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Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Reaction dynamics of the phenyl radical (C_6H_5) with 1-butyne ($HCCC_2H_5$) and 2-butyne (CH_3CCCH_3)

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ARTICLE INFO

Article history:

Received 5 May 2009

In final form 16 September 2009

Available online 19 September 2009

ABSTRACT

The reactions of the phenyl radical (C_6H_5) with 1-butyne ($HCCC_2H_5$) and 2-butyne (CH_3CCCH_3) were studied in a crossed molecular beam machine to shed light on the formation of $C_{10}H_{10}$ isomers in combustion flames. Combining these data with electronic structure calculations, we find that both reactions involve indirect scattering dynamics and are initiated by additions of the phenyl radical with its radical center to the acetylenic carbon atoms. The reaction intermediates fragmented through the ejection of hydrogen atoms yielding 1-phenyl-3-methylallene and 1-phenyl-1-butyne (both from 1-butyne) as well as 1-phenyl-1-methylallene (from 2-butyne).

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1. Introduction

During the last decades, the $C_{10}H_{10}$ potential energy surface (PES) has received considerable attention due to the importance of one of its isomers, the dihydronaphthalene molecule, a precursor of aromatic naphthalene in combustion processes and in the interstellar medium (ISM). Here, polycyclic aromatic hydrocarbons (PAHs) [1] and related molecules such as partially hydrogenated species like dihydronaphthalene [2–4] and ionized PAHs [5,6] are ubiquitous in terrestrial and extraterrestrial settings. On Earth, they are generated in combustion processes of fossil fuel as toxic byproducts and, hence, represent severe air and marine pollutants [7–9]. They further enhance global warming and hold mutagenic [10] and carcinogenic [11–13] potential. On the other hand, in the interstellar medium, PAH-like species are considered as carriers of the unidentified infrared emission bands (UIBs) [14,15] and of the diffuse interstellar bands (DIBs) [16]. Consequently, PAH-like species are of major importance to rationalize the chemical processing of carbon-rich environments including planetary nebulae and circumstellar envelopes of carbon stars, among them IRC+10216 as the most prominent member.

Due to the importance of the $C_{10}H_{10}$ PES, various laboratory experiments involving crossed molecular beams and kinetic studies as well as computations have been conducted. These projects accessed the related $C_{10}H_{11}$ surfaces via bimolecular gas phase reactions of phenyl radicals (C_6H_5) with four thermodynamically stable C_4H_6 isomers: 1,3-butadiene ($H_2CCHCHCH_2$) [17–19], 1,2-butadiene ($H_2CCCHCH_3$) [20], 1-butyne ($HCCC_2H_5$), and 2-butyne (CH_3CCCH_3). It should be stressed that these C_4H_6 isomers have

been detected in combustion flames of, for instance, ethylene, at concentrations similar to those of vinylacetylene [21,22]. The 1,3-butadiene isomer was monitored in cyclohexane [23], isobutene [24], heptane [25], ethane [26], and methane flames [27]. Utilizing the Advanced Light Source in Berkeley, Cool et al. probed, for instance, the 1,3-butadiene isomer via photoionization mass spectrometry using tunable vacuum ultraviolet photons from 8.5–10.0 eV [28]. It should be emphasized that 1,3-butadiene can exist in its cis and trans-form, the latter is more stable by about 12 kJ mol^{-1} compared to the cis isomer. At typical flame temperatures of up to 3000 K, up to 60% of the 1,3-butadiene molecules prevail in its cis-form. The 1-butyne isomer prevails in cyclohexane and in n-heptane as well as iso-octane flames, note that 2-butyne (dimethylacetylene) is present in combustion processes of polyethylene [29], as well as in acetylene, propyne, propadiene, and 1,3-butadiene flames [30,31]. Most importantly, these isomers can be interconverted via hydrogen atom addition–hydrogen atom elimination pathways. For instance, a recent investigation of the unimolecular decomposition of the 1-buten-2-yl radical, $H_2CCC_2H_5$, verified the formation of the 1-butyne and 1,2-butadiene isomers via an atomic hydrogen emission [32]. Therefore, a reversed reaction sequence is expected to convert a significant fraction of 1-butyne to the 1,2-butadiene isomer via atomic hydrogen addition–elimination pathways. Recently, we have started a systematic study of the reactions of phenyl radicals with C_4H_6 isomers 1,3-butadiene [19] and 1,2-butadiene [20] and identified two distinct $C_{10}H_{10}$ products. Here, we are expanding these studies and present crossed molecular beam data on the reactions of phenyl radicals with two additional isomers: 1-butyne ($HCCC_2H_5$) and 2-butyne (CH_3CCCH_3). The experiments are combined with electronic structure calculations aimed to elucidate the nature of the $C_{10}H_{10}$ isomers formed. We also investigated the methyl (CH_3) and ethyl

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(C₂H₅) elimination channels as well as multiple hydrogen abstraction pathways by the phenyl radical to form C₄H₅ isomers plus benzene. Finally, RRKM calculations were conducted on both surfaces.

2. Experimental section

A supersonic beam of helium-seeded phenyl radicals (C₆H₅, X²A₁) at fractions of about 0.1% was formed via flash pyrolysis of nitrosobenzene (C₆H₅NO, Fluka) [33,34] in the primary source chamber employing a modified Chen source [35]. The mixture of the helium carrier gas and the nitrosobenzene vapor was introduced by a piezoelectric valve operated at a rate of 200 Hz and a backing pressure of about 900 Torr and passed a heated silicon carbide tube (1200–1500 K). Under our experimental conditions, the decomposition of nitrosobenzene to yield nitrogen monoxide (NO) and the phenyl radical (C₆H₅) was quantitative [34]. After passing a skimmer, a part of the phenyl radical beam was selected by a four-slot chopper wheel. This section of the beam crossed perpendicularly a pulsed supersonic beam of 1-butyne (HCCC₂H₅) and 2-butyne (CH₃CCCH₃) (Fluka, 530–550 Torr) generated in the secondary source chamber. Table 1 compiles the peak velocities together with the speed ratios of the crossing segments of the beams. During the crossed beam experiments, reactively scattered products were detected in the time-of-flight (TOF) mode by a rotatable quadrupole mass spectrometric detector after electron impact ionization of the neutral reaction products at 80 eV. The detector is rotatable within the plane defined by both supersonic beams inside the main chamber. After recording TOF spectra at several angles and integrating them, a laboratory angular distribution (LAB) of the reactively scattered species at a defined mass-to-charge (*m/z*) ratio was derived. By fitting the TOF spectra and LAB angular distribution of products, the center-of-mass (CM) angular distribution $T(\theta)$ and product translational energy distribution $P(E_T)$ were obtained utilizing a forward-convolution routine [36–38]. Best fits were derived with an entrance barrier (E_o) to the reaction of about 10–30 kJ mol⁻¹ incorporating an energy dependent cross section, $\sigma(E_c)$, of the form $\sigma(E_c) \sim [1 - E_o/E_c]$, utilizing the line-of-center model with the collision energy E_c for $E_c \geq E_o$ [39]. Due to the low signal counts, we had to record up at least 4×10^6 TOF spectra to obtain a reasonable signal-to-noise ratio of the reactively scattered species.

3. Results

3.1. Laboratory data

Considering reactive scattering signal, TOF spectra were monitored at mass-to-charge ratios, *m/z*, from *m/z* = 130 (C₁₀H₁₀⁺) to *m/z* = 128 (C₁₀H₈⁺). For each system, the TOF data at different *m/z* values depicted identical pattern and – after scaling – overlapped. Consequently, signal at lower *m/z* = 129 and *m/z* = 128 originated only from dissociation ionization of the parent molecule (C₁₀H₁₀) in the electron impact ionizer of the detector. It is important to

Table 1

Peak velocities (v_p), speed ratios (S), center-of-mass angle (θ_{CM}), and the collision energies (E_c) of the reaction of phenyl radicals with 1-butyne (HCCC₂H₅) and 2-butyne (CH₃CCCH₃).

	v_p (ms ⁻¹)	S	E_c (kJ mol ⁻¹)	θ_{CM}
C ₆ H ₅ (X ² A ₁)	2974 ± 42	6.7 ± 0.9	150 ± 4	10.6 ± 0.4
HCCC ₂ H ₅ (X ¹ A')	791 ± 16	6.1 ± 0.5	–	–
C ₆ H ₅ (X ² A ₁)	2974 ± 42	6.7 ± 0.9	152 ± 6	10.6 ± 0.5
CH ₃ CCCH ₃ (X ¹ A _{1g})	800 ± 23	5.8 ± 0.8	–	–

stress that both data sets for the 1-butyne and 2-butyne systems could be fit with identical, one-channel fit, center-of-mass functions. Further, the detection of signal at *m/z* = 130 (C₁₀H₁₀⁺) clearly indicated that the phenyl radical versus hydrogen atom pathway is open in both reactions studied, due to the best signal-to-noise ratio, time-of-flight data were recorded at a mass-to-charge ratio of *m/z* = 130 (Fig. 1). Due to the unfavorable kinematics, we did not detect the methyl loss channel (from 1-butyne and 2-butyne) and the ethyl pathway (from 1-butyne). Similar to the reactions of phenyl radicals with 1,3-butadiene and 1,2-butadiene, the noise level at *m/z* = 78 (¹³CC₅H₅⁺) from the inelastically scattered phenyl radicals was too high to detect the hydrogen abstraction pathway to form benzene (C₆H₆). Finally, after integrating the TOF spectra at each angle and accounting for the data accumulation times, the laboratory angular distributions of signal recorded at *m/z* = 130 (C₁₀H₁₀⁺) could be derived for both reactions (Fig. 2). Both LAB distributions look very similar, are very narrow, and are spread over only about 13° within the scattering plane defined by both reactant beams. It should be stressed that due to the limited signal-to-noise of even the kinematically favorable hydrogen loss pathway, it is difficult to probe the methyl loss. This would require the operation of continuous pyrolytic sources to enhance the duty cycle; this is planned in the future.

3.2. Center-of-mass translational energy, $P(E_T)$ s, and angular distributions, $T(\theta)$ s

Having discussed the laboratory data, we are turning our attention now to the center-of-mass angular ($T(\theta)$) and translational energy distributions ($P(E_T)$) (Fig. 3). Based on the time-of-flight data, it is evident that for the phenyl plus 1-butyne and 2-butyne reactions, C₁₀H₁₀ isomer(s) together with the light hydrogen atom counter fragment are formed via bimolecular collisions. In order to derive information on the reaction dynamics and on the underlying mechanism(s), the laboratory data (Figs. 1 and 2) are transformed into the center-of-mass frame to yield the center-of-mass angular $T(\theta)$ and translational energy $P(E_T)$ distributions (Fig. 3). A crucial result is that both data sets from the phenyl plus 1-butyne and phenyl plus 2-butyne reactions could be fit with identical center-of-mass functions. We shall address the derived center-of-mass angular distribution, $T(\theta)$, first. The angular flux distributions show intensity over the complete angular range from 0° to 180°. For the best fit function, the distribution is asymmetric around 90° and depicts an enhanced flux in the forward hemisphere with respect to the phenyl radical beam. Best fits were derived with ratios at the poles, $I(0^\circ)/I(180^\circ)$, of 1.22. However, within the error limits, an isotropic fit or slightly more forward-pronounced peaking with $I(0^\circ)/I(180^\circ) = 1.47$ could fit the laboratory data for both systems as well. The shape of the center-of-mass angular distribution has important implications for the reaction mechanism. First, the flux present over the complete angular range strongly indicates that *both* reactions are dictated by indirect scattering dynamics involving complex formation (here: C₁₀H₁₁ reaction intermediate(s)). Further, the slight asymmetry of the center-of-mass angular distributions let us conclude that the lifetime(s) of the C₁₀H₁₁ intermediate(s) is shorter than (or comparable with) its rotational period (osculating complex model). The relatively mild polarization of the center-of-mass angular distribution results from the poor coupling between the initial and final orbital angular momentum due to the light mass of the departing hydrogen atom [39]. Here, angular momentum conservation suggests that most of the initial orbital angular momentum channels into the rotational excitation of the polyatomic C₁₀H₁₀ molecule.

Considering the $P(E_T)$, it is worth mentioning that best fits were derived with distributions extending to maximum translational energy releases, E_{Tmax} , of 165 ± 30 kJ mol⁻¹. Here, the high-energy

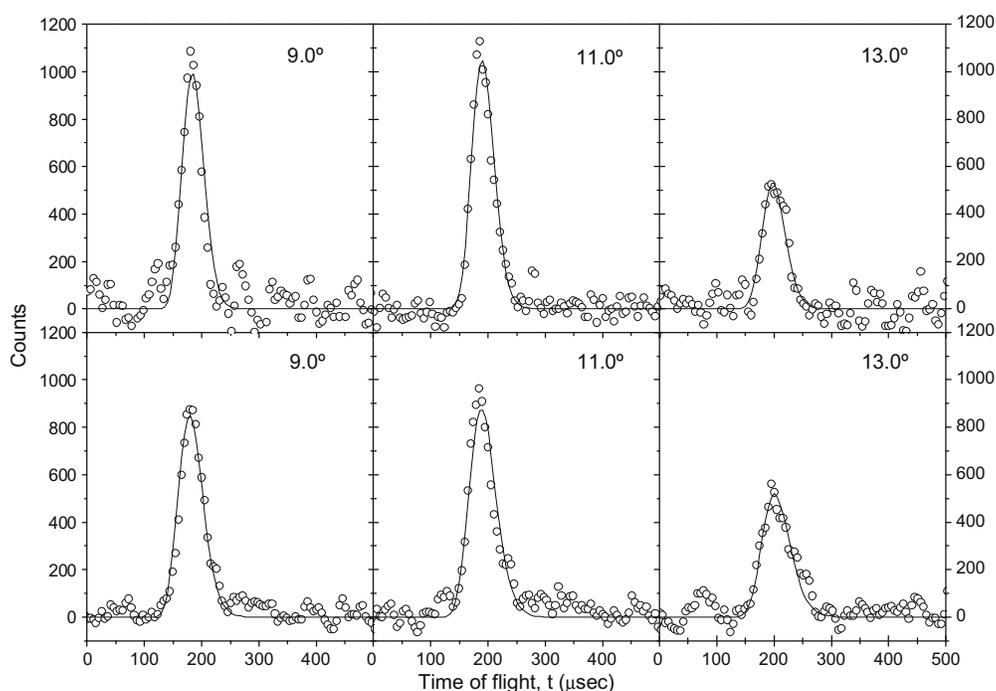


Fig. 1. Selected time-of-flight data of the $C_{10}H_{10}$ molecule(s) formed in the reactions of phenyl radicals with 1-butyne and 2-butyne at collision energies of 150 kJ mol^{-1} (upper row) and 152 kJ mol^{-1} (lower row), respectively, recorded at mass-to-charge ratio ($m/z = 130; C_{10}H_{10}^+$). The open circles are the experimental data, and the solid lines are the fits by forward-convolution routine.

cutoffs are equivalent to the sum of the absolute energy of the reaction and the collision energy. Based on these numbers and the collision energy (Table 1), the experimental reaction energy can be derived to be $-14 \pm 30 \text{ kJ mol}^{-1}$. We recognize that this presents a substantial error, but the weak scattering signal coupled with the light hydrogen atom leaving the fragmenting complex and the reduced recoil sphere of the $C_{10}H_{10}$ product(s) make an exact determination of the reaction energy very difficult. Two important conclusions can be further derived from the center-of-mass translational energy distribution. First, the center of mass translational energy distribution depicts a significant distribution maximum at about $20\text{--}35 \text{ kJ mol}^{-1}$. This suggests that the reaction intermediates decompose via a tight exit transition states to the final $C_{10}H_{10}$ products. Based on the principle of microscopic reversibility of a chemical reaction, the reverse reaction of hydrogen atom addition to the $C_{10}H_{10}$ isomer(s) should have an entrance barrier, therefore, the hydrogen atom most likely adds to a carbon-carbon triple or double bond. Finally, we can determine the fraction of the energy channeling into the translational modes of the products, i.e. $\langle E_T \rangle / E_{max}$ with $\langle E_T \rangle$ being the averaged translational energy of the products of about $45 \pm 5 \text{ kJ mol}^{-1}$. This suggests fractions of about $27 \pm 4\%$ for both systems, this order reflects indirect scattering dynamics [40].

4. Discussion

In case of polyatomic reactants, it is often beneficial to combine the experimental data with electronic structure calculations (Fig. 4). Here, we merge *ab initio* calculations on the reactions of phenyl radicals with 1-butyne and 2-butyne conducted at the G3(MP2,CC)//B3LYP/6-311G** + ZPE (B3LYP/6-311G**) level of theory [41] using the GAUSSIAN 98 [42] and MOLPRO 2002 [43] program packages. Let us focus first on the reaction of phenyl radicals with 2-butyne (dimethylacetylene). The crossed molecular beams data suggest a reaction energy of $-14 \pm 30 \text{ kJ mol}^{-1}$ to the $C_{10}H_{10}$ iso-

mer plus hydrogen. Within the error limits, the energetics agrees with the computed data of $-19 \pm 5 \text{ kJ mol}^{-1}$ to form 1-methyl-1-phenyl-allene (**p5**) plus atomic hydrogen. How can this product be formed? Recall that the center-of-mass functions suggested an entrance barrier to reaction (Section 2), indirect reaction mechanism via $C_{10}H_{11}$ intermediate(s) (based on the shape of the center-of-mass angular distribution and on the fraction of energy released into the translational degrees of freedom of the products, Section 3.2), and a tight exit transition state (Section 3.2). These experimental findings are fully supported by our electronic structure calculations. The latter predicted that the reaction of phenyl radicals with 2-butyne proceeds via addition of the phenyl radical with its unpaired electron located in the σ -symmetric A_1 orbital to one of the acetylenic carbon atoms of the 2-butyne molecule. This process has an entrance barrier of 12 kJ mol^{-1} and forms a doublet radical intermediate **i2** which is stabilized by 156 kJ mol^{-1} with respect to the separated reactants. The latter decomposes through a tight exit transition state located about 11 kJ mol^{-1} above the final products. The extracted dynamics and reaction mechanism are similar to the one found in the reaction of ground state cyano radicals ($CN, X^2\Sigma^+$) with 2-butyne studied earlier in our group except the absence of an entrance barrier in the reaction of the cyano radical [44]. It is interesting to recognize that the addition of the phenyl group to the C2 carbon atom is followed by a release of atomic hydrogen from the C4 carbon atom, therefore, the energy, which is initially 'localized' in the chemically activated and newly formed carbon-carbon bond of **i2**, has to 'flow' over three bonds to yield the carbon-hydrogen bond rupture. In the related phenyl-methylacetylene system [45], the $C_6H_5HCCCH_3$ adduct (once again formed via addition of the phenyl radical to the acetylenic, in this case the least substituted, carbon atom holding the acetylenic hydrogen atom) was found to fragment at a similar collision energy only via atomic hydrogen loss from the C1 carbon atom to form $C_6H_5CCCH_3$. No hydrogen loss from the methyl group, which would result in the formation of phenylallene ($C_6H_5HCCCH_2$),

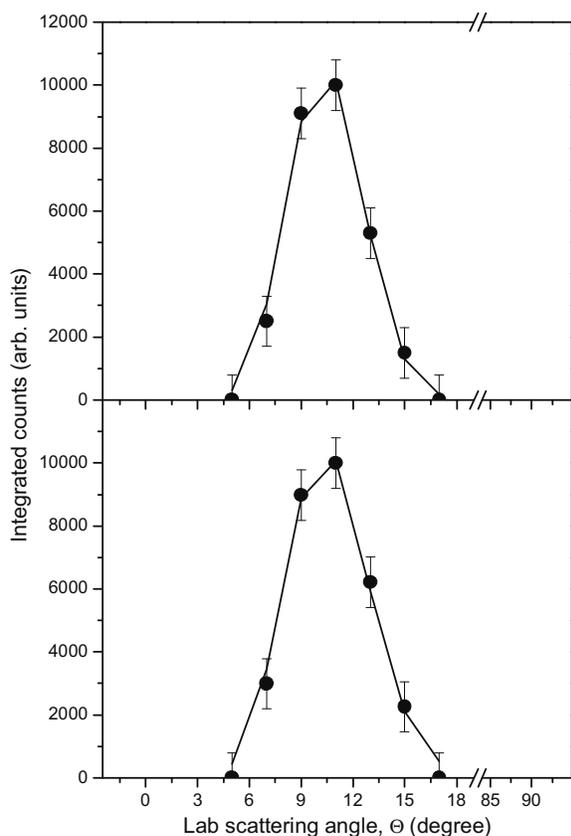


Fig. 2. Laboratory angular distributions of ion counts recorded at $m/z = 130$ ($C_{10}H_{10}^+$) in the reaction of phenyl radicals with 1-butyne and 2-butyne at collision energies of 150 kJ mol^{-1} (upper) and 152 kJ mol^{-1} (lower), respectively. The solid circles are the experimental data, and the solid lines are the fits. C.M. defines the center-of-mass angle.

was observable. This means that in the phenyl–methylacetylene system, the life time of the $C_6H_5HCCCH_3$ intermediate is too short to allow an energy randomization and ‘energy flow’ over three

bonds to occur. This correlates clearly with a rise of the life time of the radical intermediates formed in the reactions of phenyl radicals with acetylene, methylacetylene, and 2-butyne (dimethylacetylene), i.e. C_6H_5HCCH , $C_6H_5HCCCH_3$, and $C_6H_5CH_3CCCH_3$, as the numbers of atoms and hence vibrational degrees of freedom increase. Here, the longer the lifetime, the higher the chance for a complete energy randomization to occur. Likewise, this trend is also observed in the shape of the center-of-mass angular distributions of these systems. Here, at comparable collision energies, the center-of-mass angular distributions become less forward scattered when going from the acetylene and methylacetylene to the 2-butyne (dimethylacetylene) system [46].

Having proposed the underlying reaction dynamics of the phenyl-2-butyne reaction, we are turning our attention now to the reaction of phenyl radicals with the 1-butyne isomer. Again, we compare first the experimentally derived energetics to form the $C_{10}H_{10}$ isomer ($-14 \pm 30 \text{ kJ mol}^{-1}$) with the computed ones to yield 1-phenyl-1-butyne (**p1**, $-39 \pm 5 \text{ kJ mol}^{-1}$) and 1-phenyl-3-methylallene (**p2**, $-40 \pm 5 \text{ kJ mol}^{-1}$). However, within the error limits, both the synthesis of 1-phenyl-1-butyne (**p1**) (-39 kJ mol^{-1}) and 1-phenyl-3-methylallene (**p2**) (-40 kJ mol^{-1}) can explain the experimentally derived reaction energy of $-14 \pm 30 \text{ kJ mol}^{-1}$. So we have to resolve the question which is (are) the dominating reaction product(s). A closer look at the underlying reaction dynamics and a comparison with the phenyl-2-butyne system help to shed light on this question. Most importantly, the indirect scattering dynamics to generate **p1** and/or **p2** is apparent from the shapes of the center-of-mass angular distributions as discussed in Section 3.2 and also from the computational studies which suggest that the phenyl radical adds to the sterically less hindered α -carbon atom. Only this addition process and subsequent hydrogen atom emission can explain the formation of **p1** and/or **p2**. The larger cone of acceptance of the sterically less hindered, non-substituted carbon atom was found to be the more accessible pathway for the initial addition step of the phenyl radical in related reactions with methyl-substituted unsaturated hydrocarbons such as methylacetylene (CH_3CCH) [45] and propylene ($CH_3C_2H_3$) [47]. The presence of tight exit transition states, which are correlated with a significant change in electron density from the intermediate to the final products, is also obvious from the off-zero peaking of the center-of-mass translational energy distributions. Having established an indirect reaction mechanism via a phenyl radical addition to the sterically less hindered, terminal carbon atom

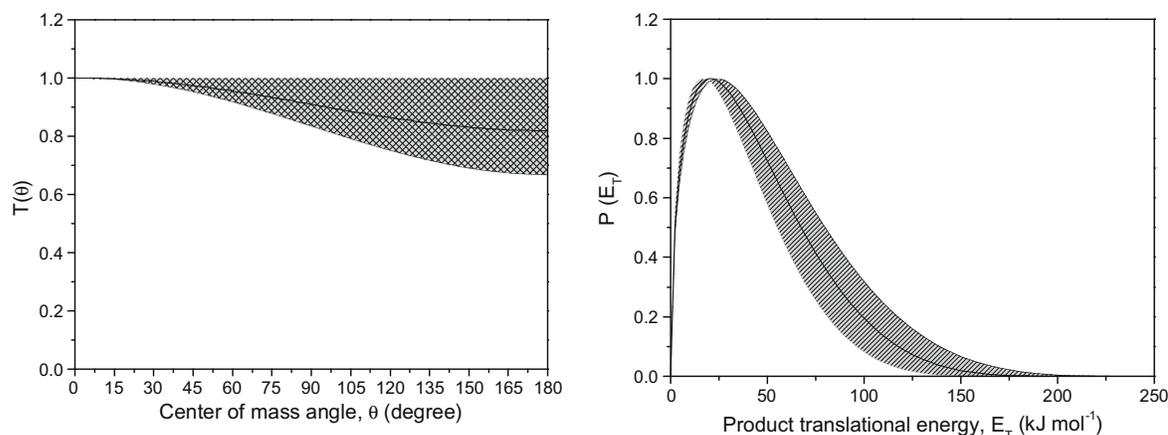


Fig. 3. Center-of-mass translational energy $P(E_T)$ s (right) and angular $T(\theta)$ s (left) distributions of the $C_{10}H_{10}$ products formed in the reaction of phenyl radical with 1-butyne and 2-butyne. The hatched areas account for the experimental error limits of the TOF spectra (Fig. 1) and laboratory angular distribution (Fig. 2) as well as the error limits of peak velocities and speed ratios of both supersonic beams (Table 1). The TOF and laboratory angular distributions for both the 1-butyne and 2-butyne isomers could be fit with identical center-of-mass functions.

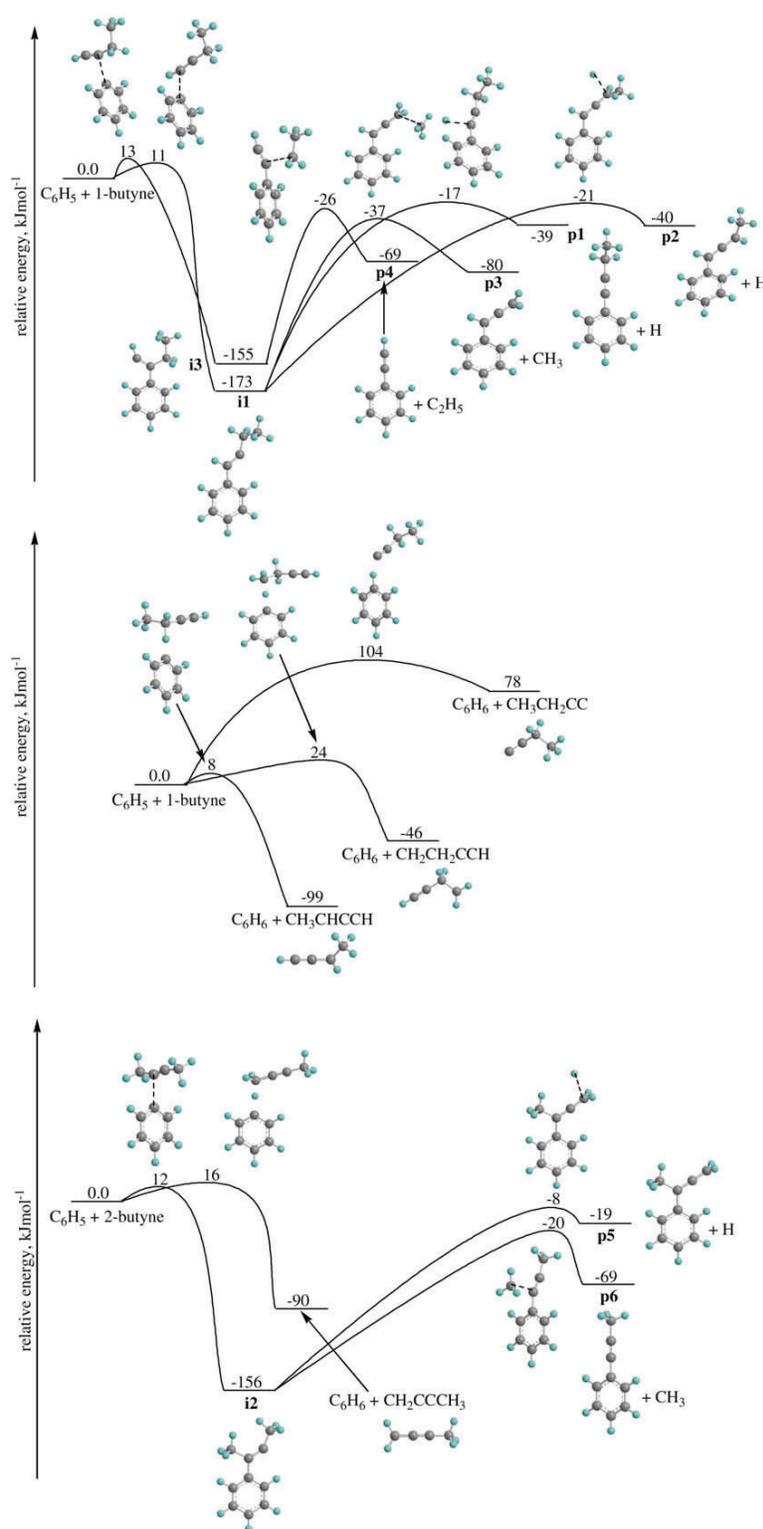


Fig. 4. Potential energy surfaces (PESs) for the reaction of phenyl radicals with 1-butene and 2-butene calculated at the G3(MP2,CC)//B3LYP/6-311G** + ZPE(B3LYP/6-311G**) level of theory. The calculations were conducted for methyl and ethyl group losses, hydrogen atom replacement pathways, and hydrogen abstraction routes leading to benzene.

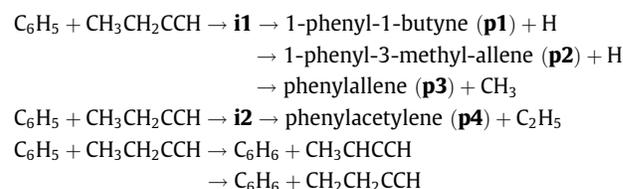
(C1) of 1-butene to form a doublet reaction intermediate **i1**, we still have to elucidate if isomer **p1** and/or **p2** are the final reaction products. For this, it is important to compare this reaction with the

dynamics of related systems studied at similar collision energies in our laboratory [20]. The reaction of phenyl radicals with methylacetylene was found to proceed through addition to the C1 carbon

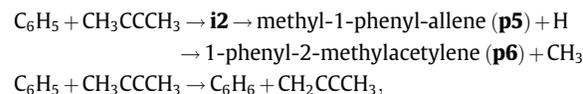
atom – to a $C_6H_5HCCCH_3$ intermediate, the latter decomposed to phenyl-methylacetylene ($C_6H_5CCCH_3$) plus atomic hydrogen. At collision energies between 91 and 161 kJ mol^{-1} , the lifetime of the reaction intermediate was too low to allow an ‘energy flow’ from the initially activated bond to the acetylenic carbon–hydrogen bond yielding the phenylallene molecule via hydrogen loss from the acetylenic group to occur. Compared to this, the increase of the life time of the $C_6H_5H_2CCHCH_3$ intermediate formed in the reaction of phenyl radicals with propylene allowed an energy randomization and ‘flow’ from the activated carbon–carbon bond to the carbon–hydrogen bonds in the methyl group, this resulted in the formation of two structural isomers as discussed previously: *cis/trans*-1-phenylpropene ($CH_3CHCHC_6H_5$) (80–90%) and 3-phenylpropene ($H_2CCHCH_2C_6H_5$). Here, the enhanced life time of the $C_6H_5H_2CCHCH_3$ intermediate (phenyl-propylene reaction) compared to the $C_6H_5HCCCH_3$ intermediate (phenyl-methylacetylene reaction) was the result of an increased numbers of vibration modes of the reaction intermediates. This likely allowed an energy ‘flow’ from the initially activated bond to the carbon–hydrogen bond rupture in the methyl group of the propylene reactant. In a similar way, the reaction of phenyl radicals with 1,2-butadiene was suggested to form two isomers: 1-phenyl-3-methylallene and 1-phenyl-butyne-2. Based on this qualitative concept, which has been verified under single-collision conditions involving phenyl radical reactions, we would like to propose that intermediate **i1** fragments via atomic hydrogen emission to form two $C_{10}H_{10}$ product(s): 1-phenyl-1-butyne (**p1**) and 1-phenyl-3-methylallene (**p2**). According to our RRKM calculations, if the fragmentation of **i1** follows a statistical behavior, the branching ratio of **p1/p2** would be about 2.4:1 at the experimental collision energy of 150 kJ mol^{-1} .

For completeness, although it is not the primary target of this investigation which focuses on the formation of distinct $C_{10}H_{10}$ isomers, we have studied theoretically other possible pathways of the reactions of phenyl radical with 1- and 2-butyne (Fig. 4). The **i1** intermediate in the reaction of phenyl radicals with 1-butyne can lose not only a hydrogen atom but also the methyl group producing a C_9H_9 isomer phenylallene (**p3**). The calculated barrier for the methyl loss from **i1** is 136 kJ mol^{-1} , with the transition state residing 37 kJ mol^{-1} below the reactants and also 16–20 kJ mol^{-1} lower in energy than the transition states for hydrogen atom elimination yielding **p1** and **p2**. Therefore, the methyl loss channel is energetically preferable as compared to the hydrogen elimination pathway. We conducted RRKM calculations on the three dissociation channels of **i1** and obtained branching ratios as 11.8:4.9:83.3 for the formation of 1-phenyl-1-butyne (**p1**), 1-phenyl-3-methylallene (**p2**), and phenylallene (**p3**), respectively, at the collision energy of 150 kJ mol^{-1} , if the reaction is statistical. However, the pathways passing via **i1** do not exhaust all possibilities for the $C_6H_5 + 1$ -butyne reaction to occur. Phenyl radical can add to the second acetylenic carbon in 1-butyne linked to the C_2H_5 moiety producing another initial intermediate **i3**. **i3** resides in a 155 kJ mol^{-1} potential energy well, is 18 kJ mol^{-1} less stable than **i1**, and its formation from the reactants requires a slightly higher barrier of 13 kJ mol^{-1} (compare to 11 kJ mol^{-1} for C_6H_5 addition to the terminal acetylenic C atom leading to **i1**). Hydrogen atom eliminations from **i3** are unfavorable because they would lead to either biradical or carbene-like product structures and the only feasible dissociation channel is the loss of the ethyl group, C_2H_5 , with the production of phenylacetylene (**p4**), 69 kJ mol^{-1} exothermic relative to the reactants. The transition state for the C_2H_5 loss lies 26 kJ mol^{-1} lower in energy than $C_6H_5 + 1$ -butyne, in the middle between the transition states for H and CH_3 eliminations. Besides the addition channels described above, the reaction can also proceed by direct H abstractions by the phenyl radical from C_4H_6 producing benzene in conjunction with C_4H_5 isomers. The H abstraction from the CH_2 group in 1-butyne is most favorable, as

it occurs with a barrier of only 8 kJ mol^{-1} . This process would result in the formation of C_6H_6 together with the CH_3CHCCH isomer of the C_4H_5 radical residing 99 kJ mol^{-1} below $C_6H_5 + 1$ -butyne. The H abstraction from the CH_3 group requires a 24 kJ mol^{-1} barrier and produces $C_6H_6 + CH_2CH_2CCH$ with the exothermicity of 46 kJ mol^{-1} . Finally, the H abstraction from the terminal acetylenic carbon is unfavorable because it leads to the endothermic $C_6H_6 + CH_3CH_2CC$ products (78 kJ mol^{-1} above the reactants) and involves a very high barrier of 104 kJ mol^{-1} . In summary, the following reaction channels as summarized below are feasible and can be competitive depending on the reaction conditions. Unfortunately, RRKM theory cannot be applied here for the prediction of branching ratios for all potential products under single-collision conditions of crossed molecular beams because it treats only unimolecular reactions. Nevertheless, statistical theories can be applied to compute temperature and pressure dependent reaction rate constants and relative product yields at thermal conditions relevant to combustion and this will be a subject of our future theoretical work.



The **i2** intermediate formed in the $C_6H_5 + 2$ -butyne reaction can lose the CH_3 group attached to the C atom also linked to the phenyl moiety. The product is then another C_9H_9 isomer, 1-phenyl-2-methylacetylene (**p6**), residing 69 kJ mol^{-1} below the reactants. The barrier for the CH_3 elimination from **i2** is computed to be 12 kJ mol^{-1} lower than that for the H loss to form 1-methyl-1-phenylallene (**p5**) and RRKM calculations suggest that the CH_3 pathway dominates with a fraction above 99%. Because of the high symmetry of 2-butyne, only one direct H abstraction channel is possible. It leads to $C_6H_6 + CH_2CCCH_3$ with exothermicity of 90 kJ mol^{-1} via a barrier of 16 kJ mol^{-1} . In this case, the H abstraction channel is slightly less favorable than the phenyl radical addition producing **i2**. The competitive reaction pathways can be summarized as stated below.



One can see that the electronic structure calculations predict a greater variety of products in the reactions of phenyl radical with 1- and 2-butyne than the $C_{10}H_{10}$ isomers detected in the present crossed molecular beams study. This deviation may be attributed to several factors, such as possible non-statistical behavior of the reactions at the high collision energy of 150 kJ mol^{-1} , experimental difficulties in detection of product pairs containing heavier fragments (CH_3 , C_2H_5 , C_4H_5).

5. Conclusion

The reactions of the phenyl radical (C_6H_5) with 1-butyne ($HCCC_2H_5$) and 2-butyne (CH_3CCCH_3) were investigated under single-collision conditions utilizing a crossed molecular beams machine. In combination with electronic structure calculations, we found that the reactions involved indirect scattering dynamics and are initiated by additions of the phenyl radical with its radical center to the (sterically more accessible) acetylenic carbon atoms of the reactants. With respect to the formation of $C_{10}H_{10}$ isomers,

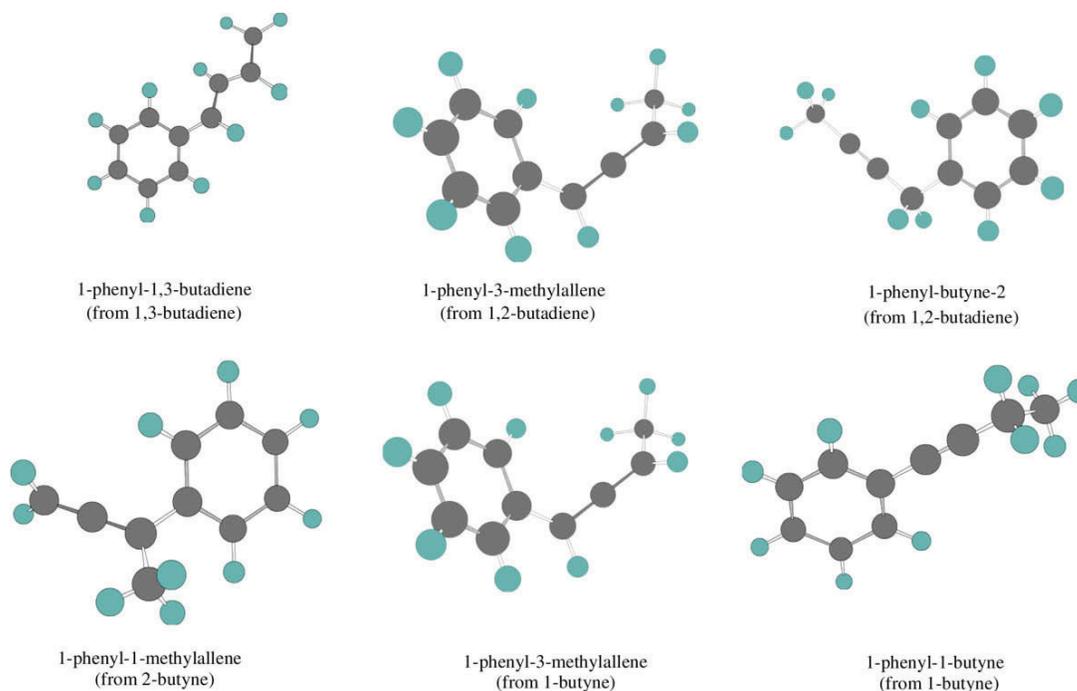


Fig. 5. Structures of the $C_{10}H_{10}$ products formed in the reaction of phenyl radicals with four the C_4H_6 isomers: 1,3-butadiene ($H_2CCHCHCH_2$; trans), 1,2-butadiene ($H_2CCCH(CH_3)$), 1-butyne ($HCCC_2H_5$), and 2-butyne (CH_3CCCH_3).

the reaction intermediates fragmented through the ejection of hydrogen atoms yielding 1-phenyl-3-methylallene (**p2**) and 1-phenyl-1-butyne (**p1**) (both from 1-butyne) and 1-phenyl-1-methylallene (**p5**) (from 2-butyne). All fragmentation proceeded via tight exit transition states. Calculations indicate that other reaction products are also feasible, including C_9H_9 (phenylallene (**p3**) from 1-butyne and 1-phenyl-2-methylacetylene (**p6**) from 2-butyne) + CH_3 , C_8H_6 (phenylacetylene) + C_2H_5 from 1-butyne, and C_6H_6 + C_4H_5 isomers, however, they were not observed here.

This study completes the investigation of the reaction dynamics of phenyl radicals with C_4H_6 isomers to form $C_{10}H_{10}$ isomers at high (>100 kJ mol $^{-1}$) collision energies. We found that the chemical dynamics of these reactions involving 1,3-butadiene, 1,2-butadiene, 1-butyne, and 2-butyne can be characterized as follows: all reactions are initiated by an addition of the phenyl radical with its radical center to the (sterically less hindered) carbon atom. This leads via indirect scattering dynamics to reaction intermediates which are stabilized by 154 – 207 kJ mol $^{-1}$ with respect to the separated reactants. The indirect nature of the reactions was also verified in terms of the fraction of available energy channeling into the translational degrees of freedom, i.e. about 27–35%. It should be noted that these addition processes have, with the possible exception of 1,3-butadiene, entrance barrier in the order of 8–12 kJ mol $^{-1}$. All intermediates decomposed via atomic hydrogen loss involving tight transition states which were located 11–30 kJ mol $^{-1}$ above the energy of the separated products. The overall reactions were found to be exoergic by 19–43 kJ mol $^{-1}$ forming distinct $C_{10}H_{10}$ isomers as compiled in Fig. 5. However, in all systems, the life time of the reaction intermediates was found to be too short to allow ring closure processes and/or hydrogen migrations to occur. Future experiments utilizing photolytic phenyl radical sources will be conducted at lower collision energies. This lower collision energy in turn will likely result in an enhanced life time of the reaction intermediate leading – hopefully – to hydrogen migration and ring closure processes yielding ultimately to hydrogenated naphthalene isomers.

Acknowledgements

This work was supported by the US Department of Energy, Basic Energy Sciences DE-FG02-03ER15411 to the University of Hawaii and DE-FG02-04ER15570 to Florida International University.

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