Crossed beam reaction of phenyl radicals with unsaturated hydrocarbon molecules. I. Chemical dynamics of phenylmethylacetylene \( \left( \text{C}_6\text{H}_5\text{CCCH}_3; \chi^1A' \right) \) formation from reaction of \( \text{C}_6\text{H}_5(\chi^2A_1) \) with methylacetylene, \( \text{CH}_3\text{CCH}(\chi^1A_1) \)

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(Received 31 August 1999; accepted 9 December 1999)

The chemical reaction dynamics to form phenylmethylacetylene, \( \text{C}_6\text{H}_5\text{CCCH}_3(\chi^1A') \), via reactive collisions of the phenyl radical \( \text{C}_6\text{H}_5(\chi^2A_1) \) with methylacetylene, \( \text{CH}_3\text{CCH}(\chi^1A_1) \), are unraveled under single collision conditions in a crossed molecular beam experiment at a collision energy of 140 \( \text{kJ mol}^{-1} \). The laboratory angular distribution and time-of-flight spectra of \( \text{C}_6\text{H}_5^+ \) at \( m/e = 116 \) indicate the existence of a phenyl radical versus hydrogen replacement pathway. Partially deuterated methylacetylene, \( \text{CH}_3\text{C}^2\text{H}_2(\chi^1A_1) \), was used to identify the site of the carbon–hydrogen bond cleavage. Only the loss of the acetylenic hydrogen atom was observed; the methyl group is conserved in the reaction. Electronic structure calculations reveal that the reaction has an entrance barrier of about 17 \( \text{kJ mol}^{-1} \). Forward-convolution fitting of our data shows that the chemical reaction dynamics are on the boundary between an osculating complex and a direct reaction and are governed by an initial attack of the \( \text{C}_6\text{H}_5 \) radical to the \( \pi \) electron density of the \( \text{C}1 \) carbon atom of the methylacetylene molecule to form a short lived, highly rovibrationally excited \( \text{C}_6\text{H}_5\text{HCCCH}_3 \) intermediate. The latter loses a hydrogen atom to form the phenylmethylacetylene molecule on the \( ^2A' \) surface. The phenyllallene isomer channel was not observed experimentally. The dynamics of the title reaction and the identification of the phenyl versus hydrogen exchange have a profound impact on combustion chemistry and chemical processes in outflows of carbon stars. For the first time, the reaction of phenyl radicals with acetylene and/or substituted acetylene is inferred experimentally as a feasible, possibly elementary reaction in the stepwise growth of polycyclic aromatic hydrocarbon precursor molecules and alkyl substituted species in high temperature environments such as photospheres of carbon stars and oxygen poor combustion systems. © 2000 American Institute of Physics. [S0021-9606(00)01409-4]

I. INTRODUCTION

The reactions of phenyl radicals, \( \text{C}_6\text{H}_5 \), in their \( ^2A_1 \) electronic ground state with unsaturated hydrocarbons are strongly considered to be elementary processes leading to the synthesis of polycyclic aromatic hydrocarbons (PAHs) and ultimately to soot formation in oxygen-poor combustion processes as well as in the outflow of carbon-rich stars. Current chemical models postulate a stepwise PAH formation via phenyl radicals reacting with acetylene molecules, followed by a reactive collision of the radical intermediate with a second acetylene molecule, and a final ring closure to a naphthalene like PAH species. The phenyl radicals themselves are thought to be generated either by dimerization of propargyl radicals, \( \text{C}_6\text{H}_5(\chi^2B_2) \), via a benzene intermediate [reaction (1)] or from reaction of \( \text{C}_6\text{H}_5(\chi^2A') \) with acetylene, \( \text{C}_2\text{H}_2(\chi^1\Sigma^+_g) \) [reaction (2)]:

\[
\begin{align*}
\text{C}_6\text{H}_3(\chi^2B_2) + \text{C}_2\text{H}_2(\chi^1\Sigma^+_g) & \rightarrow \text{C}_6\text{H}_5(\chi^2A_1) + \text{H}(\chi^2S_{1/2}), \\
\text{C}_6\text{H}_3(\chi^2A') + \text{C}_2\text{H}_2(\chi^1\Sigma^+_g) & \rightarrow \text{C}_6\text{H}_5(\chi^2A_1).
\end{align*}
\]

Due to the potential significance of phenyl radicals in both combustion processes and extraterrestrial environments, a multitude of kinetic and spectroscopic investigations have been performed in the past. Hausman and Homann scavenged the phenyl radical as a methylhioether in sooting flames and thereby demonstrated explicitly that \( \text{C}_6\text{H}_5 \) exists in these high temperature combustion environments. Further, the rate constants for the reactions of phenyl radicals with a variety of molecules have been measured by cavity ring-down spectroscopy or other methods; data show very low rate constants at temperature ranges up to 1100 K rang-
studied by Lin and Co-workers should be benzene and Obviously, the products of the reaction of \( \text{C}_6\text{H}_5 \) with \( \text{H}_2 \) as circumstellar shells of carbon starts—were never probed. Modeling of combustion processes and PAH formation in reaction products—although crucial for a detailed chemical machine. Briefly, a pulsed supersonic beam of phenyl radi-

To obtain a complete understanding of the formation of PAHs in various interesting environments, it is crucial to set up a systematic research program for the investigation of the basic elementary chemical reactions leading to PAHs and their precursors on the most fundamental, microscopic level. In this paper, we present the first crossed molecular beam reaction of phenyl radicals reported so far, i.e., the reaction with methylacetylene, \( \text{CH}_3\text{CCH} \) [reaction (3)];

\[
\text{C}_6\text{H}_5(\text{X}^2\text{A}_1) + \text{CH}_3\text{CCH}(\text{X}^1\text{A}_1) \\
\rightarrow \text{C}_6\text{H}_5\text{CCCH}(\text{X}^1\text{A}^1') + \text{H}^2\text{S}_{1/2} \tag{3a}
\]

\[
\rightarrow \text{H}_2\text{CCCH}(\text{C}_6\text{H}_5)(\text{X}^1\text{A}^1') + \text{H}^2\text{S}_{1/2} \tag{3b}
\]

\[
\rightarrow \text{C}_6\text{H}_5\text{CCH}(\text{X}^1\text{A}_1) + \text{CH}_3(\text{X}^2\text{A}^m). \tag{3c}
\]

II. EXPERIMENTAL SETUP

All experiments are performed under single collision conditions employing the 35\(^\circ\) crossed molecular beam machine. Briefly, a pulsed supersonic beam of phenyl radicals was generated via flash pyrolysis of a nitrosobenzene, \( \text{C}_6\text{H}_5\text{NO} \) (Aldrich Chemicals), in the primary source cham-

A mixture of \(<0.1\%\text{C}_6\text{H}_5\text{NO}\) seeded in helium was expanded at a stagnation pressure of 860 Torr through a resistively heated SiC tube of 1 cm length and 0.7 mm inner diameter; the temperature of the tube was estimated to be around 1300–1400 K. The electrical heating and mounting of this tube occurs through two silicon carbide electrode sleeves and two molybdenum electrode blocks. The latter are secured through insulating alumina screws and spacers and are interfaced to a water-cooled copper block. Both electrodes are connected to the power supplies outside the vacuum system. As the SiC tube has a negative tempera-

The beam was characterized on axis employing a triply differentially pumped detector consisting of an electron impact ionizer followed by a quadrupole mass spectrometer and a Daly-type scintillation particle detector. Under the above-described operation conditions, the dissociation is complete, and we did not detect signal of the \( \text{C}_6\text{H}_5\text{NO} \) precursor at \( m/e = 107 \). Only \( \text{C}_6\text{H}_5 \) was observed; not even trace amounts of a potential hydrogen abstraction product \( \text{C}_6\text{H}_4 \) are present in our beam. We estimated a number density of about \( 10^{12} \) radicals cm\(^{-3} \) in the interaction region. No biphenyl recom-

The beam was operated at 60 Hz with pulses of 80 \( \mu \)s width. After passing a skimmer, a four slot chopper wheel rotating at 240 Hz selected a 9 \( \mu \)s slice of the beam.

FIG. 1. Schematic setup of the pulsed valve and pyrolytic source.
unavoidable 60 Hz oscillations of the pulsed valve transferred to the pyrolytic source. Operating the pulsed valve before the warm-up of the SiC tube inevitably led to a migration of the SiC tube outside the sleeves. Therefore, we recommend warming up the SiC tube prior to engaging the pulsed valve. To confirm that the signal at mass to charge ratio of \( m/e = 77 \) is actually the phenyl radical and not biphenyl which could have been fragmented in the electron impact ionizer to \( m/e = 77 \), we performed elastic scattering experiments of the primary beam with argon. Under these conditions, the scattering signal of the phenyl radicals should extend up to about 38° with respect to the primary beam, whereas the biphenyl should give a cutoff angle of 18°. Measurements of the elastic scattering signal at 25.0° confirmed the presence of phenyl radicals in our beam.

A forward-convolution technique is employed to gain information on the reaction dynamics from the laboratory data.12 This approach assumes an angular flux \( T(\theta) \) and a translational energy \( P(\varepsilon_T) \) trial distribution in the center-of-mass coordinate system assuming mutual independence. The final outcome is the generation of a velocity flux contour map \( I(\theta, \varepsilon) \) in the center-of-mass frame showing the intensity as a function of angle \( \theta \) and velocity \( \varepsilon \). This plot contains all the basic information of the reactive scattering process.

### III. ELECTRONIC STRUCTURE CALCULATIONS

The geometries of all stationary points were fully optimized at the density functional theory level with the 6-31 G* and 6-311+G** basis sets and Becke’s three parameter hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr13 (B3LYP) as implemented19 in GAUSSIAN 94,16 The spin-unrestricted formalism was employed for all open-shell species. Intrinsic reaction coordinates were computed at B3LYP/6-31 G* for the addition of the phenyl radical to the methylecyclyene-triple bond using the algorithm of Gonzales and Schlegel.17 Harmonic vibrational frequencies were computed at the B3LYP/6-31 G* level and the obtained zero-point vibrational energies (ZPVE) were used for the ZPVE correction of the B3LYP/6-311+G** energies.

### IV. RESULTS

#### A. Reactive scattering signal

In our experiment, the phenyl radical versus hydrogen exchange pathway was observed, and reactive scattering signal was detected at mass to charge ratio \( m/e = 116(C_8H_6D) \). All TOF spectra observed at lower \( m/e \) ratios down to \( m/e = 108(C_8H_4) \) depicted identical patterns. Since they were fit with the same center-of-mass functions as the parent ions, these ions originate from cracking of the parent in the electron impact ionizer. No radiative association was found. Since the H atom loss can occur from the \( CH_3 \) group as well as from the acetylenic carbon, we performed a crossed beam experiment with partially deuterated methylecyclyene, \( CH_3CCD \). If a H atom loss occurred at the \( CH_3 \) group, we should have seen signal at \( m/e = 117(C_8H_5D^+) \) and \( m/e = 116(C_8H_6D^+) \); fragmentation from \( C_8H_7D^+ \). On the other hand, if only a D atom loss occurred, a signal should be present only at \( m/e = 116(C_8H_6^+) \). We observed only a \( m/e = 116 \) signal. These studies show unambiguously that under our experimental conditions the H atom is released from the acetylenic unit, whereas the \( CH_3 \) group is conserved in the reaction. Due to the unfavorable kinematics of the reaction and low signal-to-noise ratio no \( CH_3 \) loss channel could be observed.

#### B. TOF spectra and laboratory angular distribution (LAB)

The laboratory angular distribution of the product and the calculated curve are depicted in Fig. 2 together with the most probable Newton diagram. Figure 3 shows the TOF spectrum recorded at 8.5° and the best fit. The LAB distribution is very narrow and extends from 3.5° to 11.5°, i.e., only 8.0° in the scattering plane. This narrow range is based on the mass combination of the products of 116 vs 1 and the dominant translational energy release into the \( H \) atom product together with a low reaction exothermicity is observed, cf. Sec. V A. Further, the LAB distribution peaks at 7.5°, slightly forward with respect to the center-of-mass angle of 8.0° ± 0.2°.

#### C. Center-of-mass translational energy distribution, \( P(\varepsilon_T) \)

The best fits of the translational energy \( P(\varepsilon_T) \) and angular flux distribution \( T(\theta) \) are shown in Fig. 4. Both the LAB distribution and TOF spectra were fit with a single \( P(\varepsilon_T) \) extending to a maximum translational energy release...
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D. Center-of-mass angular distribution, \( T(\theta) \), and flux contour map, \( I(\theta,\mu) \)

The shape of the flux distribution \( T(\theta) \) and the contour map \( I(\theta,\mu) \), Fig. 5, contain important information on the chemical reaction dynamics of the title reaction. In the \( \text{C}_5\text{H}_5/\text{CH}_3\text{CCH} \) system, the angular flux distribution is asymmetric around \( 90^\circ \) and shows predominantly flux in the forward hemisphere with respect to the phenyl beam; the initial and final angular momenta \( L \) and \( L' \) are strongly correlated. The best fit was achieved with the flux peaking at \( 0^\circ \) and zero intensity at angles larger than \( 150^\circ \). Within the error limits, a minor intensity at these larger angles can provide an acceptable fit as well. These results suggest that the reaction does not proceed through a long-lived complex, but shows characteristics of “direct” dynamics: the reaction involves either a highly rovibrationally excited collision complex in a very shallow potential energy well with a lifetime of less than 0.1 ps, or only one transition state \([\text{C}_5\text{H}_5]^*\) along the reaction coordinate without a bound intermediate. We like to stress that despite the unfavorable kinematics of the reaction the information gained from the \( T(\theta) \) distribution shows unambiguously that this distribution is strongly forward peaked. We did a careful error analysis, and no fit could be gained with a forward–backward symmetric center-of-mass angular distribution.

V. DISCUSSION

A. The potential energy surface

The addition of the phenyl radical \( 1 \) to the \( \pi \) electron density of the methylenecyclohexane \( 2 \) triple bond can yield the trans-1-phenylpropene-2-yl as well as the trans-2-phenylpropene-1-yl structural isomers \( 3 \) and \( 4 \) via transition states \( \text{TS}1 \) and \( \text{TS}2 \), cf. Figs. 6 and 7 and Table I. The latter lie 17.1 and 28.2 kJ mol\(^{-1} \) above the reactants. In agreement with the Bell–Evans–Polyani principle, the barrier for the exothermic addition to the terminal acetylenic C1 atom of \( 2 \) to form \( 3 \) (\(-149.9 \) kJ mol\(^{-1} \)) is lower than for addition to the C2 atom to give \( 4 \) (\(-126.0 \) kJ mol\(^{-1} \)). Our calculations show that the addition of the phenyl radical to methylenecyclohexane does not yield the more stable cis-2-phenylpropene-1-yl or 1-phenylpropene-2-yl conformation isomers \( 5 \) or \( 6 \) directly. However, the barriers for cis–trans isomerization of \( 3/5 \) and \( 4/6 \) via \( \text{TS}3 \) and \( \text{TS}4 \) are very small (18.5 and 14.1 kJ mol\(^{-1} \), respectively) and well below the total available energy of the reaction.

The 1-phenylpropene-2-yl radicals \( 3 \) and \( 5 \) can emit either a methyl or a vinyl H atom. The first pathway yields phenylmethylenecyclohexane \( 7 \) via tight transition states \( \text{TS}5 \) and \( \text{TS}6 \) both of which are about 2 kJ mol\(^{-1} \) above the separated reactants. Alternatively, \( \text{TS}7 \) and \( \text{TS}8 \) which lead to the phenylalkyne isomer \( 8 \) are located slightly below the reactants, i.e., \(-0.3 \) and \(-1.0 \) kJ mol\(^{-1} \), respectively. Further, our calculations show that the reaction between the phenyl radical \( 1 \) and methylenecyclohexane \( 2 \) to give phenylmethylenecyclohexane \( 7 \) plus a H atom is exothermic by 12.0 kJ mol\(^{-1} \) at B3LYP/6-311+G\(^{*}\)* level of theory; the formation of phenylalkyne isomer \( 8 \) and a H atom is the least exothermic process (\(-5.7 \) kJ mol\(^{-1} \)) according to the calculations.
The fragmentation of 2-phenylpropene-1-yl isomers 4 and 6 into phenylacetylene 9 and a CH$_3$ radical is the thermodynamically most favorable pathway of the title reaction as it is exothermic by $-56.0$ kJ mol$^{-1}$. The transition state TS9 for this C–C bond cleavage is slightly higher in energy than the reactants (+1.3 kJ mol$^{-1}$). We were not able to locate a TS for CH$_3$ elimination from 6 as all attempts resulted in TS9. All transition states for the fragmentation of

FIG. 5. Center-of-mass velocity contour flux map distribution for the C$_6$H$_5$(X$^2A'$) + CH$_3$CCH(X$^1A_1$) reaction at a collision energy of 140 kJ mol$^{-1}$; top: two-dimensional view, bottom: three-dimensional view. The contour lines connect data points with an identical flux. Units of the x and y axis are given in ms$^{-1}$. 

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the C₉H₉ radicals lie late on the reaction coordinate and are characterized by significantly stretched dissociating bonds.

Finally, we would like to point out that the H atom elimination from the C₁ atom in the 2-phenylpropene-1yl radicals 4 and 6 results in the formation of phenylmethylvinylidene, (CH₃)(C₆H₅)CC. As this carbene is a very high lying species (+209 kJ mol⁻¹ with respect to the reactants), its formation is energetically not feasible at our collision energy of 140 kJ mol⁻¹.

B. The reaction pathway

Our experimental and theoretical data suggest that the reaction of the phenyl radical with methylacetylene proceeds according to the following reaction dynamics. The indisputable identification of the phenyl versus hydrogen replacement together with the assignment of the H loss site as acetylenic strongly indicate formation of the phenylmethylacetylene, C₆H₅CCCH₃(X₁A⁺) isomer. The high energy cut-

FIG. 6. Schematic representation of the C₉H₉ potential energy surface at the B3LYP/6-311+G** level of theory. Computational details are given in the text.

FIG. 7. Bond distances in angstrom and bond angles in degrees of reactants and potential products on the C₉H₉ potential energy surface at the B3LYP/6-311+G** level of theory. 7a and 7b are isoenergetic and differ only in the orientation of the methyl group.
off, i.e., the sum of the reaction energy and the collision energy of the \( P(E_F) \) yields a reaction exothermicity of 20 ± 10 kJ mol\(^{-1}\), which is in good agreement with our calculated value of 12.0 kJ mol\(^{-1}\). An alternative reaction channel which results in an acetylenic hydrogen loss to yield phenylmethylvinylidene, CH\(_3\)C\(_6\)H\(_5\)CC, is endothermic by about 209 kJ mol\(^{-1}\) and hence energetically not open at our collision energy of 140 kJ mol\(^{-1}\). These findings suggest an initial attack of the C\(_2\)H\(_5\) with the unpaired electron in an A\(_1\) orbital on the \( \pi \) electron density at C1 of the CH\(_3\)C\(_6\)H\(_5\)CH molecule to form 3 which could isomerize to 5. A subsequent homolytic C–H bond rupture releases the vinylc H atom. We would like to stress that a phenyl radical addition to the C1 atom of the methylacetylene giving 4 and/or 6 is energetically feasible as well, but this pathway cannot yield the experimentally observed site specific H atom loss channel. Here, two factors may direct the carbon–carbon–σ bond formation to the C1 atom. First, the \( \pi \)-group orbitals of the methyl group increase the spin density on the C1 atom at the expense of the C2 position. Second, the sterical hindrance of the CH\(_3\) group reduces the cone of acceptance at the C2 position. Both effects together might direct the electrophilic phenyl addition at C1. This preferential site-specific radical attack was observed previously in the crossed beam reaction of methylacetylene with CN radicals,\(^{19}\) C\(_2\)D radicals,\(^{20}\) and C\(^{3}\)P\(_J\)\(^{21}\) as well.

Since however the unpaired electron of phenyl is localized in an A\(_1\) orbital, the reactive scattering signal depends strongly on the orientation angle of the radical center toward the acetylenic bond. In combination with the calculated entrance barrier of 17.1 kJ mol\(^{-1}\), the reaction cross section is expected to be much lower compared to the analogous reactions of atomic carbon and cyano radicals which follow almost gas kinetics behavior. Based on the intensity of our signal, the data accumulation time, different exothermicities, and beam intensities we estimate that the cross section of our title reaction is about 2–3 orders of magnitude less than the one in both C\(^{3}\)P\(_J\)/CH\(_3\)C\(_6\)H\(_5\)CH and CN/CH\(_3\)C\(_6\)H\(_5\)CH systems. This finding is well reflected in the temperature-dependent reaction rate constants \( k \) obtained from bulk experiments (cf. Sec. I): here, data with unsaturated hydrocarbons range from \( 10^{-12} \) to \( 10^{-14} \) cm\(^{-3}\) whereas those of C\(^{3}\)P\(_J\) and CN are in the order of \( 10^{-10} \) cm\(^{-3}\).

It is worth taking a closer look at the chemical dynamics. Even if the isomers 3 and/or 5 are bound by about 150–160 kJ mol\(^{-1}\), the reaction does not go through a long-lived complex. Here, the reactive scattering signal was found predominantly in the forward sphere with respect to the phenyl beam, cf. \( I(\theta, u) \). The strong correlation of the initial and final angular momentum \( L \) and \( L' \) is characteristic for a typical direct reaction following stripping dynamics. This preferential forward scattering indicates an attractive interaction between the phenyl radical and the methylacetylene molecule. Furthermore, the process of reaction is complete before the colliding pairs of reactants have time for a full rotation around their rotation axis. Hence the complex 3 and/or 5 is very short lived. Since an acceptable fit was achieved with some minor intensity at angles larger than 150° as well, we propose that the reaction is likely on the boundary between a direct process and a short-lived oscillating complex with a lifetime of about 0.1 ps. Therefore, the initial collision complex must be highly rovibrationally excited to result in this short lifetime and translates into an incomplete energy randomization in 1 and/or 2 and hence in a preferential loss of the acetylenic hydrogen atom although the latter is more strongly bound than an aliphatic, cf. Sec. V C. In addition, direct reactions are often found to have an increased fraction of total available energy channeling into the translational degrees of freedom compared to complex forming encounters. This is consistent with our data showing a fraction of 50 ± 5%; in comparison, all reactions of C\(^{3}\)P\(_J\) and CN radicals with unsaturated hydrocarbons are indirect and depit fractions of only 30%–35% channeling into translational energy.

### C. Comparison with the reaction CN(\( ^{2}\Sigma^+ \)) + CH\(_3\)C\(_6\)H\(_5\)CH

It is interesting to compare the phenyl/methylacetylene system to the reaction of cyano radicals, CN(\( ^{2}\Sigma^+ \)), with methylacetylene which was studied earlier in our lab.\(^{19}\) In both systems, the unpaired electron is located in a centro-symmetrical orbital localized predominantly on the radical carbon atom of the reactant. Directed by a steric (screening) effect of the bulky methyl group and governed by an increased spin density at the C1 carbon atom of the methylacetylene molecule, this orbital interacts with the \( \pi \) electron density to form a new carbon–carbon \( \sigma \) bond and resulting in cis/trans CH\(_3\)C\(_6\)H\(_5\)CH (\( X = \text{CN}, \text{C}_6\text{H}_5 \)). Whereas the reaction of the cyano radical proceeds through an oscillating complex (indirect scattering dynamics) having a lifetime around 1–2 ps, the phenyl radical shows a direct reaction via a short lived (<0.1 ps) intermediate. This translates into reactive scattering signal preferentially in the forward hemisphere with respect to the phenyl radical beam. Likewise, the energy randomization in the CH\(_3\)C\(_6\)H\(_5\)CHCN intermediates is likely to be complete; we observe a H atom loss at the C2 carbon atom of the CH\(_3\)C\(_6\)H\(_5\)CH reactant—the site with the newly formed carbon–carbon bond—to yield the substituted methylacetylene, i.e., CH\(_3\)CCCN, and at the methyl group carbon atom to give the allene isomer H\(_2\)CCCH(C\(_6\)H\(_5\)). The shorter lifetime of the CH\(_3\)C\(_6\)H\(_5\)CH(C\(_6\)H\(_5\)) intermediate precludes an energy distribution into the methyl group. Hence,
only the \( \text{CH}_2\text{CCC}_2\text{H}_5 \) isomer is observed experimentally, and no phenyllallene isomer is formed. These findings can be rationalized comparing the average collision energies of the \( \text{CN/CH}_2\text{CCC}_2\text{H} \) (24.7 \( \text{kJ mol}^{-1} \)) versus the \( \text{C}_4\text{H}_{10}/\text{CH}_2\text{CCC}_2\text{H} \) (140 \( \text{kJ mol}^{-1} \)) reactive encounters. As a general trend, the lifetime of an intermediate in an indirect reaction decreases as the collision energy rises, and as an extreme, the reaction goes from a long lived intermediate through an oscillating complex, and finally via direct scattering dynamics.

VI. IMPLICATIONS TO INTERSTELLAR CHEMISTRY AND COMBUSTION PROCESSES

Our crossed beam experiments explicitly demonstrated the formation of a phenyl substituted methacetylene product formed under single collision conditions. This is the very first unambiguous assignment of a reactive scattering product of an elementary reaction between a phenyl radical and a substituted acetylene molecule—an elementary reaction which is thought to play a central role in the formation of PAHs in various terrestrial as well as extraterrestrial environments. Since the title reaction has an entrance barrier of 17 \( \text{kJ mol}^{-1} \), it is irrelevant for the formation of PAHs in cold molecular clouds or hydrocarbon-rich atmospheres of Jupiter, Saturn, and Titan because this entrance barrier inhibits the reaction. However, temperatures close to the photosphere of carbon stars can reach up to 4000 K, and the reaction might be important in these environments. The actual effect on PAH synthesis must be verified in extended and refined chemical modeling of these scenarios. However, if we extend previously postulated reaction pathways to substituted methacetylene, the title reaction is likely to be involved in the synthesis of methyl substituted naphthalene molecules.

VII. CONCLUSIONS

The crossed beam reaction of the phenyl radical \( \text{C}_4\text{H}_5(\text{X}^1\text{A}_1) \), with methacetylene, \( \text{CH}_2\text{CC}X(\text{X}^1\text{A}_1) \), was investigated at an average collision energy of 140 \( \text{kJ mol}^{-1} \). The chemical reaction dynamics are direct and proceed through a very short lived, highly vibrationaly excited trans-\( \text{CH}_2\text{CC}X(\text{C}_4\text{H}_5) \) complex via an initial addition of the unpaired electron to the \( \pi \) orbital of the methacetylene unit. As verified in our experiments, the reduced cone of acceptance of the carbon atom adjacent to the methyl group favors a carbon–carbon \( \sigma \) bond formation at the terminal acetylenic carbon atom of methacetylene. As supported in crossed beam experiments of partially deuterated \( d_1\) methacetylene, \( \text{CH}_2\text{CC}D(\text{X}^1\text{A}_1) \), the acetylenic carbon hydrogen bond in the cis/trans \( \text{CH}_2\text{CC}X(\text{C}_4\text{H}_5) \) intermediate(s) is cleaved to form phenylmethylacetylene; the methyl group is conserved throughout the reaction. The experimentally derived reaction exothermicity of about 20 \( \text{kJ mol}^{-1} \) is in good agreement with the 12 \( \text{kJ mol}^{-1} \) calculated. The site-specific H atom loss can be rationalized in terms of the subpicosecond lifetime of the reactive intermediate and hence a lifetime too short to allow an activation of the aliphatic carbon–hydrogen bond and/or energy randomization; this behavior is well documented in our experiments since the phenyllallene isomer is not formed. The explicit assignment of the phenyl versus H atom exchange is the first experimental proof that \( \text{C}_4\text{H}_5 \) radicals can react with substituted acetylenes to phenylacetylenes—the latter reaction thought to be the key elementary process in the formation of (substituted) polycyclic aromatic hydrocarbons (PAHs) in oxygen-deficient combustion flames and outflows of carbon stars. Finally, we would like to point out that as the collision energies decrease the lifetime of the collision complex increases. Therefore, the formation of the thermodynamically less stable phenyllallene isomer might be feasible at lower collision energies and hence in the outflow of carbon stars as well. This pathway is subject of further theoretical studies.22

ACKNOWLEDGMENTS

R.I.K. is indebted to the Deutsche Forschungsgemeinschaft for a Habilitation fellowship (IIC1-Ka1081/3-2). This work was supported by Academia Sinica, Taiwan, the National Science Council of R.O.C. Partial support from the Petroleum Research Fund of R.O.C. is also appreciated. Special thanks to Dr. Balucani for suggesting the use of nitrosobenzene as a phenyl radical precursor. The work in Athens was supported by the U.S. Department of Energy, Basic Energy Sciences.

1 G. Glassmann, Combustion (Academic, New York, 1987), and references therein.
18 Although the isomerization from 4/6 to 3/5 might be viable energetically, the extremely short lifetime observed for the collision complex rules out this possibility.