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PAPER

On the formation of phenyldiacetylene (C_6H_5CCCCH) and D5-phenyldiacetylene (C_6D_5CCCCH) studied under single collision conditions†

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The crossed molecular beam reactions of the phenyl and D5-phenyl radical with diacetylene (C_4H_2) was studied under single collision conditions at a collision energy of 46 kJ mol^{-1} . The chemical dynamics were found to be indirect and initiated by an addition of the phenyl/D5-phenyl radical with its radical center to the C1-carbon atom of the diacetylene reactant. This process involved an entrance barrier of 4 kJ mol^{-1} and lead to a long lived, bound doublet radical intermediate. The latter emitted a hydrogen atom directly or after a few isomerization steps *via* tight exit transition states placed $20\text{--}21 \text{ kJ mol}^{-1}$ above the separated phenyldiacetylene (C_6H_5CCCCH) plus atomic hydrogen products. The overall reaction was determined to be exoergic by about $49 \pm 26 \text{ kJ mol}^{-1}$ and $44 \pm 10 \text{ kJ mol}^{-1}$ as determined experimentally and computationally, thus representing a feasible pathway to the formation of the phenyldiacetylene molecule in combustion flames of hydrocarbon fuel.

1. Introduction

The formation mechanisms of polycyclic aromatic hydrocarbons (PAHs) are of interest to the combustion and astronomical communities due to their role as intermediates in soot growth¹ and interstellar dust formation.² Phenyl radicals (C_6H_5) and diacetylene molecules (C_4H_2) have been traced in hydrocarbon flames. However, the reaction of ground state phenyl radicals (C_6H_5) with diacetylene (C_4H_2) has until now not been investigated experimentally in flow studies or under single collision conditions in crossed molecular beam experiments. Previous work on the reaction of excited $C_4H_2^*$ with benzene identified that $C_{10}H_6$ molecules are formed.³ Here, diacetylene was excited to its $2_0^1 6_0$ band, which underwent rapid intersystem crossing (ISC) to the lowest triplet state before reacting with benzene in the gas phase; the products were ionized by vacuum ultraviolet (VUV) photons and subsequently monitored by mass spectrometry; alternatively, two photon ionization (R2PI) was exploited to provide the UV spectra of the products. Three product channels were found with their branching ratios given in parenthesis: $C_8H_6 + C_2H_2$ (39%), $C_{10}H_6 + H_2$ (or $H + H$) (48%), and $C_{10}H_7 + H$ (16%). Under these experimental conditions, only the phenyldiacetylene (C_6H_5CCCCH) isomer

was identified based on the UV spectra. The reaction was proposed to be initiated by addition of the benzene ring to the triple bond of the excited diacetylene molecule followed by isomerization to a ring structure consisting of two benzene carbon atoms and the diacetylene molecule; a 1,2 H-shift furnished a reaction intermediate which decomposed *via* ejection of molecular hydrogen and/or two hydrogen atoms yielding phenyldiacetylene (C_6H_5CCCCH). Further studies of phenyldiacetylene were conducted computationally on the ground state potential energy surface (PES) of ethynyl radicals (C_2H) reacting with phenylacetylene (C_6H_5CCH). Branching ratios for multiple reaction channels were derived from statistical RRKM theory calculations.⁴ Three reaction pathways were found to depend strongly on the position of the ethynyl radical addition to phenylacetylene (aromatic ring *versus* ethynyl unit). All additions were barrier-less and resulted in hydrogen emission to form a $C_{10}H_6$ isomer. Here, the formation of phenyldiacetylene from phenyl plus diacetylene was found to be exoergic by 44 kJ mol^{-1} . The RRKM calculations showed that for the channels involving ethynyl addition to the ethynyl unit the dominant $C_{10}H_6$ isomer is phenyldiacetylene with the formation of 1,2- and 2,3-didehydronaphthalene isomers never exceeding 0.1%, and phenyl plus diacetylene being the other significant product.

The energies of the possible bicyclic $C_{10}H_6$ isomers have been calculated by multi reference coupled clusters methods for both singlet and triplet states.⁵ The 1,2-didehydronaphthalene was found to be the most stable isomer followed closely by 2,3-didehydronaphthalene in their singlet states. Later, microwave

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flash pyrolysis experiments investigated the formation and reaction of benzyne (C_6H_4) with diacetylene.⁶ Here, using CCSD calculations the authors postulated a [2 + 4] addition mechanism of benzyne with diacetylene to form phenyldiacetylene intermediates, which could access the didehydronaphthalene structure located 399 kJ mol^{-1} lower in energy than the reactants. Recent mass spectra of acetylene pyrolysis found increasing signals at $m/z = 126$ ($C_{10}H_6$) with temperature from 1347 K to 1476 K, which was tentatively assigned to 1,3-diethynylbenzene based on the most probable structure from the HACA (hydrogen abstraction - acetylene addition) mechanism from phenylacetylene.⁷ Flame tests of gasoline in oxygen/argon mixture also monitored mass to charge ratios, m/z , of 126 ($C_{10}H_6^+$) assigned to 1,4-diethynylbenzene based on the ionization energy.⁸ Recent flame experiments tests of toluene identified $C_{10}H_6$ molecular masses to 1,4-diethynylbenzene and 1,2-didehydronaphthylene; this indicates a mass growth process to higher mass PAHs such as pyrene *via* the HACA mechanism.^{9,10} The isomers are too close in ionization energy making their identification non-trivial. The previous literature compilation suggests that no consistent picture has emerged on the formation of phenyldiacetylene. To account for this, the present work utilizes cross molecular beams of phenyl radicals and diacetylene along with *ab initio* calculations and RRKM theory to investigate the reaction dynamics and products under single collision conditions and propose possible formation routes to phenyldiacetylene in combustion flames and in the interstellar medium.

2. Experimental

The experiments were conducted under single collision conditions in a crossed molecular beams machine at the University of Hawaii.¹¹ Briefly, a helium-seeded molecular beam of (deuterated) phenyl radicals (C_6H_5 , C_6D_5 ; X^2A_1) at fractions of about 1% was generated by photolysis of (deuterated) chlorobenzene (C_6H_5Cl 99.9%; C_6D_5Cl 99%; Fluka) in the primary source chamber. The helium-seeded (deuterated) chlorobenzene was coupled into the piezoelectric pulsed valve (Proch-Trickl) operated at 120 Hz and a backing pressure of about 1.5 atm. The (deuterated) chlorobenzene was photolyzed by focusing the 193 nm excimer laser output operating at 60 Hz and 10 mJ per pulse 1 mm downstream of the nozzle prior to the skimmer. Under our experimental conditions, the photolysis of chlorobenzene in the part of the beam intersected by the laser was estimated to be about 90% using a $1 \times 3 \text{ mm}$ focal region with an absorption cross section of $9.6 \times 10^{-18} \text{ cm}^{-2}$ at 193 nm.¹² The supersonic (deuterated) phenyl radical beam passed a skimmer and a four-slot chopper wheel. The latter selected segments of the pulsed (deuterated) phenyl radical (C_6D_5 , X^2A_1) beam of well-defined peak velocities (v_p) and speed ratios (S) as compiled in Table 1. The phenyl radical beam intersected a pulsed molecular beam of the diacetylene reactant seeded in argon (Airgas, 99.9999%) at fractions of 5% at a backing pressure of 550 Torr; the secondary pulsed valve was 20 μs prior to the pulsed valve in the primary source. Diacetylene (99.5% +) was synthesized in house according to a modified literature procedure as described in ref. 13. The reaction products were monitored with a triply differentially pumped quadrupole mass spectrometer (QMS) in the time-of-flight (TOF) mode after electron-impact ionization

Table 1 Peak velocities (v_p), speed ratios (S), center-of-mass angles (Θ_{CM}), and the collision energies of the phenyl radical with the diacetylene reactant (E_c) of the segments crossing at the interaction region

	v_p (ms^{-1})	S	E_c (kJ mol^{-1})	Θ_{CM}
$C_4H_2(X^1\Sigma_g^+)/Ar$	620 ± 20	26.0 ± 1.0		
$C_6H_5(X^2A_1)/He$	1672 ± 20	11.6 ± 1.5	46.6 ± 1.0	13.7 ± 0.5
$C_4H_2(X^1\Sigma_g^+)/Ar$	620 ± 20	26.0 ± 1.0		
$C_6D_5(X^2A_1)/He$	1652 ± 20	11.3 ± 1.3	45.6 ± 1.0	13.8 ± 0.5

of the neutral molecules at 80 eV with an emission current of 2 mA.¹⁴ The TOF spectra recorded at each angle and the product angular distribution in the laboratory frame (LAB) were fit with Legendre polynomials using a forward-convolution routine.¹⁵ This method uses an initial choice of the product translational energy $P(E_T)$ and the angular distribution $T(\theta)$ in the center-of-mass reference frame (CM) to reproduce TOF spectra and a product angular distribution. The TOF spectra and product angular distribution obtained from the fit were then compared to the experimental data. The parameters of the $P(E_T)$ and $T(\theta)$ were iteratively optimized until the best fit was reached.

3. Theoretical

Geometries of all intermediates and transition states on the $C_{10}H_7$ PES accessed *via* the reaction of phenyl radicals with diacetylene and the reaction reactants and products were optimized employing the hybrid density functional B3LYP method^{16,17} with the 6-311G** basis set. The same method was used to obtain vibrational frequencies, molecular structural parameters, zero-point energy (ZPE) corrections, and to characterize the stationary points as minima or first-order saddle points. To obtain more accurate energies, we utilized the G3(MP2,CC)//B3LYP modification^{18,19} of the original Gaussian 3 (G3) scheme²⁰ for high-level single-point energy calculations. The final energies at 0 K were obtained using the B3LYP optimized geometries and ZPE corrections according to the following formula $E_0[G3(MP2,CC)] = E[CCSD(T)/6-311G(d,p)] + \Delta E_{MP2} + E(ZPE)$, where $\Delta E_{MP2} = E[MP2/G3large] - E[MP2/6-311G(d,p)]$ is the basis set correction and $E(ZPE)$ is the zero-point energy. $\Delta E(SO)$, a spin-orbit correction, and $\Delta E(HLC)$, a higher level correction, from the original G3 scheme were not included in our calculations, as they do not make significant contributions into relative energies. We used the Gaussian 98²¹ program package for the B3LYP and MP2 calculations and the MOLPRO 2006²² program package for the calculations of spin-restricted coupled cluster RCCSD(T) energies. Relative yields of various products of the reaction of phenyl radicals with diacetylene under single-collision conditions were evaluated employing Rice-Ramsperger-Kassel-Marcus (RRKM) calculations²³⁻²⁵ of energy-dependent rate constants for individual unimolecular steps and of branching ratios of different channels. The computational procedure was described in detail previously.²⁶ We calculated rate constants as functions of available internal energy of each intermediate or transition state; the internal energy was taken as a sum of the energy of chemical activation in the reaction of phenyl radicals with diacetylene and the collision energy, assuming that a dominant fraction of the latter is converted to internal

vibrational energy. Only a single total-energy level was considered throughout, as for single-collision conditions (zero-pressure limit). The harmonic approximation was used to compute numbers and densities of state needed for evaluating the rate constants. Next, using the calculated rate constants, we computed product branching ratios by solving first-order kinetic equations within the steady-state approximation for unimolecular isomerization and fragmentation steps of initial reaction intermediates formed as a result of the addition of phenyl to the carbon atoms C1 and C2 in diacetylene.

4. Results

For the phenyl-diacetylene reaction, we recorded reactive scattering signal at mass-to-charge ratios of $m/z = 126$ ($C_{10}H_6^+$) (Fig. 1) and $m/z = 125$ ($C_{10}H_5^+$). Note that the time-of-flight spectra recorded at both m/z ratios are identical after scaling indicating that signal at $m/z = 125$ originated from dissociative ionization of the $C_{10}H_6$ parent molecule in the electron impact ionizer of the detector. Therefore, we can conclude that in the reaction of the phenyl radical with diacetylene, the phenyl *versus* atomic hydrogen pathway is open, but the molecular hydrogen elimination pathway is closed within the signal-to-noise limitation of our detector. The corresponding laboratory angular distribution (LAB) of $m/z = 126$ is depicted in Fig. 2. This distribution is relatively narrow, peaks at 13.5° close to the center-of-mass angle of $13.7 \pm 0.5^\circ$, and spreads over about 20° within the scattering plan as defined by the primary and secondary beams.

Since both the phenyl radical and the diacetylene molecule can in principle emit a hydrogen atom, we investigated to see to what degree the hydrogen atom is ejected from the diacetylene reactant. Therefore, we carried out the crossed beam reaction of D5-phenyl with diacetylene, and recorded signal at $m/z = 131$, *i.e.* $C_{10}D_5H^+$. The corresponding TOF spectra and LAB distributions are shown in Fig. 3 and 4, respectively. It is interesting to note that the intensity of the hydrogen loss channel in the phenyl-diacetylene and D5-phenyl-diacetylene systems as detected *via* the ionized $C_{10}H_6$ and $C_{10}D_5H$ products are essentially identical. Also, the LAB distributions show the same distributions apart from a difference due to the heavier mass of the deuterium atoms. Based on these laboratory data alone, we propose that the hydrogen atom is emitted almost

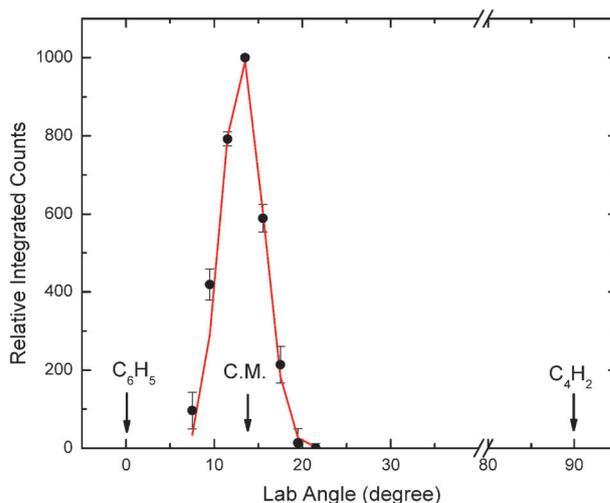


Fig. 2 Laboratory angular distribution of the $C_{10}H_6$ reaction product recorded at $m/z = 126$ by reaction of the phenyl radical ($C_6H_5 X^2A_1$) with diacetylene ($C_4H_2 X^1\Sigma_g^+$). Circles signify experimental data, red line denotes best fit to the data and C.M. designates center-of-mass angle.

exclusively from the diacetylene reactant, but—at least in the D5-phenyl-diacetylene reactant—not from the phenyl group.

Considering the almost identical LAB distributions and TOF spectra, it is not surprising that the laboratory data for both systems could be fit with identical center-of-mass functions as depicted in Fig. 5. A reasonable fit of the TOF data and LAB distributions for both reactions could be obtained with a single reaction channel. Best fits of the center-of-mass translational energy distributions, $P(E_T)$ s, were obtained with distributions extending to maximum translational energy releases, E_{max} , of about $105 \pm 25 \text{ kJ mol}^{-1}$. Since this high energy cutoff equals the sum of the absolute of the reaction energy plus the collision energy, the reactions leading to $C_{10}H_6/C_{10}D_5H$ plus atomic hydrogen are exoergic by $49 \pm 26 \text{ kJ mol}^{-1}$. Further, the $P(E_T)$ s depict a clear distribution maximum at 7 to 16 kJ mol^{-1} ; this finding suggests the presence of a tight exit transition state. Finally, the fraction of available energy channeling into the translational degrees of freedom of the products was computed to be $28 \pm 6\%$. Note that the center-of-mass angular distribution gains further information on the underlying reaction dynamics. The angular flux distributions of the hydrogen loss channel are

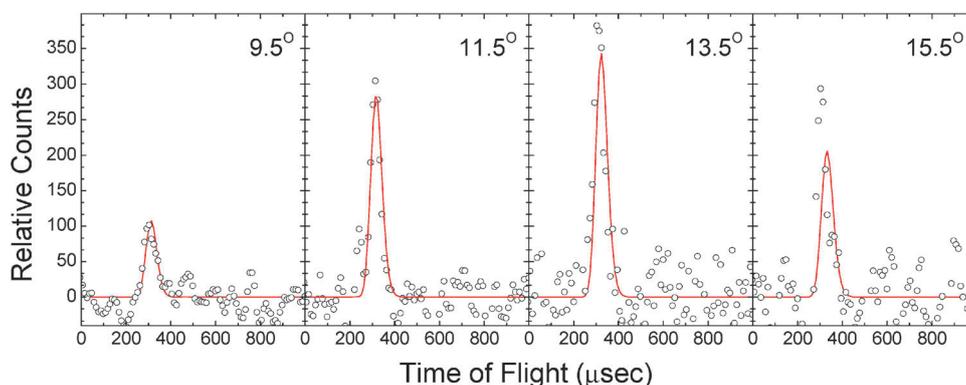


Fig. 1 Time-of-flight data for the reaction of the phenyl radical ($C_6H_5 X^2A_1$) with diacetylene ($C_4H_2 X^1\Sigma_g^+$) monitored at $m/z = 126$.

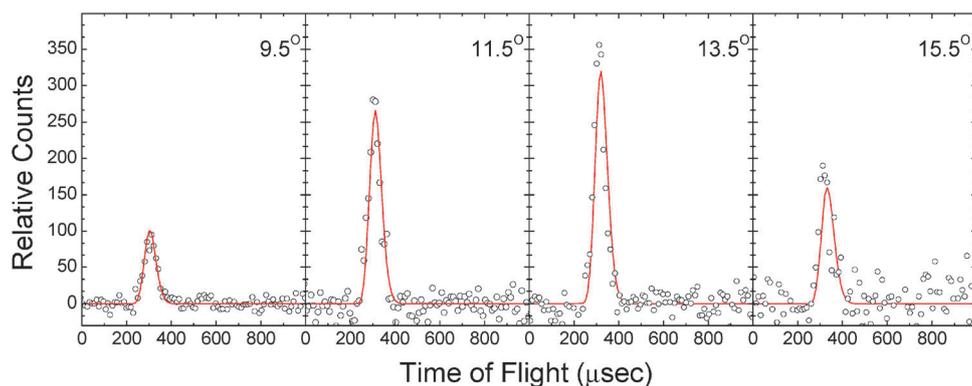


Fig. 3 Time-of-flight data for the reaction of the D5-phenyl radical ($C_6D_5 \ X^2A_1$) with diacetylene ($C_4H_2 \ X^1\Sigma_g^+$) monitored at $m/z = 131$.

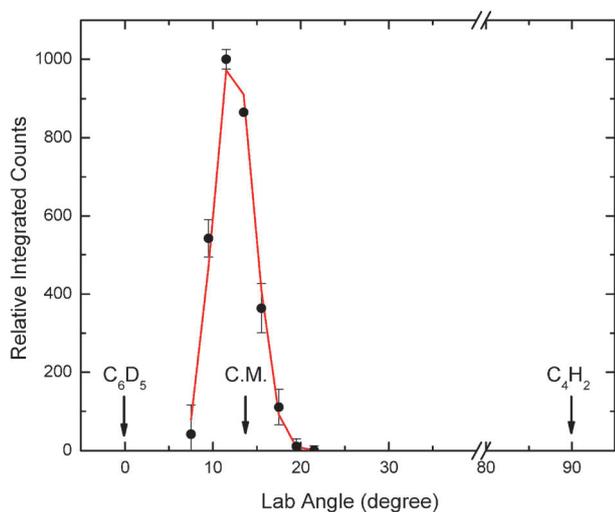


Fig. 4 Laboratory angular distribution of the $C_{10}D_5H$ reaction product recorded at $m/z = 131$ by reaction of the D5-phenyl radical ($C_6D_5 \ X^2A_1$) with diacetylene ($C_4H_2 \ X^1\Sigma_g^+$). Circles signify experimental data, red line denotes best fit data and C.M. designates center-of-mass angle.

essentially forward-backward symmetric around 90° depicting flux over the complete angular range from 0° to 180° . This finding indicates that the reaction follows indirect scattering dynamics *via* formation of $C_{10}H_7/C_{10}D_5H_2$ complexes holding lifetimes longer than their rotation periods.²⁷ The fits were found to be insensitive to a maximum or dip at 90° . However, the rather weak polarization of the center-of-mass angular distribution proposed that the initial and final angular momentum are only weakly coupled and that most of the total angular momentum is coupled into rotational excitation of the polyatomic products.²⁸ This is due the inability of the departing, light hydrogen atom to carry away a significant fraction of the angular momentum.

5. Discussion

In the case of crossed beam reactions involving polyatomic reactants, it is often useful to combine the crossed beam data with electronic structure calculations (Fig. 6). First, we are comparing the experimentally determined reaction energy with

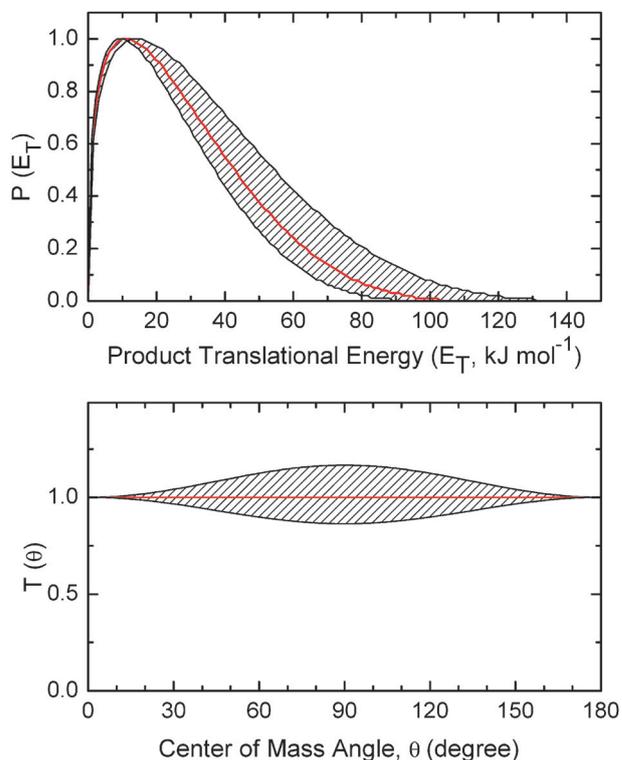


Fig. 5 Center-of-mass translational energy flux distribution (upper) and angular distribution (lower) utilized to fit data at $m/z = 126$ for the reaction of phenyl radicals with diacetylene and $m/z = 131$ for the reaction of D5-phenyl radicals with diacetylene. Hatched areas indicate the acceptable upper and lower error limits of the fits and the solid red line defines the best-fit function.

those obtained for low-lying $C_{10}H_6$ isomers relevant to the reaction of phenyl plus diacetylene. Our computation suggests that two isomers can be formed: phenyldiacetylene (p1; -44 kJ mol^{-1}) and 2,3-didehydronaphthalene (p2; -54 kJ mol^{-1}) with the calculated reaction energies indicated in parentheses; a third potential product isomer, 1-H-indenyl-ylidenemethylene (p3; $+109 \text{ kJ mol}^{-1}$), cannot be formed in our reaction considering our collision energy of 46 kJ mol^{-1} , since the collision energy is about 54 kJ mol^{-1} lower than the reaction endoergicity. The experimental reaction exoergicity of $49 \pm 26 \text{ kJ mol}^{-1}$ can account for the formation

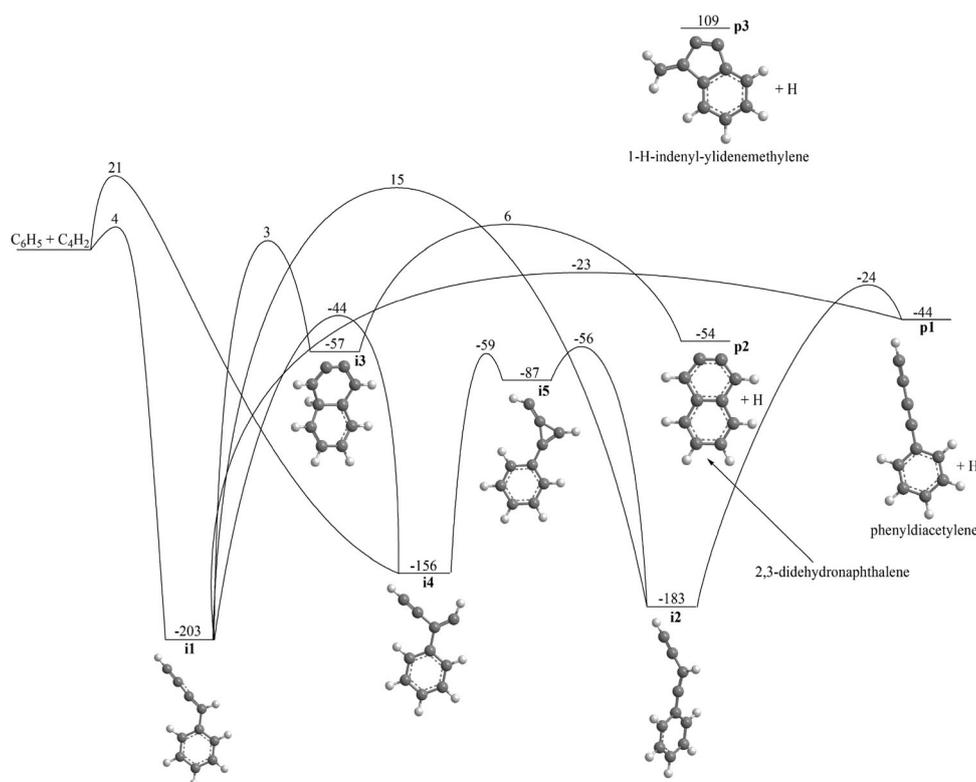


Fig. 6 Potential energy surface of the reaction of phenyl radicals with diacetylene. Relative energies calculated at the G3(MP2,CC)//B3LYP/6-311G** level of theory are given in units of kJ mol^{-1} for the reaction of phenyl with diacetylene; for the reaction of D5-phenyl with diacetylene, relative energies do not differ from those for phenyl plus diacetylene by more than 1 kJ mol^{-1} .

of both phenyldiacetylene and 2,3-didehydronaphthalene. Therefore, the energetics alone cannot untangle which of these isomers is formed.

Therefore, we are expanding our discussion to a comparison of the theoretically predicted pathways to form phenyldiacetylene and 2,3-didehydronaphthalene and compare these findings with our experimental data, in particular the observance of the hydrogen atom loss in the phenyl-diacetylene and D5-phenyl-diacetylene systems and the identical nature of the derived center-of-mass functions (Fig. 5). The computations predict three reaction pathways to form the phenyldiacetylene product (Fig. 6). Initiated by an addition of the phenyl radical with its radical center to the C1-carbon atom (the terminal carbon atom) of the diacetylene molecule *via* a barrier of 4 kJ mol^{-1} , a bound doublet radical intermediate (**i1**) is formed. The latter can lose a hydrogen atom from the C1 carbon atom yielding the phenyldiacetylene product *via* a tight exit transition state located 21 kJ mol^{-1} above the separated products. Alternatively, intermediate **i1** can isomerize *via* a C1–C2 hydrogen atom shift to intermediate **i2** before ejecting the hydrogen atom from C2 to yield phenyldiacetylene; this pathway also involves a tight exit transition state being placed 20 kJ mol^{-1} above the final products. However, the calculated barrier for the 1,2-H shift from **i1** to **i2** is high, 218 kJ mol^{-1} , with the corresponding transition state residing 15 kJ mol^{-1} above the initial reactants. Another, lower energy path exists between **i1** and **i2**. It starts with migration of the C_6H_5 moiety over the C1–C2 bond of C_4H_2 leading to **i4** *via* a barrier of 159 kJ mol^{-1} . Note that **i4** can be

also produced directly from the reactants, by addition of C_6H_5 to the C2 carbon of diacetylene, but the barrier for this addition is 21 kJ mol^{-1} , significantly higher than that for the addition to C1 to form **i1**. Intermediate **i4** can rearrange to **i2** *via* a two-step mechanism involving three-member ring opening and ring closure in the C_4H_2 fragment effectively swapping the C1 and C2 atoms. The highest in energy transition state on the **i4** → **i5** → **i2** pathway resides 147 kJ mol^{-1} above **i1** and 56 kJ mol^{-1} below the reactants. Alternatively, intermediate **i1** ring closes to **i3** *via* a 206 kJ mol^{-1} barrier, and **i3** can undergo unimolecular decomposition by a hydrogen atom loss from the bridged carbon atom forming 2,3-didehydronaphthalene; note that this hydrogen atom would be released from the former phenyl moiety, but *not* from the diacetylene molecule.

Which of the computed pathways can explain our experimental findings? If intermediate **i3** is formed *via* ring closure from **i1**, a deuterium atom loss should dominate the chemical dynamics in the D5-phenyl plus diacetylene reaction. However, the TOF and LAB distributions as well as the corresponding center-of-mass functions are essentially identical both qualitatively and quantitatively. Considering the fact that the intensity of the scattering signal for the atomic hydrogen loss for the phenyl-diacetylene and D5-phenyl-diacetylene system was also identical within the error limits, we can conclude that the hydrogen atom only originated from the diacetylene reactant. If hydrogen is emitted also from the phenyl group, the intensity of the hydrogen loss channel in the phenyl-diacetylene reaction should be stronger than in the D5-phenyl-diacetylene system.

This was not observed. Consequently, we propose that within the limits of our detection, the hydrogen atom originates rather from the diacetylene molecule. The experimental observations are corroborated by the results of our RRKM calculations of product branching ratios which show that phenyldiacetylene is practically the exclusive reaction product in the collision energy range of 0–60 kJ mol⁻¹. The calculations also indicate that at zero collision energy 62% and 38% of phenyldiacetylene are produced from **i2** and **i1**, respectively, with the pathway branching ratio changing to 47/53 at 60 kJ mol⁻¹. At the experimental collision energy of 46 kJ mol⁻¹ the calculated contributions of the two pathways are nearly equivalent.

We therefore propose that the reaction of the phenyl radical with diacetylene is initiated by an addition of the phenyl radical *via* an entrance barrier of 4 kJ mol⁻¹ to the C1 carbon atom of diacetylene forming the doublet radical intermediate **i1**. The latter ejects a hydrogen atom *via* a tight exit transition state placed 21 kJ mol⁻¹ above the separated products or isomerizes to **i2** *via* the **i1** → **i4** → **i5** → **i2** pathway and then eliminates an H *via* a barrier located 20 kJ mol⁻¹ above the phenyldiacetylene + H products. The overall reaction was found to be exoergic by 49 ± 26 kJ mol⁻¹ (experiment) and 44 ± 10 kJ mol⁻¹ (theory). Note that this reaction follows a similar pattern as the reaction of the phenyl radical with acetylene studied earlier in our group.²⁹ Here, the phenyl radical also added to the carbon atom of the hydrocarbon reactant (acetylene) forming a doublet radical intermediate which ejected a hydrogen atom *via* a tight exit transition state. This reaction was found to be exoergic as well by 41 ± 10 kJ mol⁻¹. It should be noted, that the reaction path proposed here has been derived in earlier studies on the C₁₀H₇ potential energy surface investigating successive ethynyl additions to phenyl.⁴ Another high energy route was found to lead from **i2** to 2-naphthyl radical and then to 1,2-didehydronaphthalene plus hydrogen located 21 kJ mol⁻¹ below the products phenyldiacetylene plus hydrogen. This pathway has been omitted here since it has a transition state located 45 kJ mol⁻¹ above the reactants, an energy barrier prohibiting it from being a competitive reaction channel.

The formation of phenyldiacetylene, like in the exoergic reaction through addition of a phenyl radical to diacetylene shown here, becomes relevant to combustion modeling aimed at understanding soot formation. Phenyldiacetylene can also be reached through the HACA mechanism *via* formation of phenylacetylene²⁹ or through ethynyl addition to phenylacetylene.⁴ From phenyldiacetylene further molecular mass growth processes by the HACA mechanism, diacetylene or ethynyl additions can reach PAHs. For example, ethynyl addition to phenyl diacetylene has been shown to reach 1-ethynyl-2-butadiynylbenzene from which a subsequent ethynyl addition can result in formation of substituted naphthyl radicals, such as 3,4-diethynyl-1-naphthyl plus hydrogen and 3,4-diethynyl-1,2-didehydronaphthalene plus hydrogen.⁴ Ethynyl-naphthyl radicals can also be formed directly by hydrogen addition to 1-ethynyl-2-butadiynylbenzene, a process which possesses a small energy barrier that is easily surmountable in the high temperatures of combustion environments.

6. Conclusion

We conducted the crossed molecular beam reactions of the phenyl and D5-phenyl radicals with diacetylene at a collision energy of 46 kJ mol⁻¹. The chemical dynamics were found to be indirect (complex forming reaction mechanisms) and initiated by an addition of the phenyl/D5-phenyl radical with its radical center to the C1-carbon atom of the diacetylene reactant. This process involved an entrance barrier of 4 kJ mol⁻¹ and lead to a bound doublet radical intermediate(s), which emitted a hydrogen atom *via* tight exit transition states placed 20–21 kJ mol⁻¹ above the separated phenyldiacetylene plus atomic hydrogen products. The overall reaction was determined to be exoergic by 49 ± 26 kJ mol⁻¹ (experiment) and 44 ± 10 kJ mol⁻¹ (theory) and depicts an efficient pathway to the formation of the phenyldiacetylene molecule in sooting combustion flames.¹⁰

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