

A crossed molecular beams study of the reaction of dicarbon molecules with benzene

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Abstract

We conducted the reaction of dicarbon molecules in their electronic ground, $C_2(X^1\Sigma_g^+)$, and first excited state, $C_2(a^3\Pi_u)$, with benzene, $C_6H_6(X^1A_{1g})$. The phenylethynyl radical (C_6H_5CC ; X^2A') and atomic hydrogen were inferred to be the reaction products under single collision conditions. The reactions were indirect via short-lived C_8H_6 intermediates which decomposed via atomic hydrogen elimination without exit barrier (singlet surface) and via a tight exit transition state (triplet surface). Our experiments suggest that the phenylethynyl radical can be likely formed via bimolecular reactions involving dicarbon molecules with benzene in extreme environments such as circumstellar envelopes of carbon stars, planetary nebulae, and combustion flames.

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1. Introduction

An investigation of the detailed reaction mechanisms leading to the formation of polycyclic aromatic hydrocarbons (PAHs) and their hydrogen-deficient precursor molecules presents an important means to understand the chemical evolution of the interstellar medium [1] and of combustion processes [2–7]. PAH-like molecules have been suggested to be precursors to soot in combustion systems [8–14] and to carbonaceous grain particles in outflows of carbon stars [15]. In recent years, an exploration of the C_8H_6 and C_8H_5 potential energy surfaces (PESs) has received considerable attention. Here, the phenylacetylene (C_6H_5CCH) molecule and the ethynylphenyl radicals (C_6H_4CCH) have been proposed to be central reaction intermediates in the formation of the naphthyl radical ($C_{10}H_7$) and higher PAHs (Fig. 1) via an addition of acetylene to the 2-ethynylphenyl-1 radical (C_8H_5) and consecutive isomerization plus hydrogen atom elimination [16].

However, despite the potential importance of the C_8H_5 radicals in combustion flames as precursors to PAHs and related molecules, not many investigations accessing the C_8H_6 and C_8H_5 PESs experimentally have been conducted. Coleman et al. suggested the phenylethynyl isomer (C_6H_5CC) to be formed as a photolysis product of the iodine precursor [17]. The existence of this radical was verified in low temperature argon matrices suggesting that the unpaired electron resides in an π orbital from mixing of the π_z orbital of the ethynyl group with the E_{1a} orbital of the phenyl group [18,19]. Broadus and Kass identified a hitherto unobserved C_8H_5 isomer, i.e. the anti-aromatic benzocyclobutadienyl radical (Fig. 1) [20]. Hofman et al. claimed to have accessed the C_8H_5 potential energy surface via pyrolysis of phenyl acetylene by atomic hydrogen elimination [16]. However, Suits et al. examined the unimolecular decomposition of phenylacetylene under single collision conditions upon excitation at 193 nm. The authors provided evidence that acetylene and C_6H_4 isomers – some of them were found to decompose via molecular hydrogen elimination to 1,3,5-hexatriene – were the sole photodissociation products [21]. In this Letter, we access the singlet and triplet C_8H_6 potential energy surfaces experimentally via

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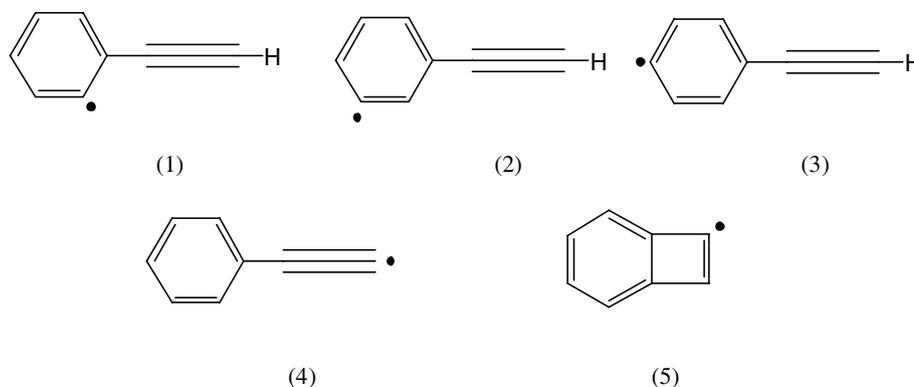


Fig. 1. Structures of various C₈H₅ radicals: (1) *ortho*-ethynylphenyl, (2) *meta*-ethynylphenyl, (3) *para*-ethynylphenyl, (4) phenylethynyl, and (5) benzocyclobutadienyl.

the crossed beams reactions of dicarbon molecules, C₂, in their singlet ground ($X^1\Sigma_g^+$) and excited triplet state ($a^3\Pi_u$) with benzene (C₆H₆). By focusing on the formation of C₈H₅ and possible C₈H₄ isomers via atomic and molecular hydrogen elimination pathways we can provide information on the nature of the reaction products, intermediates involved, and the underlying formation routes.

2. Experimental

The experiments were carried out under single collision conditions utilizing a crossed molecular beams machine [22]. Pulsed dicarbon beams were produced via laser ablation of graphite at 266 nm by focusing 8 mJ per pulse on a rotating carbon rod. The ablated species were seeded in neat helium carrier gas (Gaspro, 99.9999%, 3040 torr, Table 1) which was released by a pulsed valve. After passing a skimmer, a four-slot chopper wheel mounted after the ablation zone selected a part of the seeded dicarbon beam which then crossed a pulsed, neon seeded (about 5%) benzene beam (C₆H₆; Aldrich, 99.9%). 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; at the present stage, the concentration of the singlet versus triplet states are unknown. We monitored the reactively scattered species 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 taking and integrating the TOF spectra, we obtain the laboratory angular distribution (LAB).

Information on the chemical dynamics were obtained by fitting the TOF spectra and the LAB distributions using a forward-convolution routine [23]. Best fits of the TOF and laboratory angular distributions were achieved by refining the $T(\theta)$ and $P(E_T)$ parameters.

3. Electronic structure calculations

The reactants, products, various intermediates, and transition states on C₈H₆ the potential energy surfaces for the C₂($X^1\Sigma_g^+$)/C₂($a^3\Pi_u$) plus benzene reactions were optimized using the hybrid density functional B3LYP method with the 6-311G(d,p) basis set [24,25]. Vibrational frequencies were also computed at the B3LYP/6-311G(d,p) level for the characterization of stationary points and to obtain zero-point energy (ZPE) corrections. The energies were then refined by single-point calculations using the G3(MP2,CCSD)//B3LYP method [26] which approximated the coupled cluster [27] CCSD(T)/G3MP2 large energy. All calculations were carried out using the GAUSSIAN 98 [28] and MOLPRO 2000 [29] programs.

4. Results

In our experiments, we monitored the reactive scattering signal at mass-to-charge ratios of $m/z = 101$ (C₈H₅⁺), 100 (C₈H₄⁺), and 99 (C₈H₃⁺). At each laboratory angle, the TOF spectra at both lower $m/z = 100$ and 99 are super imposable with the TOF spectra recorded at $m/z = 101$ (Fig. 2). This finding suggests that the molecular hydrogen elimination channel to form any C₈H₄ isomer is closed; the ion counts at $m/z = 100$ and 99 originated from a dissociative ionization of the C₈H₅ parent species in the ionizer.

Table 1
Peak velocities (v_p), speed ratios (S) and center-of-mass angles (θ_{CM}) together with the nominal collision energies of the dicarbon and the benzene reactants (E_c)

Beam	v_p (m s ⁻¹)	S	E_c (kJ mol ⁻¹)	θ_{CM}
C ₆ H ₆ (X^1A_{1g})/Ne	762 ± 2	21.6 ± 0.5	–	–
C ₂ ($X^1\Sigma_g^+$ / $a^3\Pi_u$)/He	2369 ± 50	3.4 ± 0.2	56.8 ± 2.2	46.3 ± 0.7
C ₂ ($X^1\Sigma_g^+$ / $a^3\Pi_u$)/He	2704 ± 98	2.7 ± 0.3	72.4 ± 5.0	42.5 ± 1.1

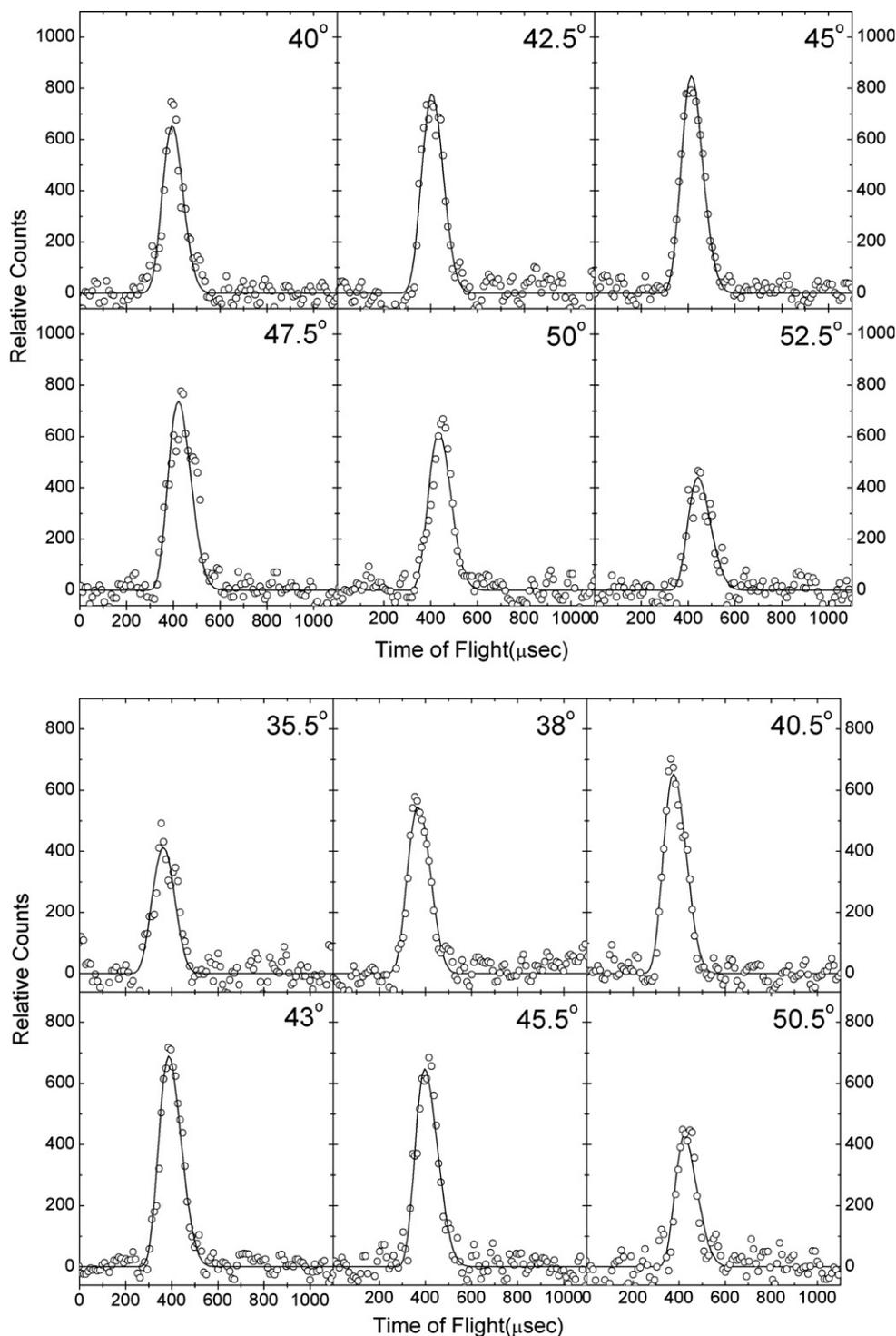


Fig. 2. Selected time-of-flight data for $m/z = 101$ ($C_8H_5^+$) recorded at collision energies of 56.8 kJ mol^{-1} (top) and 72.4 kJ mol^{-1} (bottom) at various laboratory angles. The circles indicate the experimental data, the solid lines the calculated fit.

Therefore, we can conclude that molecule(s) of the generic formula C_8H_5 together with atomic hydrogen are formed. The TOF data can now be integrated and scaled; this enables us to derive laboratory angular distributions of the C_8H_5 radical product at both collision energies. The most probable Newton diagrams of the reactions of dicarbon $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ with benzene and the corresponding labo-

ratory angular distributions of the C_8H_5 product recorded via $m/z = 101$ are shown in Fig. 3 at both collision energies.

The translational energy distributions in the center-of-mass-frame, $P(E_T)$, together with the center-of-mass angular distributions, $T(\theta)$, are depicted in Fig. 4. We achieved best fits of the TOF spectra and of the LAB distributions with a single $P(E_T)$ at each collision energy extending to

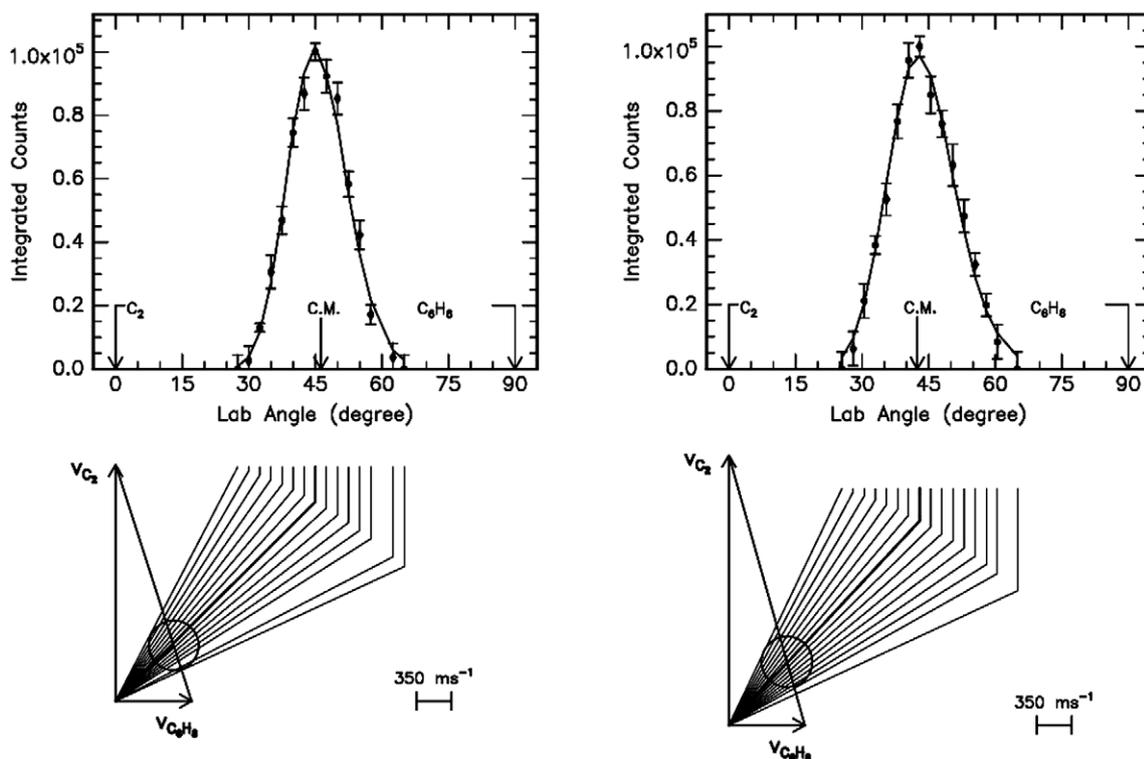


Fig. 3. Newton diagrams for the reaction of dicarbon with benzene at two collision energies of 56.8 kJ mol^{-1} (left) and 72.4 kJ mol^{-1} (right) together with the corresponding laboratory angular distribution of the C_8H_5 radical(s) recorded at $m/z = 101$ (C_8H_5^+). Circles and error bars indicate experimental data, the solid line the calculated distribution with the best-fit center-of-mass functions.

a maximum translational energy, E_{max} , of 121 kJ mol^{-1} ($E_c = 56.8 \text{ kJ mol}^{-1}$) and 132 kJ mol^{-1} ($E_c = 72.4 \text{ kJ mol}^{-1}$). We would like to note that because of the kinematics of the reaction, i.e. the emission of a light hydrogen atom, the fits are relatively insensitive to the high energy cutoff: adding or cutting the high energy tail by $\pm 20 \text{ kJ mol}^{-1}$ does not change the fit. It should be stressed that the maximum translational energy portrays the sum of the collision energy plus the absolute value of the exoergicity of the reaction; consequently, we can compute the reaction exoergicity with the help of E_{max} . Averaging over both collision energies, we establish that the reaction to form the C_8H_5 plus atomic hydrogen is exoergic by $62 \pm 20 \text{ kJ mol}^{-1}$. Besides the reaction energy, we can analyze the shape of the center-of-mass translational energy distributions. Here, both $P(E_T)$ s depict a flat and very broad plateau between 3 kJ mol^{-1} and about 40 kJ mol^{-1} . These data may suggest that at least one reaction channel exhibits a significant exit barrier and, hence, a significant geometry as well as electron density change from the fragmenting C_8H_6 intermediate to the products resulting in a repulsive bond rupture from a tight transition state [30]. It is worth mentioning that indirect, bimolecular reactions involving polyatomic reactants holding an exit barrier from the decomposing intermediate to the reaction products are frequently associated with a $P(E_T)$ peaking away from zero translational energy. Besides the translational energy distributions, the center-of-mass angular distributions hold valuable information on the reaction dynamics. Most

important, the angular distribution shows intensity over the complete angular scan. This indicates indirect scattering dynamics and the involvement of C_8H_6 intermediate(s). Also, as the collision energy increases, the shapes of the $T(\theta)$ s change significantly from a forward scattered distribution at lower to a backward-scattered distribution at higher collision energy. This yielded intensity ratios of $T(\theta)$ at $\theta = 0-180^\circ$ of $T(0^\circ)/T(180^\circ) = 2.3 \pm 0.3$ and 0.7 ± 0.1 at lower and higher collision energy, respectively.

5. Discussion

Our experiments suggest that the formation of C_8H_5 plus atomic hydrogen is exoergic by $62 \pm 20 \text{ kJ mol}^{-1}$. We can compare this value with the computed reaction energies to form various C_8H_5 isomers and a hydrogen atom (Fig. 5). Our experimental reaction energy is in good agreement to form the phenylethynyl radical ($\text{C}_6\text{H}_5\text{CC}\cdot$; X^2A'). Here, the computed energies on the singlet and triplet surfaces, i.e. -33 ± 10 and $-41 \pm 10 \text{ kJ mol}^{-1}$, respectively, correlate – within the error limits – with the experimentally derived data of $62 \pm 20 \text{ kJ mol}^{-1}$. The reactions to form *ortho*, *meta*, and *para*-phenyl radicals are too exoergic by about 70 kJ mol^{-1} to account for the product translational energy distributions (Fig. 4). It is interesting to note that the thermodynamically most favorable isomer(s) are not formed in this reaction. This is similar to the reactions of, for instance, carbon atoms with benzene and carbon atoms with 1,2-butadiene [31]. Here, non-RRKM and dynamical

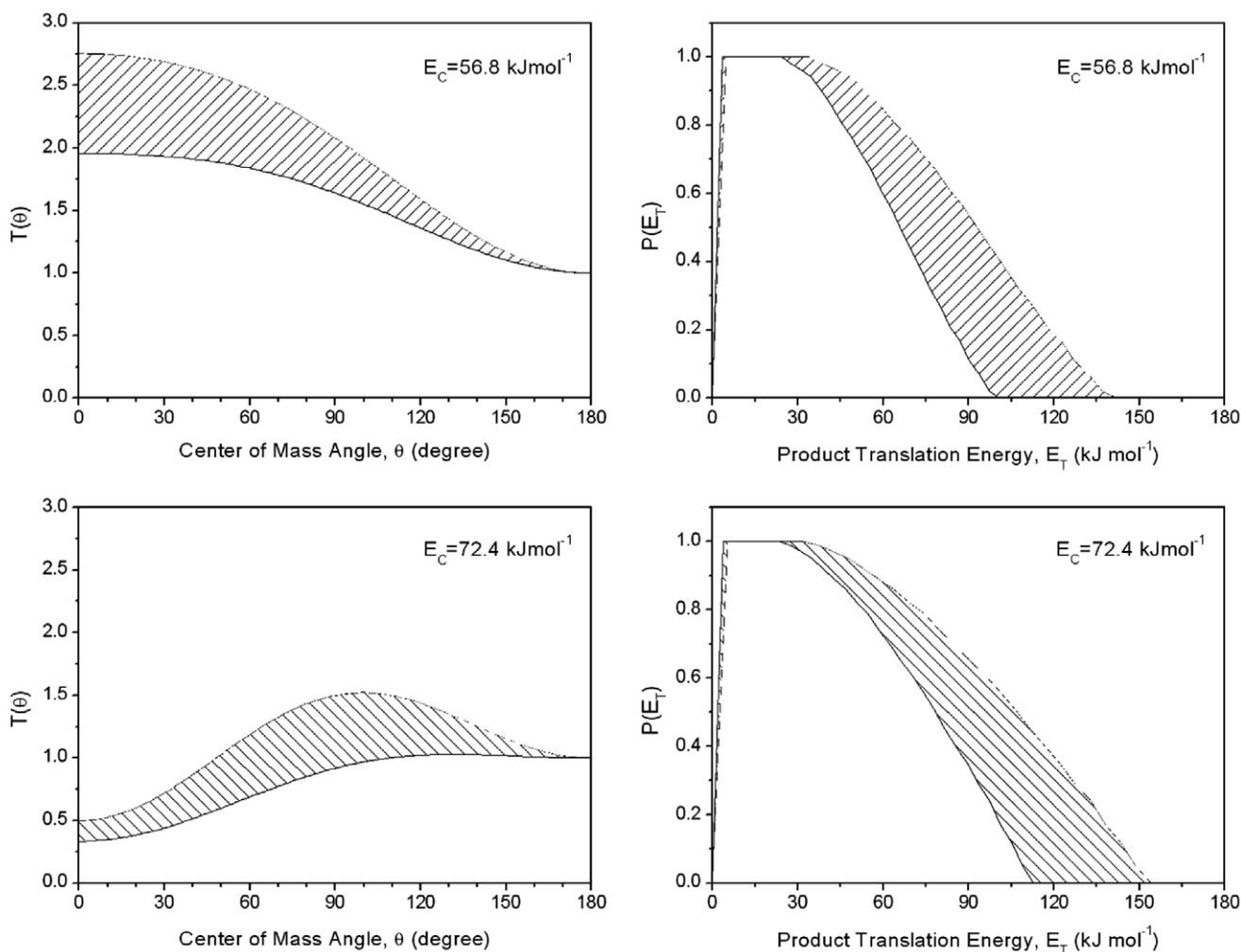


Fig. 4. Center-of-mass translational energy flux (right) and angular distributions (left) for the reaction of dicarbon with benzene. The hatched areas indicate the error limits of the distributions.

effect clearly block the formation of the thermodynamically most stable structures. Likewise, the channels to yield 1,2,4-tridehydrocyclooctatetraene ($\Delta_r G = 87 \text{ kJ mol}^{-1}$) and 1,2,3-tridehydrocyclooctatetraene ($\Delta_r G = 145 \text{ kJ mol}^{-1}$) are energetically not accessible even at our highest collision energy of 72.4 kJ mol^{-1} . Upper limits of 5–10% of the 1,2,5-tridehydrocyclooctatetraene radical ($\Delta_r G = 36 \text{ kJ mol}^{-1}$) can be derived. Summarized, the experimental and computed reaction energies are in line with the formation of the phenylethynyl radical ($\text{C}_6\text{H}_5\text{CC}$; $\text{X}^2\text{A}'$). Having assigned the phenylethynyl radical as the reaction product, we can exploit the center-of-mass translational energy distributions to extract the fraction of the energy channeling into the translational modes of the products. Here, the averaged fraction of the translational energy was computed to be $46 \pm 10\%$ invariant on the collision energy.

We attempt now to solve the underlying reaction dynamics to form the phenylethynyl radical ($\text{C}_6\text{H}_5\text{CC}$; $\text{X}^2\text{A}'$) on the singlet and triplet surfaces, respectively. First, it is necessary to associate the structures of the phenylethynyl radical product ($\text{C}_6\text{H}_5\text{CC}$) with the geometry of the dicarbon (CC) and benzene (C_6H_6) reactants. Most importantly,

the shapes of the $T(\theta)$ s (Fig. 4) reveal that the reaction is indirect involving the formation of C_8H_6 intermediate(s). Comparing the structures of the reactants with the reaction products, it is clear that the aromatic benzene unit is conserved; one hydrogen atom is formally replaced by the dicarbon unit. To correlate benzene with the phenylethynyl radical, we propose that the dicarbon molecule adds to either one carbon atom of the benzene molecule to form a $\text{C}_6\text{H}_6\text{-CC}$ reaction intermediate. Here, the hybridization of the attacked benzene carbon atom changes from sp^2 to sp^3 . Subsequently, this reaction intermediate could lose a hydrogen atom to yield the experimentally observed phenylethynyl radical. This reaction sequence is similar to the bimolecular collision of cyano radicals (CN , $\text{X}^2\Sigma^+$) with benzene which proceeds via a barrier-less addition of the cyano radical to a carbon atom of the aromatic benzene ring followed by an atomic hydrogen atom elimination yielding the cyanobenzene molecule ($\text{C}_6\text{H}_5\text{CN}$) [32]. Alternatively, the dicarbon molecule could add across the carbon-carbon double bond in a similar way the dicarbon-ethylene reaction proceeds [33]. This intermediate could undergo a hydrogen migration to the terminal carbon atom

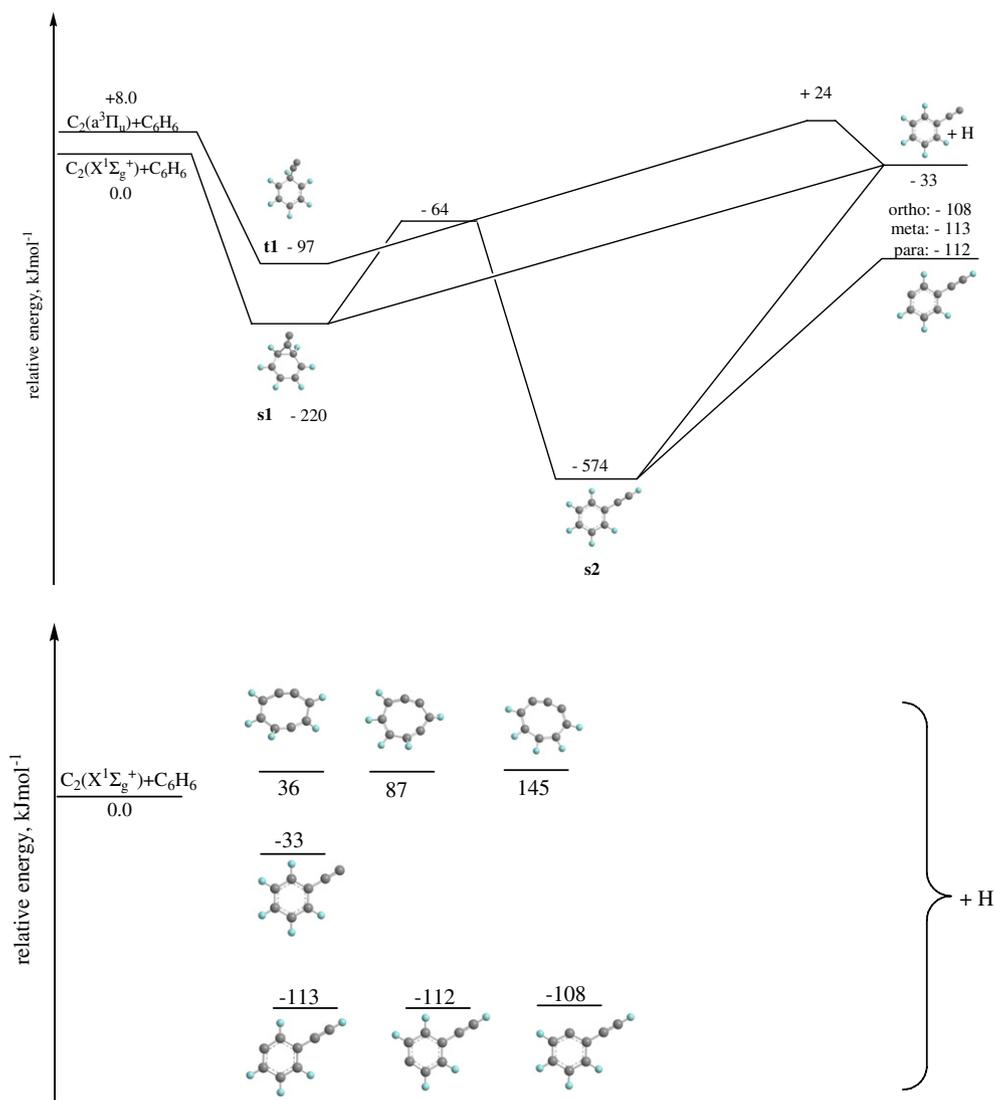


Fig. 5. Relevant stationary points on the singlet and triplet C₈H₆ potential energy surfaces of the reaction of dicarbon with benzene.

of the dicarbon molecule prior to its elimination. It should be noted that in principle, the initial collision complex could also lose a hydrogen atom undergoing a simultaneous ring opening to the phenylethynyl radical in one step. These proposed dynamics could explain the experimental findings of indirect reaction mechanisms via C₈H₆ intermediates. On the singlet surface, we would expect a barrier-less decomposition of the C₈H₆ intermediate via a simple bond rupture process (lose exit transition state); however, the triplet surface is expected to have an exit barrier. Here, the reversed addition of a hydrogen atom to the carbon atom of the phenylethynyl radical holding the former dicarbon unit is similar to the addition of a hydrogen atom to an aromatic benzene ring depicting an entrance barrier of about 37 kJ mol⁻¹ [34]. Therefore, the decomposition of the intermediates via loose (singlet) and tight (triplet) exit transition states can account for the broad plateau of the center-of-mass translational energy distributions. Similar patterns of broad plateaus which reflect the existence of distinct pathways on the singlet and triplet surfaces have been

observed for the reaction of singlet/triplet dicarbon with acetylene [35] and ethylene [33].

Having proposed reaction mechanisms, we attempt to verify these recommended reaction pathways computationally (Fig. 5). Our calculations confirm the derived mechanisms. On the singlet surface, dicarbon was found to add to a carbon-carbon double bond forming **s1** which is stabilized by 220 kJ mol⁻¹ with respect to the reactants. This intermediate could either isomerize via hydrogen migration to the phenylbenzene intermediate **s2** or fragments directly via atomic hydrogen elimination to form the phenylethynyl radical via a loose exit transition state. Alternatively, phenylbenzene can eject a hydrogen atom to yield either the *ortho*, *meta*, and/or *para*-ethynylphenyl radical or the phenylethynyl radical. Since neither the *ortho*, *para*, nor *meta*-ethynylphenyl molecule were observed experimentally, our experiments suggest that the life time of the **s1** intermediate is likely to be too short for a hydrogen migration to **s2** to occur. Based on the shape of the center-of-mass angular distribution, the life time is shorter than the

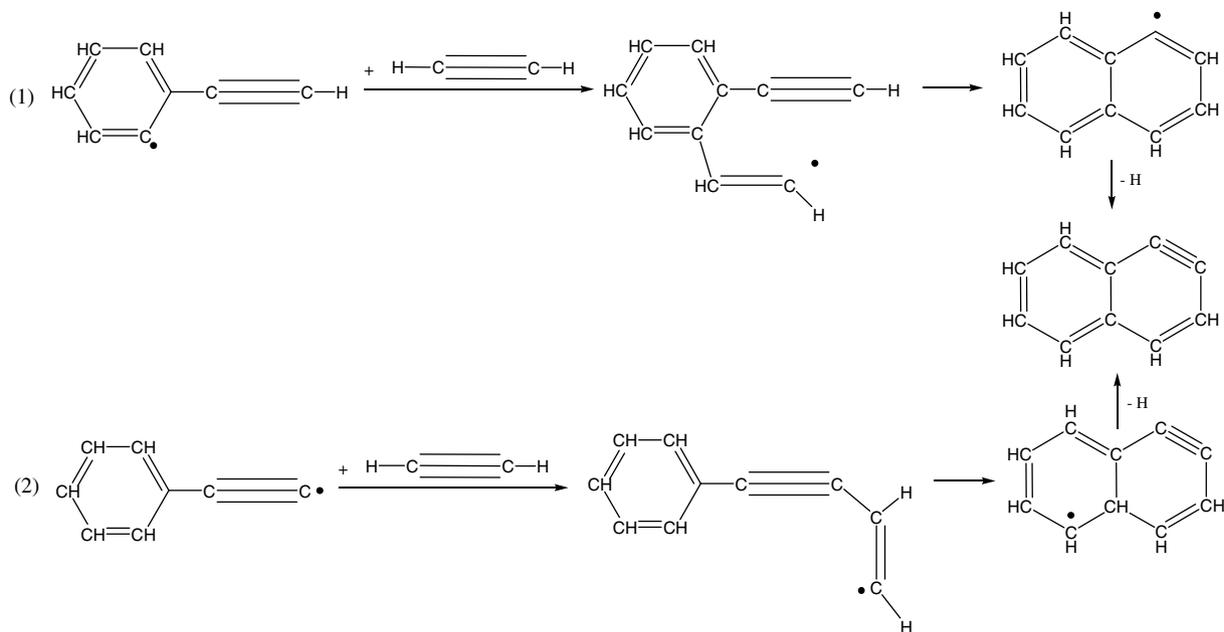
rotation period of the decomposing complex, i.e. a few picoseconds. Considering our electronic structure calculations and vibrational frequencies, we can compute the isomerization rates and hence life times of about 237 ps and 114 ps. However, we have to stress that these are timescales *if* the energy randomization is complete. Timescales of hundreds of picoseconds would result in long-lived complexes and symmetric center of mass angular distributions. This was clearly not observed in our experiments; recall that the asymmetric center-of-mass angular distributions suggest lifetimes of less than a few picoseconds. Therefore, we have to conclude that the dicarbon–benzene system is clearly a non-RRKM case, here, in which the thermodynamically most stable isomer(s) are not formed. On the triplet surface, the dicarbon adds to one carbon atom of the benzene molecule forming **t1**. The latter resides in a relatively shallow potential energy well of only 97 kJ mol^{-1} with respect to the reactants. This structure was found to decompose by an atomic hydrogen elimination via a tight exit transition state located 57 kJ mol^{-1} above the separated products to the phenylethynyl radical. Therefore, the reaction of triplet dicarbon with benzene proceeds in a similar way as the reaction of the cyano radical with benzene as discussed in the previous paragraph.

Finally, we would like to discuss the energy dependence of the center-of-mass angular distributions. Here, a switch from a forward to a pronounced backward scattering is obvious. Note that this finding was also observed in the crossed beams reactions of dicarbon with acetylene [35]. Since the reaction on the singlet and triplet surfaces have no entrance barrier, this finding could be explained in terms of impact parameters. As the collision energy rises, the maximum reactive impact parameter decreases. Larger impact parameters could lead to a forward scattered center-of-mass angular distribution via a short lived reaction intermediate where the dicarbon molecule ‘picks up’

the phenyl unit and leaves behind a hydrogen; smaller impact parameters could result in a backward scattering of the heavy phenylethynyl radical product. However, we acknowledge that the ratio of triplet to singlet dicarbon in our beam is currently unknown. Therefore, the pronounced backward scattering could be also the result of a change in the singlet versus triplet ratio with increasing collision energy. Nevertheless, despite this open question, the crossed beams experiments and electronic structure calculations correlate nicely with the formation of the phenylethynyl radical under single collision conditions. Also, the presence/absence of the exit barriers and the existence of short lived reaction intermediates should be stressed.

6. Conclusions

We carried out the crossed beams reaction of dicarbon molecules in their electronic ground, $\text{C}_2(\text{X}^1\Sigma_g^+)$, and first excited state, $\text{C}_2(\text{a}^3\Pi_u)$, with benzene, $\text{C}_6\text{H}_6(\text{X}^1\text{A}_{1g})$, to synthesize the phenylethynyl radical ($\text{C}_6\text{H}_5\text{CC}\cdot$; $\text{X}^2\text{A}'$) and atomic hydrogen under single collision conditions. On the singlet and triplet surface, the reactions were found to be indirect via short-lived C_8H_6 intermediates decomposing via atomic hydrogen elimination. The formation of the thermodynamically less stable phenylethynyl radical could be rationalized in terms of the short life time of the reaction intermediates. Our experiments provide a clean pathway to form phenylethynyl radical ($\text{C}_6\text{H}_5\text{CC}\cdot$; $\text{X}^2\text{A}'$) and could pave the way to further spectroscopic studies of this potential combustion intermediate. In combustion flames, for instance, a reaction with acetylene could present an alternative pathway to form 1,2-didehydronaphthalene not only via equation (1), but also via route (2) – a pathway which was thought previously to involve solely ethynylphenyl radical isomers.



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