

Crossed-Molecular-Beam Study on the Formation of Phenylacetylene from Phenyl Radicals and Acetylene**

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During the last decades, polycyclic aromatic hydrocarbons (PAHs)^[1] and other related aromatic compounds, such as ionized PAHs,^[2] have received considerable attention from astronomers,^[3] astrobiologists,^[4] environmentalists,^[5] and the combustion community.^[6] In the interstellar medium, PAH-like species account for up to 10% of the cosmic carbon budget,^[7] have been suggested as carriers of both the unidentified infrared (UIR) emission bands^[8] and the diffuse interstellar bands (DIBs),^[9] and are also associated with the origin of life. On Earth, however, PAHs are severe pollutants and are considered as airborne toxic chemicals because of their mutagenic and carcinogenic character.^[10] Considering a yearly emission rate of 1.6 million tons in combustion processes,^[5] PAHs and soot also contribute significantly to global warming.^[11] A quantitative understanding of the formation of PAHs is therefore essential to develop clean combustion devices and understand the astrochemical and astrobiological evolution of the interstellar medium.

Despite the crucial importance of PAHs, even the formation route of the very first building block of this type of compounds (namely, the phenylacetylene molecule, C₆H₅CCH) is unknown. Chemical reaction networks that model the formation of PAH in combustion flames^[12] and in the interstellar medium^[13] imply that the phenyl radical (that is, C₆H₅) represents the most important transient species to initiate the formation of the very first PAH.^[14] The crucial steps of these reaction models are hydrogen abstraction–acetylene addition sequences. The chemical networks concur that the reaction of the phenyl radical with acetylene initiates the synthesis of PAH through the addition of phenyl to the acetylene molecule. Because of the central role of the phenyl–acetylene reaction, the kinetics of this system have been well-established (covering the temperature range up to 1500 K).^[15]

Theoretical studies of this benchmark system predicted the initial formation of a [C₈H₇]* adduct which either decomposed back to the reactants or fragmented into the phenylacetylene molecule (C₆H₅CCH) plus atomic hydrogen [Eq. (1)].^[16] Nevertheless, despite the central role of the

$$\text{C}_6\text{H}_5(\text{X}^2\text{A}_1) + \text{C}_2\text{H}_2(\text{X}^1\sum_g^+) \rightarrow [\text{C}_8\text{H}_7]^* \rightarrow \text{C}_6\text{H}_5\text{CCH}(\text{X}^1\text{A}_1) + \text{H}(^2\text{S}_{1/2}) \quad (1)$$

phenyl–acetylene reaction as the trigger to PAH formation, the theoretical investigations have never been verified experimentally under single-collision conditions. Consequently, the nature of the true reaction products of this elementary reaction has remained elusive to date. To shed light on this fundamental question, we conducted a crossed-molecular-beam study of the gas-phase reaction of the phenyl radical with acetylene to synthesize phenylacetylene plus atomic hydrogen via [C₈H₇]* intermediate(s).

This system presents the prototype reaction of an aromatic radical^[17] with ubiquitous acetylene molecules to form phenylacetylene by means of a single radical–neutral collision. Benzene, a likely precursor of the phenyl radical, has been observed together with acetylene, for example, toward the carbon-rich planetary nebula CRL 618,^[18] where it might be photodissociated to form the phenyl radical. On the other hand, the phenyl radical might result from benzene in combustion flames through hydrogen abstraction processes.^[19] The reaction is also interesting from the viewpoint of a physical–organic chemist as it represents a benchmark system to unravel the chemistry of radical-substitution reactions initiated by polyatomic organic radicals.

The reactive-scattering signal was recorded at mass-to-charge ratios (*m/z*) between *m/z* 102 (C₈H₆⁺) and *m/z* 98 (C₈H₂⁺) (at distinct laboratory angles). The time-of-flight (TOF) spectra monitored at *m/z* 101–98 were superimposable—at all angles (and after scaling)—to those taken at *m/z* 98 (Figure 1). This represents a crucial finding and suggests that the phenyl-versus-atomic-hydrogen exchange pathway to form the C₈H₆ isomer(s) is open and that the signal at lower *m/z* values originates from the dissociative ionization of the reaction product in the electron-impact ionizer.

We also detected a signal at *m/z* 103. Since the patterns of the TOF spectra were identical to those recorded at *m/z* 102 and the intensity of the ion counts at *m/z* 103 was only about 10% of that observed at *m/z* 102, we concluded that the signal at *m/z* 103 originates from the ionized ¹³C isotopomer of C₈H₆, that is, from ¹³CC₇H₆, but not from the C₈H₇ adduct. The TOF spectra and laboratory angular distributions of the reactive-scattering signal at *m/z* 102 (namely, of C₈H₆) are shown in Figure 1. To pin down whether the hydrogen atom is lost from the phenyl group or from the acetylenic unit, we conducted the crossed-beam reaction of phenyl radicals with fully deuterated acetylene. In this case, the loss of a hydrogen atom from the phenyl group should result in a signal at *m/z* 104 (C₈H₄D₂⁺), while the release of atomic deuterium is expected to be monitored at *m/z* 103 (C₈H₅D⁺). We observed signals at *m/z* 103 and 104. However, both TOF spectra were superimposable, and the ion counts at *m/z* 104 were only about 10% of those at *m/z* 103. This result indicates that

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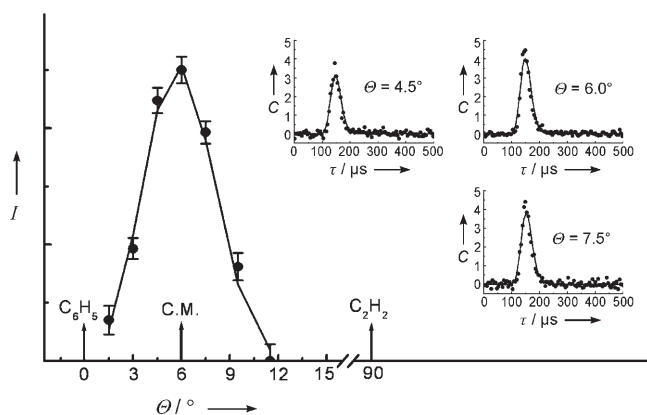


Figure 1. Representative laboratory angular distribution of the C_8H_6 product at m/z 102 and a collision energy of 96 kJ mol^{-1} . Shown is the intensity I plotted versus the laboratory angle Θ . Circles and 1σ error bars indicate experimental data, the solid lines represent the calculated distributions, and C.M. is the center-of-mass angle. Also shown are the corresponding TOF data at selected laboratory angles (inset); the flight time τ is plotted against the counts C . The circles represent the experimental data, and the solid lines show the corresponding fit.

within the signal-to-noise limitations of our experiments, only the deuterium atom was lost and that the signal at higher m/z ratio originated—similar to that at m/z 103 in the original experiment—from an ionized ^{13}C isotopomer (here, $^{13}\text{CC}_7\text{H}_5\text{D}$).

Finally, we investigated to what extent a hydrogen-abstraction pathway, by which benzene (m/z 78) and ethynyl are formed, is involved in the dynamics. When we monitored the signal at m/z 78, we detected a strong interference from elastically scattered $^{13}\text{CC}_5\text{H}_5$ radicals, which overlapped with the expected reactively scattered benzene molecules. To circumvent this interference, we monitored the deuterium-abstraction pathway to form $C_6H_5\text{D}$ from phenyl and C_2D_2 . At m/z 79, no background molecules interfered, but we were unable to detect any reactive-scattering signal. In summary, the laboratory data suggest that the phenyl ring is conserved in the phenyl-radical-versus-atomic-hydrogen/deuterium exchange reaction and that the sole reaction product(s) is (are) the C_8H_6 isomer(s). Accounting for our signal-to-noise ratio and the dynamics of the reaction, the hydrogen/deuterium-abstraction pathway was found to contribute less than 5% to the scattering signal. The identification of this phenyl-hydrogen exchange under single-collision conditions alone underlines the importance of this reaction to build up C_8H_6 isomers in interstellar environments and in combustion settings.

Next we tried to elucidate the reaction energies and gain additional information on potential entrance and exit barriers in the phenyl-acetylene reaction by untangling its dynamics. Most importantly, the dynamics assist in the identification of the nature of the product isomer(s) and the intermediate(s) involved. The center-of-mass translational energy $P(E)$ and the angular distribution $T(\theta)$ for both collision energies help us to solve this matter; the functions are depicted in Figure 2.

The translational-energy distributions assist in collecting information on the reaction dynamics. Both distributions

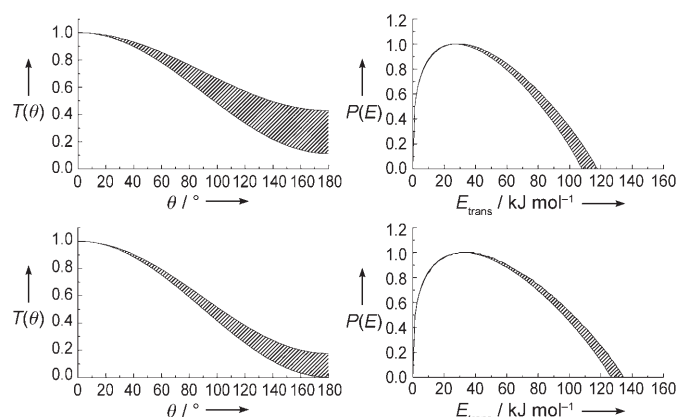


Figure 2. Center-of-mass angular-flux distributions (T , left) and translational-energy-flux distributions (P , right) for the reaction of phenyl radicals with acetylene at nominal collision energies of 71 (upper row) and 96 kJ mol^{-1} (lower row); the hatched areas limit the fits obtained within the error limits (θ : center-of-mass angle; E_{trans} : translational energy).

show maxima around $25\text{--}35 \text{ kJ mol}^{-1}$, thus indicating a tight exit transition state in the decomposition of the intermediate. In other words, the reverse reaction (hydrogen-atom addition to the C_8H_6 isomer) is expected to have an entrance barrier of about 30 kJ mol^{-1} . Most importantly, the high-energy cutoffs of the translational-energy distributions resemble the sum of the absolute value of the reaction exoergicity plus the relative collision energy; in this limit, all of the available energy goes into the translational degrees of freedom of the products. After extraction of the latter and averaging over both experiments, the data suggest that the reaction is exoergic by $(45 \pm 11) \text{ kJ mol}^{-1}$. These data are in excellent agreement with the computed values of $(41 \pm 8)^{[20]}$ and $(38 \pm 5) \text{ kJ mol}^{-1}$ ^[16] to form the phenylacetylene isomer plus atomic hydrogen. Based on this result, we can extract the fraction of available energy channeled into the translational degrees of freedom of the reactants to be about $(45 \pm 5) \%$. Finally, the best fits to the TOF data and laboratory angular distributions were achieved by adjusting the threshold energy of the reaction to be in the range of 5 to 30 kJ mol^{-1} .

Also, both center-of-mass angular distributions exhibit intensity over the complete range (from 0 to 180°). This finding indicates that the reaction dynamics are indirect and involve the formation of C_8H_7 intermediate(s) before the latter decompose—via atomic-hydrogen elimination—into the C_8H_6 product(s). Moreover, the $T(\theta)$ values show a pronounced forward scattering, that is, the flux at 0° is enhanced compared to that at 180° and, as the collision energy increases, the distribution becomes more forward-scattered. These results suggest that the lifetime(s) of the decomposing reaction intermediate(s) is(are) shorter than the rotational period. Most importantly, the center-of-mass angular distributions show an enhanced forward peaking as the collision energy increases. This energy dependence of the $T(\theta)$ values infers the existence of an osculating complex,^[21] that is, a C_8H_7 intermediate whose lifetime decreases as the collision energy is enhanced.

Our results suggest that the phenyl radical adds with its radical center to the carbon–carbon triple bond, thereby forming a C_8H_7 doublet radical intermediate (namely, 2-phenylvinyl, see Figure 3). The threshold energy indicates

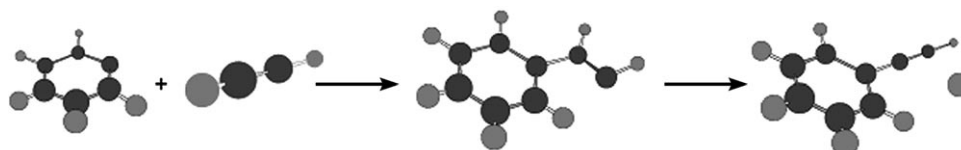


Figure 3. Schematic representation of the reaction mechanism of phenyl radicals with acetylene (left) leading to phenylacetylene plus atomic hydrogen (right) via a 2-phenylvinyl radical intermediate (center). Carbon and hydrogen atoms are depicted in black and blue, respectively. Note that the 2-phenylvinyl intermediate can exist in its *cis* and *trans* form.

that this process has an entrance barrier between 5 and 30 kJ mol^{-1} . The shapes of the center-of-mass angular distributions are indicative of complex-forming “indirect” scattering dynamics. At both collision energies used, the lifetime of the decomposing intermediate was much shorter than the rotational period. The rotational period of the 2-phenylvinyl intermediate acts as a clock in the molecular-beam experiment and can be utilized to estimate the lifetime τ of the decomposing complex. A quantitative inspection of the $T(\theta)$ values (Figure 2) suggests that the lifetime of the intermediate is less than half of its rotational period.

The short timescale of this reaction was also verified by the relatively large fraction of energy that channels into the translational modes, that is, $(45 \pm 5)\%$ of the total available energy. The initial collision complex decomposed by atomic-hydrogen elimination through a tight exit transition state located 25–35 kJ mol^{-1} above the separated reaction products (namely, phenylacetylene and atomic hydrogen). This reaction mechanism fully supports a previous theoretical study,^[16] in which the authors concluded that the phenyl radical added with its unpaired electron to the acetylene molecule through a barrier of about 16 kJ mol^{-1} , leading to an intermediate which was stabilized by 170 kJ mol^{-1} . This shallow potential-energy well can nicely account for the relatively short timescale of the reaction (as found experimentally). The fate of this intermediate was dictated by an atomic-hydrogen loss upon passing an exit transition state located 28 kJ mol^{-1} above the products; note that this intermediate could also undergo a *cis*–*trans* isomerization prior to its decomposition.^[16] Finally, the experiments verify the sole existence of the hydrogen-loss pathway—and the absence of any hydrogen-abstraction pathways—to form benzene.

In summary, we have identified the phenylacetylene molecule as the sole product in the radical–neutral reaction of phenyl radicals with acetylene molecules under single-collision conditions. The proposed chemical dynamics infer the existence of a reaction intermediate, which decomposed in the crossed-beam experiments through the loss of atomic hydrogen. However, in low-temperature and high-pressure combustion flames, this intermediate may either be stabilized or react with another acetylene molecule if the time between collisions is short enough; this can ultimately lead to the

formation of naphthalene. In the interstellar medium, however, only bimolecular reactions take place, and the intermediate always fragments, for example, in planetary nebulae, to phenylacetylene plus atomic hydrogen.

Consequently, future infrared spectroscopic surveys of planetary nebulae should search for infrared features of the phenylacetylene molecule—a crucial building block of complex PAHs in the interstellar medium. Since the reaction between phenyl and acetylene has an entrance barrier, it should be noted that it does not contribute to the formation of PAHs in cold

molecular clouds, where averaged translational temperatures of the reactants of only 10 K reside. However, reactants in planetary nebulae close to the central star can have temperatures of up to a few 1000 K (which are sufficiently high to overcome the entrance barrier). We anticipate that this generalized concept of a phenyl-radical-versus-atomic-hydrogen exchange is a starting point in a systematic investigation of phenyl-radical reactions with unsaturated hydrocarbons under single-collision conditions and a search for hitherto unobserved reaction intermediates of these reactions in space and in combustion flames.

Experimental Section

The reaction was conducted under single-collision conditions, at collision energies of 71 and 96 kJ mol^{-1} , using a crossed-molecular-beam machine.^[22] The supersonic phenyl-radical beam was generated by flash pyrolysis of helium-seeded nitrosobenzene (Aldrich) at seeding fractions of less than 0.1 %. This mixture was expanded, at a stagnation pressure of 920 Torr, through a resistively heated silicon carbide tube held at temperatures of 1200–1500 K. The pulsed valve was operated at 200 Hz, with pulses that were 150 μs wide (under these conditions, the decomposition of nitrosobenzene is quantitative). A chopper wheel, mounted after the skimmer, selected a component of the phenyl-radical beam before it crossed a pulsed acetylene beam at a right angle in the interaction region.^[23] To extract the position of the hydrogen-atom loss, we also performed experiments with $[D_2]$ acetylene. TOF spectra and laboratory angular distributions of the reactively scattered products were probed utilizing a quadrupole mass spectrometer with an electron-impact ionizer. Information on the reaction dynamics was gained by fitting the laboratory data using a forward-convolution routine, thereby yielding the angular-flux distribution $T(\theta)$ and the translational-energy-flux distribution $P(E)$ in the center-of-mass system.^[24]

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