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Crossed beam reaction of phenyl radicals with unsaturated hydrocarbon molecules. I. Chemical dynamics of phenylmethylacetylene ($C_6H_5CCCH_3; X^1A'$) formation from reaction of $C_6H_5(X^2A_1)$ with methylacetylene, $CH_3CCH(X^1A_1)$

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The chemical reaction dynamics to form phenylmethylacetylene, $C_6H_5CCCH_3(X\,^1A')$, via reactive collisions of the phenyl radical $C_6H_5(X\,^2A_1)$ with methylacetylene, $CH_3CCH(X\,^1A_1)$, are unraveled under single collision conditions in a crossed molecular beam experiment at a collision energy of 140 kJ mol^{-1}. The laboratory angular distribution and time-of-flight spectra of $C_9H_8^+$ at $m/e = 116$ indicate the existence of a phenyl radical versus hydrogen replacement pathway. Partially deuterated methylacetylene, $CH_3CCD(X\,^1A_1)$, 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 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 C_6H_5 radical to the π electron density of the C1 carbon atom of the methylacetylene molecule to form a short lived, highly rovibrationally excited $(C_6H_5)HCCCH_3$ intermediate. The latter loses a hydrogen atom to form the phenylmethylacetylene molecule on the $^2A'$ surface. The phenylallene 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, C_6H_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.[1] 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.[2] The phenyl radicals themselves are thought to be generated either by dimerization of propargyl radicals, $C_3H_3(X\,^2B_2)$, via a benzene intermediate [reaction (1)] or from reaction of $C_4H_3(X\,^2A')$ with acetylene, $C_2H_2(X\,^1\Sigma_g^+)$ [reaction (2)]:[3]

$$C_3H_3(X\,^2B_2) + C_3H_3(X\,^2B_2) \rightarrow C_6H_6(X\,^1A_g) \rightarrow C_6H_5(X\,^2A_1) + H(^2S_{1/2}), \tag{1}$$

$$C_4H_3(X\,^2A') + C_2H_2(X\,^1\Sigma_g^+) \rightarrow C_6H_5(X\,^2A_1). \tag{2}$$

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 methylthioether in sooting flames and thereby demonstrated explicitly that C_6H_5 exists in these high temperature combustion environments.[4] 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;[5] data show very low rate constants at temperature ranges up to 1100 K rang-

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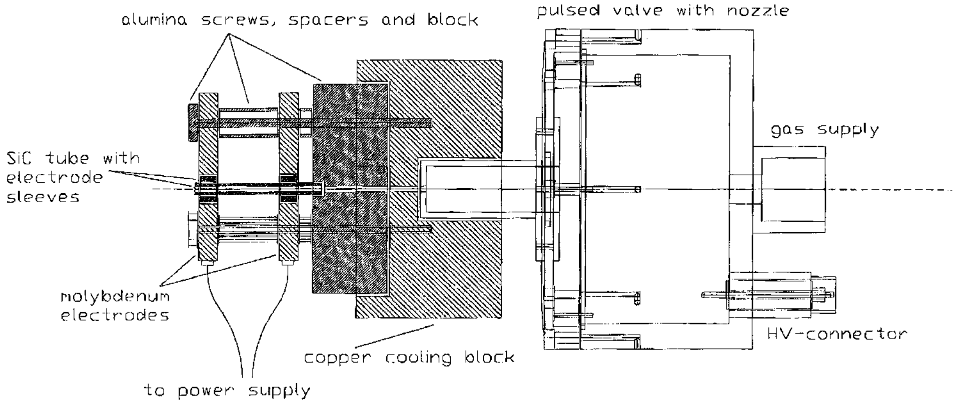

FIG. 1. Schematic setup of the pulsed valve and pyrolytic source.

ing between 10^{-12} and $10^{-14}\,\mathrm{cm^3\,s^{-1}}$. These studies further show an entrance barrier between 25 and 43 $\mathrm{kJ\,mol^{-1}}$ with olefines and alkynes. But despite valuable kinetic data, the reaction products—although crucial for a detailed chemical modeling of combustion processes and PAH formation in circumstellar shells of carbon starts—were never probed. Obviously, the products of the reaction of C_6H_5 with H_2 as studied by Lin and Co-workers[6] should be benzene and atomic hydrogen, but the problem is more complex in the case of unsaturated and substituted hydrocarbons.

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, CH_3CCH [reaction (3)]:

$$C_6H_5(X\,^2A_1)+CH_3CCH(X\,^1A_1)$$

$$\rightarrow C_6H_5CCCH_3(X\,^1A')+H(^2S_{1/2}) \tag{3a}$$

$$\rightarrow H_2CCCH(C_6H_5)(X\,^1A')+H(^2S_{1/2}) \tag{3b}$$

$$\rightarrow C_6H_5CCH(X\,^1A_1)+CH_3(X\,^2A''). \tag{3c}$$

II. EXPERIMENTAL SETUP

All experiments are performed under single collision conditions employing the 35″ crossed molecular beam machine.[7,8] Briefly, a pulsed supersonic beam of phenyl radicals was generated via flash pyrolysis of a nitrosobenzene, C_6H_5NO (Aldrich Chemicals), in the primary source chamber employing a modified Chen source[9] and a piezoelectric pulsed valve, cf. Fig. 1.[10] A mixture of $<0.1\%\,C_6H_5NO$ 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 temperature coefficient, we used a high voltage and low current power supply (200 mA, 400 V) for the warm-up phase and switched thereafter to a low voltage and high current power supply. During the experiments we used about 20 V and 2 A depending on the resistance of the SiC tube. The nitrosobenzene was kept at 277 K and shielded from light to avoid decomposition. The pulsed valve was operated at 60 Hz with pulses of 80 μs width. After passing a skimmer, a four slot chopper wheel rotating at 240 Hz selected a 9 μs slice of the beam.

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 C_6H_5NO precursor at $m/e=107$. Only C_6H_5 was observed; not even trace amounts of a potential hydrogen abstraction product C_6H_6 are present in our beam. We estimated a number density of about 10^{12} radicals $\mathrm{cm^{-3}}$ in the interaction region. No biphenyl recombination product, $C_6H_5-C_6H_5$, was detected. The velocity of the phenyl beam and its speed ratio were determined to $v_p=3150\pm 50\,\mathrm{m\,s^{-1}}$ and $S=8.5-9.0$, respectively. Due to a periodical replacement of the SiC tubes (see the following), the day-to-day velocity changed slightly, and the delay time between the chopper wheel trigger pulse and the pulsed valve had to be adjusted slightly. The phenyl radical beam crosses a methylacetylene beam (MG Industries) in the interaction region in the main chamber at a collision energy of 140 $\pm 8\,\mathrm{kJ\,mol^{-1}}$ ($v_p=850\pm 10\,\mathrm{m\,s^{-1}}$, $S=9.0$.) Reactively scattered species are detected using a triply differentially pumped detector consisting of a Brink-type electron-impact-ionizer, quadrupole mass filter, and a Daly ion detector[11] recording time-of-flight spectra (TOF). Integrating these TOF spectra at each laboratory angle and correcting for different data accumulation times yields the laboratory angular distribution (LAD). After 8–10 h of operation, we observed a background signal at almost all m/e ratios. This was probably due to reaction of the C_6H_5NO precursor or the formed C_6H_5 radicals with the SiC tube. Time-consuming daily dismantling of the source and changing of the tube was therefore necessary. Further, extreme care had to be taken with 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 $P(E_T)$ trial distribution in the center-of-mass coordinate system assuming mutual independence. The final outcome is the generation of a velocity flux contour map $I(\theta,u)$ in the center-of-mass frame showing the intensity as a function of angle θ and velocity u. 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[13] three parameter hybrid functional in conjunction with the correlation functional of Lee, Yang, and Parr[14] (B3LYP) as implemented[15] 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 methylacetylene 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 $m/e = 116(C_9H_8^+)$. All TOF spectra observed at lower m/e ratios down to $m/e = 108(C_9^+)$ 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 methylacetylene, CH_3CCD. If a H atom loss occurred at the CH_3 group, we should have seen signal at $m/e = 117\,(C_9H_7D^+)$ and $m/e = 116\,(C_9H_6D^+$; fragmentation from $C_9H_7D^+)$. On the other hand, if only a D atom loss occurred, a signal should be present only at $m/e = 116\,(C_9H_8^+)$. 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.

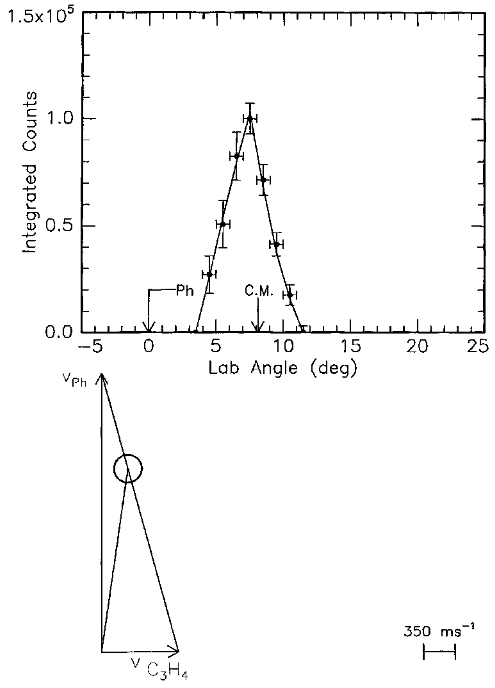

FIG. 2. Laboratory angular distribution together with the most probable Newton diagram for the $C_6H_5(X\ ^2A') + CH_3CCH(X\ ^1A_1)$ reaction at a collision energy of 140 kJ mol^{-1}. The circle centrosymmetric around the center of mass stands for the maximum center-of-mass recoil velocity of the phenylmethylacetylene product.

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, $P(E_T)$

The best fits of the translational energy $P(E_T)$ and angular flux distribution $T(\theta)$ are shown in Fig. 4. Both the LAB distribution and TOF spectra were fit with a single $P(E_T)$ extending to a maximum translational energy release

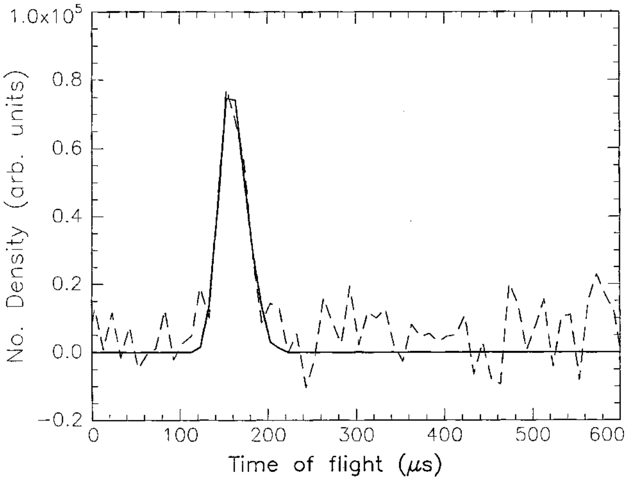

FIG. 3. Time-of-flight data at 8.5^0 for the $C_6H_5(X\,^2A')$ $+CH_3CCH(X\,^1A_1)$ reaction at a collision energy of 140 kJ mol^{-1}. The dashed line indicates the experimental data, the solid line the calculated fit.

E_{max} of 160 kJ mol^{-1}. Within the experimental error limits, extending or cutting the $P(E_T)$ by 10 kJ mol^{-1} does not influence the quality of the fit. Further, the $P(E_T)$ is very broad and peaks within the error limits at about 60–70 kJ mol^{-1} well away from zero translational energy. This finding together with the large fraction of the total available energy, i.e., the sum of the reaction energy plus the collision energy, of 50±5% released into the translational degrees of freedom of the products and the forward peaking LAB distribution suggest that the reaction proceeds via a (very) short-lived intermediate.

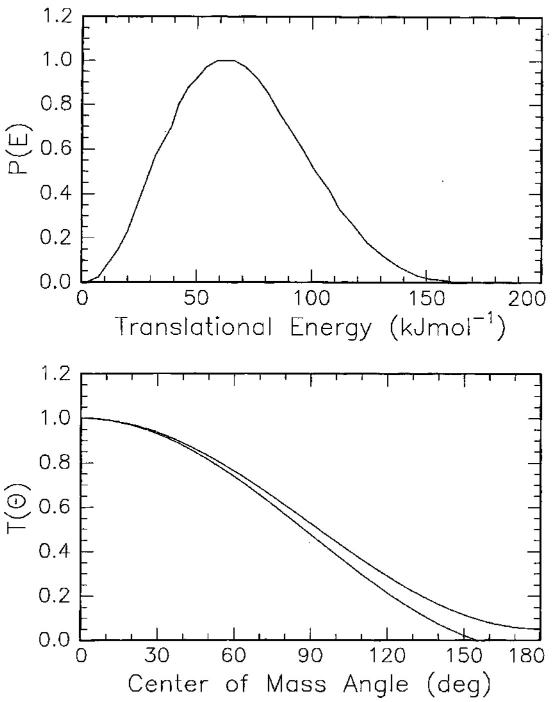

FIG. 4. Center-of-mass angular flux distribution (lower) and translational energy flux distribution (upper) for the $C_6H_5(X\,^2A')+CH_3CCH(X\,^1A_1)$ reaction at a collision energy of 140 kJ mol^{-1}.

D. Center-of-mass angular distribution, $T(\theta)$, and flux contour map, $I(\theta,u)$

The shape of the flux distribution $T(\theta)$ and the contour map $I(\theta,u)$, Fig. 5, contain important information on the chemical reaction dynamics of the title reaction. In the C_6H_5/CH_3CCH system, the angular flux distribution is asymmetric around 90° 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° and zero intensity at angles larger than 150°. 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 the 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 $[C_9H_9]^*$ 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 π electron density of the methylacetylene **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 **TS1** and **TS2**, 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 more 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 methylacetylene 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 **TS3** and **TS4** 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 phenylmethylacetylene **7** via tight transition states **TS5** and **TS6** both of which are about 2 kJ mol^{-1} above the separated reactants. Alternatively, **TS7** and **TS8** which lead to the phenylallene 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 methylacetylene **2** to give phenylmethylacetylene **7** plus a H atom is exothermic by 12.0 kJ mol^{-1} at B3LYP/6-311+G** level of theory; the formation of phenylallene isomer **8** and a H atom is the least exothermic process (−5.7 kJ mol^{-1}) according to the calculations.

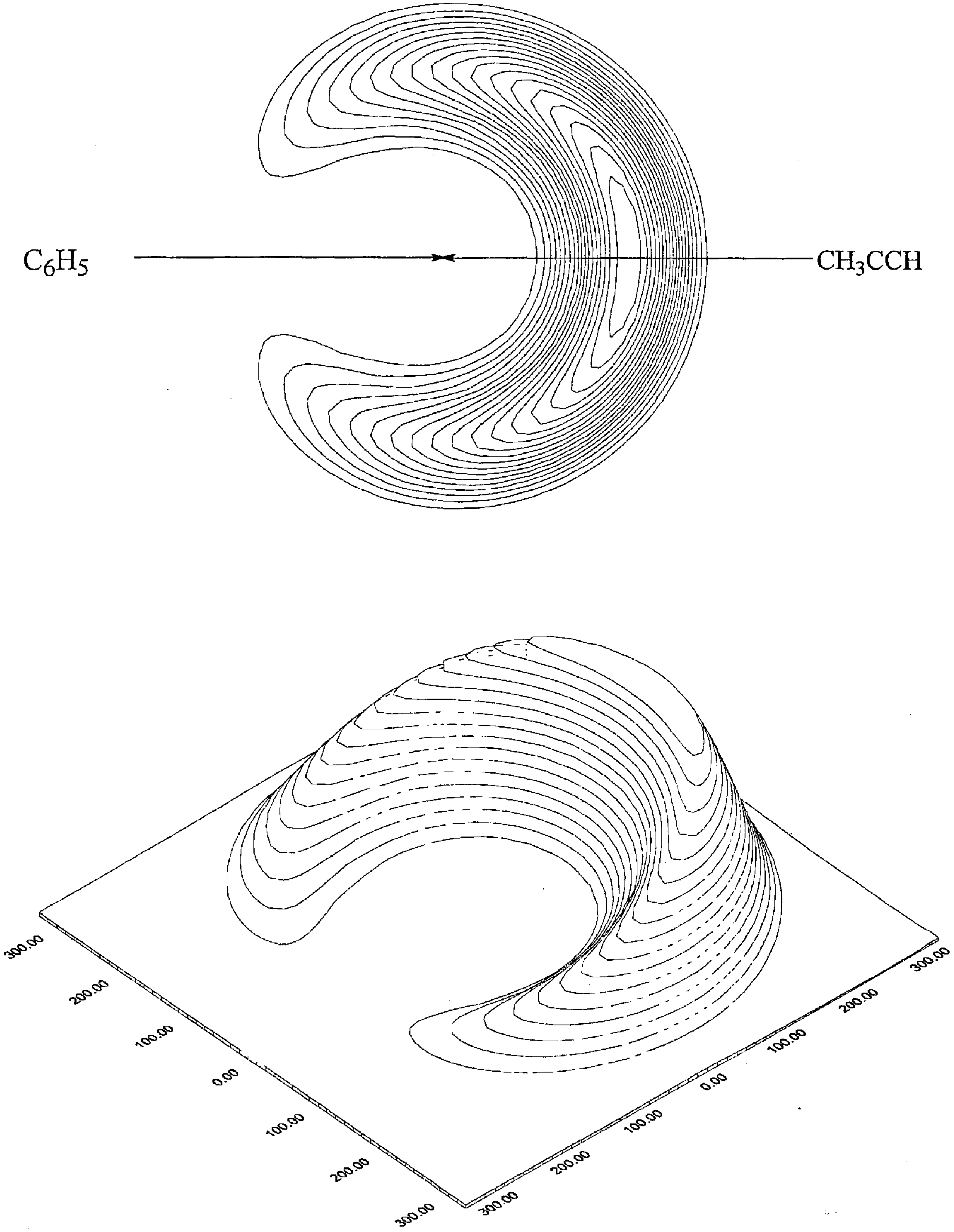

FIG. 5. Center-of-mass velocity contour flux map distribution for the $C_6H_5(X\,^2A')+CH_3CCH(X\,^1A_1)$ reaction at a collision energy of 140 kJ mol^{-1}; top: two-dimensional view, bottom: three-dimensional view. The contour lines connect data points with an identical flux. Units of the *x* and *y* axis are given in ms^{-1}.

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

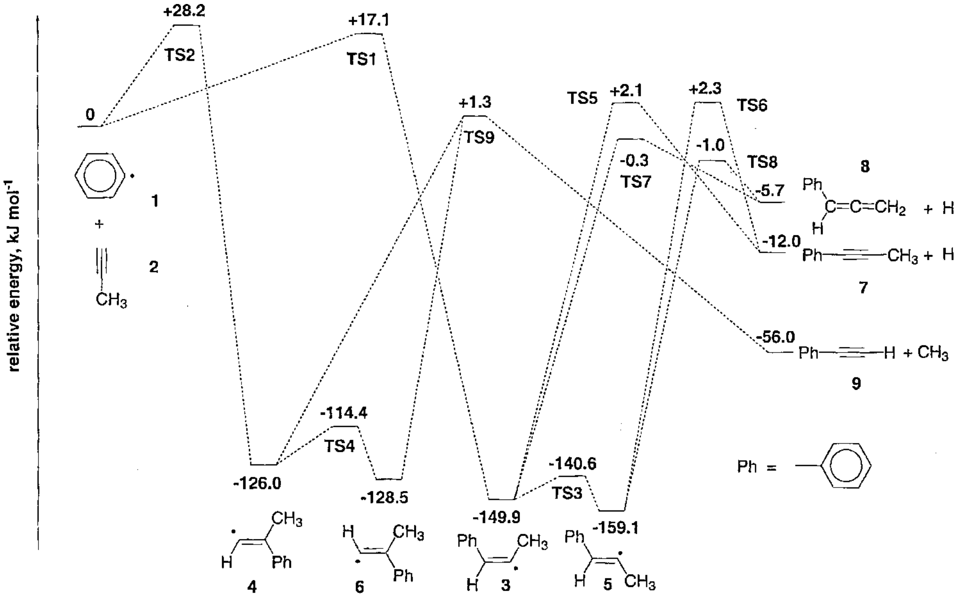

FIG. 6. Schematic representation of the C_9H_9 potential energy surface at the B3LYP/6-311+G** level of theory. Computational details are given in the text.

the C_9H_9 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, $(CH_3)(C_6H_5)CC$. 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, $C_6H_5CCCH_3(X\,^1A')$ isomer. The high energy cut-

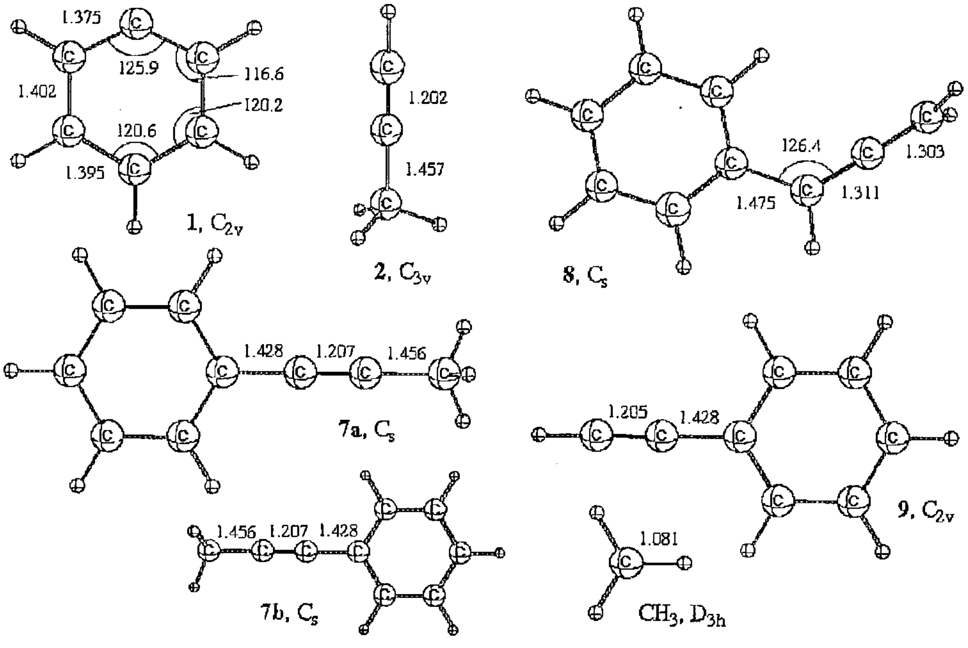

FIG. 7. Bond distances in angstrom and bond angles in degrees of reactants and potential products on the C_9H_9 potential energy surface at the B3LYP/6-311+G** level of theory. 7a and 7b are isoenergetic and differ only in the orientation of the methyl group.

TABLE I. Electronic states, dipole moments μ (in debye), and rotational constants (in GHz) for reactants, intermediates, and products obtained at the B3LYP/6-311+G** level of theory.

Molecule	Electronic state	Dipole moment (μ)
1	$^2A_1$	0.9133
2	$^1A_1$	0.8506
3	^2A	0.9174
4	^2A	0.8338
5	$^2A'$	1.1154
6	$^2A'$	0.9259
7	$^1A'$	0.5115
8	$^1A'$	0.1199
9	$^1A_1$	0.7437
CH_3	$^2A_2''$	0.0

off, i.e., the sum of the reaction energy and the collision energy of the $P(E_T)$ yields a reaction exothermicity of 20 $\pm 10\,\mathrm{kJ\,mol^{-1}}$, which is in good agreement with our calculated value of 12.0 $\mathrm{kJ\,mol^{-1}}$. An alternative reaction channel which results in an acetylenic hydrogen loss to yield phenylmethylvinylidene, $CH_3C_6H_5CC$, is endothermic by about 209 $\mathrm{kJ\,mol^{-1}}$ and hence energetically not open at our collision energy of 140 $\mathrm{kJ\,mol^{-1}}$. These findings suggest an initial attack of the C_6H_5 with the unpaired electron in an A_1 orbital on the π electron density at C1 of the CH_3CCH molecule to form **3** which could isomerize to **5**. A subsequent homolytic C–H bond rupture releases the vinylic H atom. We would like to stress that a phenyl radical addition to the C2 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.[18] Here, two factors may direct the carbon–carbon–σ bond formation to the C1 atom. First, the π-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_2D radicals,[20] and $C(^3P_j)$[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 $\mathrm{kJ\,mol^{-1}}$, 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 $C(^3P_j)/CH_3CCH$ and CN/CH_3CCH 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 $10^{-14}\,\mathrm{cm^{-3}}$ whereas those of $C(^3P_j)$ and CN are in the order of $10^{-10}\,\mathrm{cm^{-3}}$.

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 $\mathrm{kJ\,mol^{-1}}$, 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 $\mathbf{L}$ and $\mathbf{L}'$ 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 osculating 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 $\pm 5\%$; in comparison, all reactions of $C(^3P_j)$ and CN radicals with unsaturated hydrocarbons are indirect and depict fractions of only 30%–35% channeling into translational energy.

C. Comparison with the reaction $CN(^2\Sigma^+) + CH_3CCH$

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 centrosymmetrical 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 π electron density to form a new carbon–carbon σ bond and resulting in cis/trans CH_3CCHX ($X = CN, C_6H_5$). Whereas the reaction of the cyano radical proceeds through an osculating 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_3CCHCN intermediates is likely to be complete: we observe a H atom loss at the C2 carbon atom of the CH_3CCCH reactant—the site with the newly formed carbon–carbon bond—to yield the substituted methylacetylene, i.e., CH_3CCCN, and at the methyl group carbon atom to give the allene isomer $H_2CCCH(CN)$. The shorter lifetime of the $CH_3CCH(C_6H_5)$ intermediate precludes an energy distribution into the methyl group. Hence, only the $CH_3CCC_6H_5$ isomer is observed experimentally, and no phenylallene isomer is formed. These findings can be rationalized comparing the average collision energies of the CN/CH_3CCH (24.7 $kJ\,mol^{-1}$) versus the C_6H_5/CH_3CCH (140 $kJ\,mol^{-1}$) 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 osculating 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 methylacetylene 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 $kJ\,mol^{-1}$, 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 methylacetylene, 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 $C_6H_5(X\,^2A_1)$, with methylacetylene, CH_3CCH $(X\,^1A_1)$, was investigated at an average collision energy of 140 $kJ\,mol^{-1}$. The chemical reaction dynamics are direct and proceed through a very short lived, highly rovibrationally excited *trans*-$CH_3CCH(C_6H_5)$ complex via an initial addition of the unpaired electron to the π orbital of the methylacetylene unit. As verified in our experiments, the reduced cone of acceptance of the carbon atom adjacent to the methyl group favors a carbon–carbon σ bond formation at the terminal acetylenic carbon atom of methylacetylene. As supported in crossed beam experiments of partially deuterated d_1-methylacetylene, CH_3CCD $(X\,^1A_1)$, the acetylenic carbon hydrogen bond in the *cis*/*trans* $CH_3CCH(C_6H_5)$ intermediate(s) is cleaved to form phenylmethylacetylene; the methyl group is conserved throughout the reaction. The experimentally derived reaction exothermicity of about 20 $kJ\,mol^{-1}$ is in good agreement with the 12 $kJ\,mol^{-1}$ 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 phenylallene isomer is not formed. The explicit assignment of the phenyl versus H atom exchange is the first experimental proof that C_6H_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 phenylallene 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]

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