCCCH$ and $H_2CCCCCCH_2$ intermediates with the tricarbon plus methylacetylene and allene reactants, respectively. In a similar manner to the reaction of methylacetylene and allene with singlet dicarbon,[17] the carbon chains of methylacetylene and allene are enlarged by three carbon atoms. Since it is not feasible for the tricarbon reactant to 'insert' in a single step into the carbon–carbon triple (methylacetylene) and carbon–carbon double bonds (allene), we propose that the tricarbon molecule adds to the triple and double bonds of the methylacetylene and allene reactants, respectively, to form initially cyclic C_6H_4 collision complex(es) on the singlet surface. Note that our experiments predict barriers in the order of 40 and 50 kJ mol^{-1}. These predicted mechanisms are similar to the reaction pathway of tricarbon plus ethylene as investigated computationally.[26] Here, tricarbon can either add side-on or end-on to the carbon–carbon double bond of ethylene forming a five- or three-membered ring intermediate, respectively. In the ethylene system, both intermediates were suggested to isomerize to yield eventually an acyclic pentatetraene intermediate ($H_2CCCCCH_2$). In our present study, we suggest that the cyclic intermediates formed initially *via* addition of tricarbon to the unsaturated bonds undergo isomerization forming eventually acyclic $CH_3CCCCCH$ and $H_2CCCCCCH_2$ structures. Recall that we also carried out a reaction of tricarbon with partially deuterated methylacetylene, CD_3CCH. The proposed reaction mechanisms in the tricarbon–methylacetylene system is expected to yield a $CD_3CCCCCH$ intermediate which would then lose a deuterium atom to give $D_2CCCCCCH$. An atomic hydrogen loss from $CD_3CCCCCH$ can only result in the synthesis of CD_3CCCCC (**p4**). Based on energetical arguments, **p4** was excluded as a reaction product. Further, the experiments with CD_3CCH only prove the existence of the tricarbon *versus* deuterium pathway and could eliminate the importance of the atomic hydrogen ejection. Consequently, the tricarbon–CD_3CCH experiment nicely verifies the proposed reaction mechanism of a tricarbon molecule adding to the carbon–carbon triple bond, followed by isomerization(s) of the initially cyclic intermediate to form an acyclic $CH_3CCCCCH$ structure; this isomer can then lose a hydrogen atom from the methyl group leading to the 1-hexene-3,5-diynyl-2 radical. Finally, we would like to address the experimentally found off-zero peaking of the center-of-mass translational energy distributions. In the most favorable case, the unimolecular decomposition of a reaction intermediate on the singlet surface *via* a simple carbon–hydrogen bond rupture process is expected to hold a lose exit transitions state.[12] This was clearly not observed experimentally. As a matter of fact, the average fraction of energy channeling into the translational degrees of freedom of the reactants can be calculated to be about 27%–43% (lower collision energies) and 41–53%. This order of magnitude suggests that the reaction goes—at least at higher collision energies—through a relatively short-lived intermediate. These dynamical effects can result in the experimentally observed off-zero peaking of the center-of-mass translational energy distributions. The potentially short life-time of the $CH_3CCCCCH$ and $H_2CCCCCCH_2$ intermediates is in line with the large collision energies of up to 123 kJ mol^{-1} in the present experiments. Therefore, the intermediates likely decompose *via* atomic hydrogen loss to the $H_2CCCCCCH$ isomer before $CH_3CCCCCH$ and $H_2CCCCCCH_2$ can undergo hydrogen shifts. Considering the molecular structures of the C_6H_3 isomers (Fig. 5), these hydrogen shifts are required to form **p2** and **p3**. Based on the energetics, these isomers were not identified as the major reaction products. Therefore, we may conclude that indeed a hydrogen loss from the $CH_3CCCCCH$ and $H_2CCCCCCH_2$ intermediates is preferred in contrast to hydrogen atom migration(s) prior to the atomic hydrogen loss. We can also exclude here the formation of six-membered ring C_6H_3 isomers, such as 1,2,3-, 1,2,4-, and 1,3,5-tridehydrobenzenes with relative energies of −67, −64, −14 kJ mol^{-1}, respectively, on the basis of the short lifetime of intermediates and the fact that no hydrogen atom loss was observed in the C_3 + CD_3CCH reaction. Apparently, rearrangements of $CH_3CCCCCH$ and $H_2CCCCCCH_2$ to six-membered ring C_6H_4 benzyne isomers accompanied with hydrogen atom migrations are too slow to play a role in the reaction under our experimental conditions.

5. Summary

We have investigated the reaction of tricarbon molecules, $C_3(X^1\Sigma_g^+)$, with allene (H_2CCCH_2; X^1A_1), methylacetylene (CH_3CCH; X^1A_1), and D3-methylacetylene (CD_3CCH; X^1A_1) at collision energies between 74.2 and 123.0 kJ mol^{-1} in a crossed molecular beams setup. Our studies suggest that both reactions feature characteristic threshold energies, E_o, of 40–50 kJ mol^{-1} (eqn (1)). The reaction dynamics are indirect and suggested to proceed *via* initial addition of the tricarbon molecule to the unsaturated hydrocarbon forming initially cyclic reaction intermediates of the generic formula C_6H_4. The cyclic intermediates isomerize to yield eventually the acyclic isomers $CH_3CCCCCH$ (methylacetylene reaction) and $H_2CCCCCCH_2$ (allene reaction). The life time of these intermediates is proposed to be rather short; both structures decompose *via* atomic hydrogen elimination to form the 1-hexene-3,4-diynyl-2 radical (C_6H_3; $H_2CCCCCCH$). Considering the limited speed ratio of the tricarbon beam, the experimental reaction exoergicities of 50–70 kJ mol^{-1} agree reasonably well with the computed data of 53 kJ mol^{-1}. Note that the experimentally derived threshold energies could imply the existence of an entrance barrier in the initial addition step; alternatively, it could indicate the presence of an isomerization barrier on the singlet C_6H_4 which resides 40–50 kJ mol^{-1} above the energy of the separated reactants. This reaction threshold has far reaching consequences on the applications of our findings. Whereas tricarbon molecules can certainly react with methylacetylene and allene to form 1-hexene-3,4-diynyl-2 radicals in high temperature combustion flames, the reaction threshold certainly blocks this reaction in cold molecular clouds where the molecules have average translational temperatures of about 10 K. Therefore, future flame studies utilizing the Advanced Light Source should investigate the existence of 1-hexene-3,4-diynyl-2 radicals in high temperature methylacetylene and allene flames. Since the corresponding C_3H_3, C_4H_3, and C_5H_3 radicals have been identified *via* their ionization potentials in combustion flames,[4,5] the existence of the C_6H_3 isomer 1-hexene-3,4-diynyl-2 in these settings seems reasonable.

Acknowledgements

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