

# Low temperature formation of naphthalene and its role in the synthesis of PAHs (Polycyclic Aromatic Hydrocarbons) in the interstellar medium

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Polycyclic aromatic hydrocarbons (PAHs) are regarded as key molecules in the astrochemical evolution of the interstellar medium, but the formation mechanism of even their simplest prototype—naphthalene ( $C_{10}H_8$ )—has remained an open question. Here, we show in a combined crossed beam and theoretical study that naphthalene can be formed in the gas phase via a barrierless and exoergic reaction between the phenyl radical ( $C_6H_5$ ) and vinylacetylene ( $CH_2 = CH-C \equiv CH$ ) involving a van-der-Waals complex and submerged barrier in the entrance channel. Our finding challenges conventional wisdom that PAH-formation only occurs at high temperatures such as in combustion systems and implies that low temperature chemistry can initiate the synthesis of the very first PAH in the interstellar medium. In cold molecular clouds, barrierless phenyl-type radical reactions could propagate the vinylacetylene-mediated formation of PAHs leading to more complex structures like phenanthrene and anthracene at temperatures down to 10 K.

astrochemistry | reaction dynamics | molecular beams | flame chemistry

The ubiquitous presence of polycyclic aromatic hydrocarbons (PAHs)—organic molecules carrying fused benzene rings—together with their (de)hydrogenated, ionized, and protonated counterparts in the interstellar medium (1–3) has been inferred from the unidentified infrared emission bands observed in the range of 3–14  $\mu\text{m}$  (4) and through the diffuse interstellar bands (5, 6), discrete absorption features superimposed on the interstellar extinction curve ranging from the blue part of the visible (400 nm) to the near-infrared (1.2  $\mu\text{m}$ ). Because the first postulation of their interstellar relevance as the missing link between small carbon clusters and amorphous carbon particles with PAHs possibly constituting up to 10% of the interstellar carbon budget (7–12), PAHs have been associated with the prebiotic evolution of the interstellar medium and are thought to provide critical nucleation sites eventually leading to carbonaceous dust particles (13, 14). The discovery of the simplest PAH naphthalene, which consists of a pair of fused benzene rings, in at least 20 carbonaceous chondrites suggests an interstellar origin (15, 16). Contemporary astrochemical models of PAH formation have been derived from the combustion chemistry community. The most favorable routes to interstellar PAHs were suggested to involve molecular weight growth processes in the warm and dense circumstellar envelopes of carbon-rich stars through sequential reactions of aromatic (phenyl) (17–19) and resonantly stabilized radicals (propargyl) (20). Along with acetylene, these reactions are viewed as the basis for the hydrogen abstraction, acetylene addition mechanism (17–21) operating at elevated temperatures of about 1,000 K. Theoretical studies proposed that at these temperatures, naphthalene might also be formed via phenyl radical reactions with vinylacetylene (22, 23), through the reaction of benzene with o-benzyne (24), and via the self-reaction of two cyclopentadienyl radicals (25). Nevertheless, the validity of these routes to form PAHs has remained conjectural, because not a single laboratory experiment could corroborate to what extent PAHs

were formed in these elementary reactions. Consequently, the formation mechanisms of even their simplest representative—the naphthalene molecule as tentatively observed via its  $C_{10}H_8^+$  cation toward the Perseus Cloud (26) and possibly in its protonated form ( $C_{10}H_9^+$ ) (4) has remained elusive to date.

In recent years it has become quite clear that interstellar PAHs are rapidly destroyed in the interstellar medium (27–29). First, driven by laboratory studies on the loss of acetylene upon photolysis of small PAHs, theoretical studies predict lifetimes of a few times  $10^8$  y for PAHs in the diffuse interstellar medium. Second, interstellar shock waves driven by supernova explosions predict similar short lifetimes for PAHs in the interstellar medium (30). Lastly, energetic cosmic ray bombardment rapidly processes small PAHs, again on a time scale of few  $10^8$  y (27–29). These time scales are much shorter than the time scale for injection of new material into the interstellar medium by carbon-rich Asymptotic Giant Branch (AGB) stars—some  $2 \times 10^9$  y—and carbon-rich planetary nebulae as the descendants of AGB stars (13, 18, 20, 31). Hence, the ubiquitous presence of PAHs in the interstellar medium implies a crucial, hitherto unexplained route to a fast chemical growth of PAHs in the cold environment of the interstellar medium at temperatures down to 10 K.

Here, we report the results of the crossed molecular beam reactions of phenyl [ $C_6H_5(X^2A_1)$ ] and D5-phenyl [ $C_6D_5(X^2A_1)$ ] radicals with vinylacetylene [ $CH_2 = CH-C \equiv CH(X^1A')$ ]. By combining these data with electronic structure calculations, we present a barrierless formation route to interstellar naphthalene [ $C_{10}H_8(X^1A_g)$ ] via a single collision event involving a van-der-Waals complex and a submerged barrier in the entrance channel. This barrierless pathway defies conventional wisdom that PAH formation—such as naphthalene—via phenyl radical reactions only occurs in high temperature environments like circumstellar envelopes of evolved carbon stars. The facile route to naphthalene and possibly to higher order PAHs like anthracene and phenanthrene in low temperature environments presents a fundamental shift in currently “accepted” perceptions of the formation of PAHs and proposes cold molecular clouds such as carbon chain rich cores of TMC-1 and OMC-1 (32) as potential “molecular nurseries” of PAH synthesis.

## Results

**Crossed Molecular Beams Studies—Laboratory Frame.** The gas phase reactions of the phenyl and of the D5-phenyl radical with vinyl-

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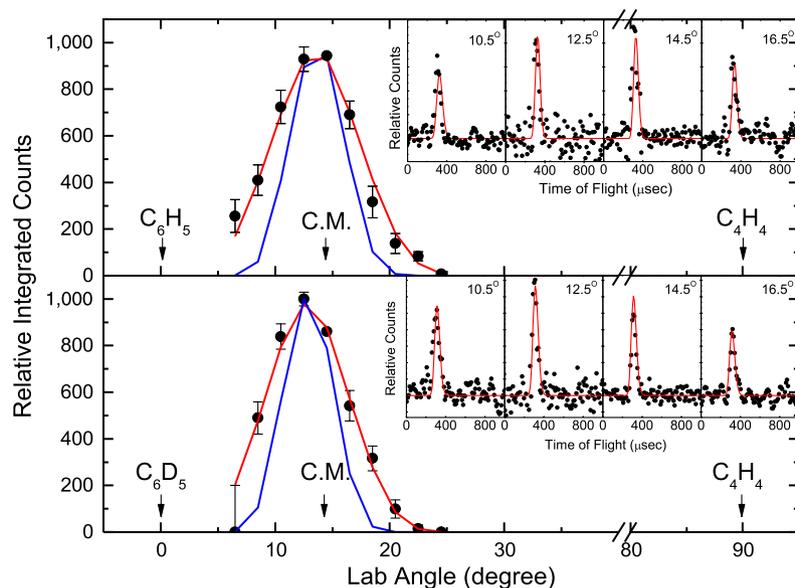
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lacetylene were examined experimentally under single collision conditions utilizing a crossed molecular beam machine by intersecting supersonic beams of phenyl and D5-phenyl radicals with vinylacetylene perpendicularly at collision energies of  $47.0 \pm 1.0 \text{ kJ mol}^{-1}$  and  $48.4 \pm 1.0 \text{ kJ mol}^{-1}$ , respectively (*SI Materials and Methods*). Within the triply differentially pumped quadrupole mass spectrometric detector, the neutral reaction products were first ionized via electron impact at 80 eV and then mass- and velocity-analyzed to collect time-of-flight (TOF) spectra of the ionized reaction products. For the phenyl–vinylacetylene system, we recorded reactive scattering signal at a mass-to-charge ratio ( $m/z$ ) of 128 ( $\text{C}_{10}\text{H}_8^+$ ) (Fig. 1); signal at  $m/z = 129$  originated from the ionized,  $^{13}\text{C}$ -substituted product ( $^{13}\text{C}_9\text{H}_8^+$ ), and within the detection limits not from a  $\text{C}_{10}\text{H}_9$  adduct. These raw data alone indicate that the reaction of the phenyl radical ( $\text{C}_6\text{H}_5$ ) with vinylacetylene ( $\text{CH}_2 = \text{CH}-\text{C}\equiv\text{CH}$ ;  $\text{C}_4\text{H}_4$ ) leads to the synthesis of a hydrocarbon molecule with the molecular formula  $\text{C}_{10}\text{H}_8$  plus atomic hydrogen via a single collision event. The reaction of the D5-phenyl radical with vinylacetylene was conducted under identical conditions as the phenyl–vinylacetylene reaction to quantify to what extent the hydrogen atom originates from the vinylacetylene reactant. We observed reactive scattering signal at  $m/z = 133$  ( $\text{C}_{10}\text{H}_3\text{D}_5^+$ ) indicating that in the reaction of D5-phenyl ( $\text{C}_6\text{D}_5$ ) with vinylacetylene ( $\text{C}_4\text{H}_4$ ), the hydrogen atom is at least released from the vinylacetylene reactant. Considering that the count rates of the hydrogen atom losses in the vinylacetylene reactions with phenyl and D5-phenyl radicals are essentially identical within the error limits, the hydrogen atom is suggested to be ejected predominantly from the vinylacetylene reactant, and not from the phenyl group.

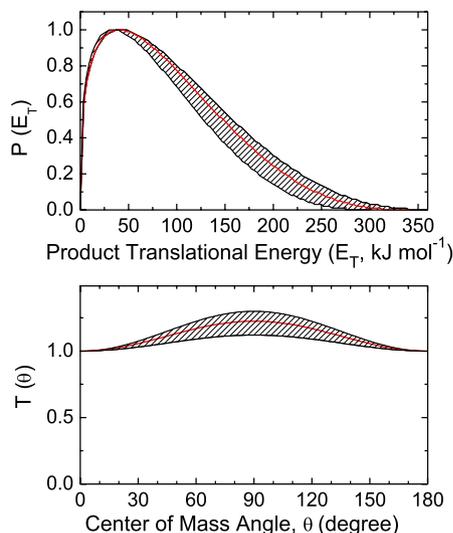
**Crossed Molecular Beams Studies—Center-of-Mass Frame.** The interpretation of the raw data provided convincing evidence that in the reaction of phenyl radicals with vinylacetylene, a hydrocarbon of the molecular formula  $\text{C}_{10}\text{H}_8$  is formed via an atomic hydrogen loss as the driving force with the hydrogen atom originating principally from the vinylacetylene reactant. We shift our attention now to the identification of the product isomer(s) formed. This identification necessitates an extraction of the underlying chemical dynamics of the (D5)-phenyl–vinylacetylene system by transforming the experimental data from the laboratory to the center-

of-mass reference frame (33). The best fits of the laboratory data are overlaid in Fig. 1 with the center-of-mass angular ( $T(\theta)$ ) and translational flux distributions ( $P(E_T)$ ) depicted in Fig. 2. The laboratory data for both reactions could be reproduced with identical center-of-mass functions utilizing a single channel fit with the mass combinations of the products of 128 ( $\text{C}_{10}\text{H}_8$ ) plus 1 (H) and 133 ( $\text{C}_{10}\text{D}_5\text{H}_3$ ) plus 1 (H) for the reactions of vinylacetylene with phenyl and D5-phenyl, respectively. We would like to stress that no fit could be obtained by assuming the signal at  $m/z = 128$  and 133 originated from dissociative ionization of potential  $\text{C}_{10}\text{H}_9$  and  $\text{C}_{10}\text{D}_5\text{H}_4$  adducts. The center-of-mass translational energy distribution,  $P(E_T)$ , helps assigning the product isomer(s). For those molecules formed without internal excitation, the high energy cutoff of the  $P(E_T)$  of  $315 \pm 30 \text{ kJ mol}^{-1}$  presents the sum of the reaction exoergicity plus the collision energy. A subtraction of the collision energy suggests that the reaction is exoergic by  $268 \pm 30 \text{ kJ mol}^{-1}$ . This value is in excellent agreement with the computed ( $-265 \pm 5 \text{ kJ mol}^{-1}$ ) and literature data ( $-276 \pm 18 \text{ kJ mol}^{-1}$ ) (34) to form naphthalene plus atomic hydrogen. The 1-phenyl-vinylacetylene isomer is less stable by  $223 \pm 5 \text{ kJ mol}^{-1}$  and cannot account for the experimentally derived reaction energy. Note that the  $P(E_T)$  depicts a pronounced distribution maximum of  $30\text{--}40 \text{ kJ mol}^{-1}$  indicating the involvement of a rather tight exit transition state to form naphthalene plus a hydrogen atom. Considering the center-of-mass angular distribution, the  $T(\theta)$  presents intensity over the complete angular range. This result indicates that the reactions follow indirect scattering dynamics through the formation of  $\text{C}_{10}\text{H}_9$  and  $\text{C}_{10}\text{H}_4\text{D}_5$  complexes with life times longer than their rotational periods (35). Most importantly, the  $T(\theta)$  depicts a pronounced distribution maximum at  $90^\circ$  with ratios of the flux intensities at the respective maxima and minima of the distribution,  $I(90^\circ)/I(0^\circ)$ , of  $1.3 \pm 0.2$  to form  $\text{C}_{10}\text{H}_8/\text{C}_{10}\text{H}_3\text{D}_5$  plus atomic hydrogen; this “sideways” scattering exposes geometrical constraints of the fragmenting  $\text{C}_{10}\text{H}_9/\text{C}_{10}\text{H}_4\text{D}_5$  intermediates with the hydrogen atom being ejected almost parallel to the total angular momentum vector and hence perpendicularly to the molecular plane of the rotating, decomposing complex(es) (35).

**Electronic Structure Calculations and Reaction Mechanisms.** Having identified the naphthalene molecule as the product of the gas



**Fig. 1.** Laboratory angular distributions and time-of-flight spectra recorded at mass-to-charges,  $m/z$ , of 128 ( $\text{C}_{10}\text{H}_8^+$ ) and 133 ( $\text{C}_{10}\text{H}_3\text{D}_5^+$ ) in the reactions of phenyl and D5-phenyl with vinylacetylene, respectively. Closed circles signify the experimental data and the red lines the calculated distribution with the best fit center-of-mass functions as depicted in Fig. 2. The blue lines demonstrate that no reasonable fit could be achieved assuming the formation of the thermodynamically less stable 4-phenyl-vinylacetylene isomer. C.M. designates the center-of-mass angles.

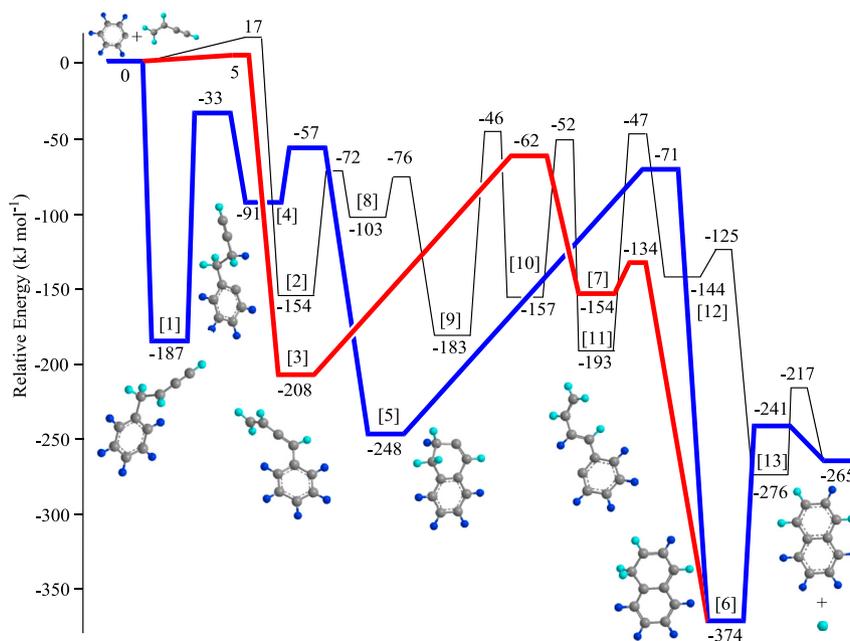


**Fig. 2.** Center-of-mass angular (top) and translational energy flux distributions (bottom) leading to the formation of the naphthalene ( $C_{10}H_8$ ) and D5-naphthalene ( $C_{10}D_5H_3$ ) in the reactions of phenyl and D5-phenyl with vinylacetylene, respectively. Hatched areas indicate the acceptable upper and lower error limits of the fits. The solid line defines the best fit functions.

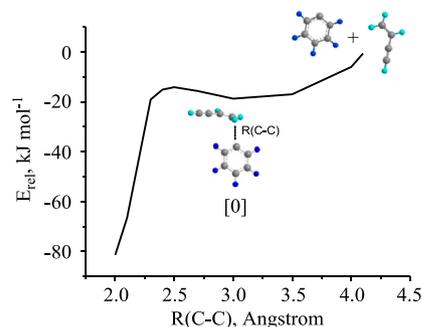
phase reaction of the phenyl radical with vinylacetylene under single collision conditions, we are merging now these findings with the computational results to untangle the underlying reaction mechanism(s) (Figs. 3 and 4) (*SI Materials and Methods*). Our electronic structure calculations exposed three pathways to naphthalene, among them one de facto barrierless route in the entrance channel. All reactions lead ultimately via addition of the phenyl radical to the C1, C3, and C4 carbon atoms of vinylacetylene to  $C_{10}H_9$  intermediates [1], [2], and [3] bound by 154 to 208  $\text{kJ mol}^{-1}$ . Most importantly, when the phenyl radi-

cal approaches the C1 carbon atom of vinylacetylene, the potential energy surface is attractive until a van-der-Waals complex [0], which is bound by 19  $\text{kJ mol}^{-1}$  with respect to the separated reactants, is formed. The further approach leading to the formation of a covalent carbon-carbon bond and hence intermediate [1] is hindered by a barrier of 5  $\text{kJ mol}^{-1}$ , but the corresponding transition state lies lower in energy than the separated phenyl plus vinylacetylene reactants. In this sense, a barrier to addition exists, but this barrier is located below the energy of the separated reactants and hence called a *submerged barrier*. In such a situation, the kinetics are controlled by two transition states: a loose, indistinct outer variational transition state and a tight inner transition state corresponding to the *submerged barrier*. The outer transition state is rate controlling at low temperatures and the inner one at high temperatures. For the overall reaction from phenyl plus vinylacetylene to intermediate [1], the reaction is de facto barrierless. The existence of the van-der-Waals complex and of the submerged barrier was verified by a careful examination of the potential energy surface in the entrance channel (*SI Materials and Methods*).

This barrierless pathway deserves further discussion. Conventional wisdom dictates that the addition of the phenyl radical to an olefinic double and acetylenic triple bond is associated with entrance barriers, for example 15  $\text{kJ mol}^{-1}$  and 10  $\text{kJ mol}^{-1}$  for acetylene (36) and ethylene (37), respectively, as the “building blocks” of vinylacetylene. Even though these barriers are quite low, they cannot be overcome at low temperatures of 10 K as prevailing, for example, in cold molecular clouds. However, the enhanced polarizability of vinylacetylene of 7.70  $\text{\AA}^3$ , which correlates with greater attractive long range dispersion forces between the phenyl radical and vinylacetylene compared to phenyl and acetylene (3.48  $\text{\AA}^3$ ) or ethylene (4.15  $\text{\AA}^3$ ), triggers first the formation of the weakly bound van-der-Waals complex [0], which then isomerizes via a submerged barrier. Our results are also in line with a semiempirical criterion for a reaction between an unsaturated hydrocarbon with an open shell reactant to be



**Fig. 3.** Potential energy surface of the reaction of phenyl radicals with vinylacetylene leading to naphthalene. Relative energies are given in units of  $\text{kJ mol}^{-1}$  for the reaction of phenyl with vinylacetylene; for the reaction of D5-phenyl with vinylacetylene (with deuterium atoms shown in dark blue, and hydrogen atoms in light blue), relative energies do not differ from those for the phenyl plus vinylacetylene reaction by more than 1  $\text{kJ mol}^{-1}$ . The barrierless reaction pathway highlighted in blue dominates the naphthalene formation in cold molecular clouds holding temperatures as low as 10 K. The pathway denoted in red is also relevant at elevated temperatures as present, for instance, in circumstellar envelopes of evolved carbon stars. Our study suggests that the reaction sequence in black is—if at all—only of minor importance to form naphthalene. Optimized Cartesian coordinates for all structures and a full version of this surface including the pathways to monocyclic isomers and hydrogen abstraction yielding benzene are given in the Supporting Information.



**Fig. 4.** Barrierless formation of the van-der-Waals complex [0] and its isomerization via a submerged barrier to intermediate [1].

barrierless and fast at low temperatures as derived by Smith, et al. (38). The authors suggested that if the difference of the ionization energy of the molecule (I.E.) and electron affinity of the open shell reactant (E.A.) is below 8.75 eV and the reaction rate constant at 298 K,  $k_{298}$ , is above  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , the reaction is likely to accelerate to lower temperatures with rate coefficients approaching the collision-determined limit at very low temperatures. Both criteria are satisfied for the reaction of phenyl radicals with vinylacetylene with  $\text{I.E.} - \text{E.A.} = 8.48 \text{ eV}$  (27) and our computed phenyl to vinylacetylene (at C1) addition rate constant being  $1.5 \times 10^{-11}$  and  $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 and 100 K, respectively\* (39). For comparison, it is important to note that reactions of the cyano ( $\text{C} \equiv \text{N}$ ) and ethynyl ( $\text{C} \equiv \text{CH}$ ) radicals with unsaturated hydrocarbons are all barrierless, (39) even for acetylene and ethylene reactants. Once again, this observation can be rationalized in terms of the energy difference between the I.E. of the closed shell hydrocarbon and the E.A. of the radical reactant.

After isomerization to intermediate [1], the latter undergoes a hydrogen shift from the phenyl ring to the vinylacetylene moiety via intermediate [4] followed by ring closure to [5] and hydrogen shift forming [6]. A hydrogen ejection from the C1 carbon atom of the 1-hydro-naphthalene intermediate [6] leads via a tight exit transition state located  $24 \text{ kJ mol}^{-1}$  above the products to naphthalene. Both competing pathways to naphthalene via addition to C4 and C3 involve entrance barriers of 5 and  $17 \text{ kJ mol}^{-1}$ , respectively. The resulting doublet radicals [3] and [2] undergo either a hydrogen shift followed by cyclization and naphthalene formation ( $[7] \rightarrow [6] \rightarrow \text{naphthalene plus atomic hydrogen}$ ) or involve a multistep isomerization sequence via intermediates [8] to [13] to be terminated by a hydrogen atom loss via a tight exit transition state to naphthalene. Which presents the dominant route to naphthalene formation under our experimental conditions? Considering our collision energy of  $47 \text{ kJ mol}^{-1}$ , each entrance channel to addition might be open. However, the results from the D5-phenyl—vinylacetylene system provide vital guidance to exclude the highest energy pathway via intermediate [2]. Fig. 3 traces the incorporated deuterium atoms from the D5-reactants in dark blue. Naphthalene formation requires intermediates [6] (C1/C4 addition) or [13] (C3 addition). This formation would involve the emission of a hydrogen atom from the  $\text{sp}^3$  hybridized C1 carbon atom of the  $\text{CH}_2$  moiety in [6], but requires the ejection of atomic deuterium from the bridging carbon atom

in [13]. Because the experimental data implied an atomic hydrogen loss from the vinylacetylene moiety, we suggest that in our experiments, naphthalene is formed preferentially via both low-energy pathways through addition of the phenyl radical to the C1 and C4 carbon atoms ultimately leading via intermediate [6] to naphthalene. The pathway via addition at C3 is proposed to be of minor importance; this can be rationalized in terms of a higher barrier to addition ( $17 \text{ kJ mol}^{-1}$ ); also, the resulting intermediate [2] would require seven reaction steps to naphthalene compared to four at most via intermediate [6]. Our computations also revealed that three monocyclic products cis-1-phenyl-vinylacetylene, 4-phenyl-vinylacetylene, and trans-1-phenyl-vinylacetylene are accessible; these isomers, however, are more than  $200 \text{ kJ mol}^{-1}$  less stable than naphthalene. At zero pressure and collision energies lower than  $5 \text{ kJ mol}^{-1}$ , our calculations predict an almost exclusive formation of naphthalene with branching ratios of about 99%. At collision energies from 5 to  $50 \text{ kJ mol}^{-1}$ , the computed naphthalene production eventually decreases to about 70% of the products, with cis/trans-1-phenyl-vinylacetylene and 4-phenyl-vinylacetylene yields increasing to 15% and 13%, respectively. Note that our calculations indicate that the branching ratios with and without tunneling corrections are nearly identical because the tunneling corrections are insignificant due to the high internal energy content of chemically activated  $\text{C}_{10}\text{H}_9$  intermediates. Finally, it is important to address a competing reaction pathway at elevated collision energies: the hydrogen abstraction from the C2 and C1 carbon atoms forming the benzene molecule and  $i\text{-C}_4\text{H}_3$  and  $n\text{-C}_4\text{H}_3$ , respectively. These reactions are exoergic by 46 and  $3 \text{ kJ mol}^{-1}$ , but involve abstraction barriers of 21 and  $37 \text{ kJ mol}^{-1}$ , respectively (*SI Materials and Methods*). Therefore, these pathways cannot compete in cold molecular clouds.

**Chemical Dynamics.** To summarize the chemical dynamics, the reaction of the phenyl radical with vinylacetylene is proposed to be initiated by an addition of the phenyl radical to the terminal carbon atoms of the vinylacetylene reactant at the vinyl- and acetylene moieties leading eventually to doublet radical intermediates. At the vinyl group, the addition is initiated via the formation of a van-der-Waals complex followed by an isomerization of the latter through a submerged barrier, whereas the competing addition at the acetylene group involves a barrier of  $5 \text{ kJ mol}^{-1}$ . Both intermediates ultimately isomerize to the bicyclic 1-hydro-naphthyl intermediate, which emits atomic hydrogen to form naphthalene. As predicted experimentally based on the off-zero peaking of the center-of-mass translational energy distribution and also theoretically, the exit transition state is rather tight and located about  $24 \text{ kJ mol}^{-1}$  above the separated products. This result can be easily rationalized because the reversed reaction involves the addition of a hydrogen atom to a closed shell aromatic hydrocarbon, which is associated with an entrance barrier. Considering the computed structures of the exit transition state, the hydrogen atom leaves the decomposing complex almost perpendicularly to the molecular plane; i.e.,  $86^\circ$ , as predicted based on the center-of-mass angular distribution peaking at  $90^\circ$ . Note that our experiment was conducted at a collision energy of  $47 \text{ kJ mol}^{-1}$ , which would be equivalent to a temperature of about 5,400 K. Hence, the temperature equivalent of our collision energy is significantly higher than the average translational temperature in cold molecular clouds (10 K); it is however comparable with temperatures in the circumstellar envelopes of carbon-rich stars with temperatures of about 1,000 K. Consequently, in cold molecular clouds, naphthalene is formed almost exclusively with fractions of 99 % via the low temperature route (C1 addition). At elevated temperatures, the higher energy addition pathway is accessible, which leads preferentially to naphthalene as well.

**Interstellar Chemistry and Conclusions.** Having revealed the facile synthesis of naphthalene under single collision conditions, we

\*It is noteworthy that the phenyl reaction with 1,3-butadiene with a polarizability of  $8.50 \text{ \AA}^3$  was also found to be barrierless Ismail J Park, B.M. Wong, W.H. Green Jr., M.C. Lin, Proc. Combust. Inst. 30, 1049 (2005). However, although this reaction has  $\text{I.E.} - \text{E.A.} = 7.97 \text{ eV}$  and satisfies the first criterion, its experimentally measured and theoretically calculated  $k_{298}$  are  $2.9 \times 10^{-13}$  and  $2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively, and the second criterion is not fulfilled (38). Theoretical calculations predict the activation energy for this reaction to be zero, and experimental measurements in the 298–450 K range suggest an activation energy of  $2 \pm 5 \text{ kJ mol}^{-1}$  and thus the low-temperature behavior of the rate coefficient for the related reaction of phenyl radicals reacting with 1,3-butadiene remains uncertain

discuss these findings in the context of “real” interstellar environments. Our combined experimental and computational investigation uncovered an exoergic and barrierless route to the simplest representative of polycyclic aromatic hydrocarbons—naphthalene—under single collision conditions via the gas phase reaction of the phenyl radical with vinylacetylene with all isomerization barriers located below the energy of the separated reactants. Considering that the hydrogen atoms in vinylacetylene and at the meta- and para- position of the phenyl radical can be substituted by organic side groups, the reaction of vinylacetylene with the phenyl radical represents the prototype reaction of a previously disregarded, unique reaction class leading to the formation of naphthalene derivatives even in cold molecular clouds. Because photodissociation of naphthalene can further lead via atomic hydrogen loss from the C1 and C2 positions to 1- and 2-naphthyl radicals with high yields of about 80% ( $C_{10}H_7$ ), (40, 41) reactions of the latter with vinylacetylene might propagate PAH extension to systems with three fused benzene rings: anthracene and phenanthrene ( $C_{14}H_{10}$ ). These reactions are also expected to be barrierless due to the much stronger bound van-der-Waals complex between vinylacetylene and the naphthyl radical in the entrance channels. Hence, we consider the reaction of vinylacetylene with the phenyl radical the prototype of a class of reactions for growth of PAHs in cold environments. Barriers above the energy of the separated reactants, such as those involved in previously proposed high energy acetylene addition routes cannot be overcome at the low temperatures of 10 K as present in molecular clouds like Taurus Molecular Cloud (TMC-1). Our key finding—the formation of naphthalene as a result of a fast neutral–neutral reaction at low temperatures—challenges conventional theories that PAHs can only be synthesized in high temperature environments as present in circumstellar envelopes of evolved carbon stars like IRC+10216.

Indeed, reactions of doublet PAH radicals, formed via photodissociation through an atomic hydrogen loss, with vinylacetylene open up a versatile chemical route to a step-wise growth of PAHs via fast, barrierless bimolecular collisions at temperatures as low as 10 K. Our proposed chemical route to PAH growth requires the presence of vinylacetylene as well as phenyl and doublet PAH radicals (phenyl-like radicals). Note that neither phenyl radicals nor vinylacetylene have been detected in interstellar clouds, presumably due to their very low dipole moments of 0.9 Debye and 0.4 Debye, respectively (42, 43), or their high reactivity resulting in low fractional abundances. However, in molecular clouds, vinylacetylene can be synthesized via the barrierless and exoergic reaction of ethynyl radicals (CCH), formed from photodissociation of acetylene ( $C_2H_2$ ), with ethylene ( $C_2H_4$ ) (44); the phenyl radical can be rapidly generated in photon dominated regions via photolysis, where ultraviolet photons photolyze benzene ( $C_6H_6$ ) (45, 46).

Therefore, the edges of molecular clouds, where atomic gas is transformed into molecular gas and the carbon drives a complex hydrocarbon chemistry, are likely the prime growth locations of PAH formation via de facto barrierless routes. The reaction pathway proposed here may provide the key to understanding the high abundance of PAHs in the harsh environment of the interstellar medium, where their destruction is rapid (11). A postulated, but hitherto unconfirmed model suggests that the processing of large carbonaceous grains in interstellar shocks by grain-grain collisions forms PAHs as fragmentation products (28). An alternative reformation pathway proposed the build-up of PAHs via unstudied reaction pathways involving insertion reactions of neutral and singly ionized carbon atoms, reactions with molecular hydrogen, and dissociative recombination (47, 48). On the other hand, our combined experimental and theoretical study provides compelling evidence that the prototype PAH—naphthalene—can be synthesized even in cold interstellar environments through a fast,

barrierless reaction involving two neutral reactants: the phenyl-type radical and vinylacetylene.

To conclude, our study opens up a versatile, hitherto overlooked reaction class growing PAHs such as naphthalene at low temperatures down to 10 K as prevailing in cold molecular clouds thus challenging conventional wisdom that PAHs can only be formed at elevated temperatures as found in circumstellar envelopes of evolved carbon stars and on Earth in combustion systems.

## Materials and Methods

**Experimental.** The experiments were conducted under single collision conditions in a crossed molecular beams machine (33). A helium-seeded molecular beam of (deuterated) phenyl radicals ( $C_6H_5$ ,  $C_6D_5$ ;  $X^2A_1$ ) at fractions of 1% was prepared by photolysis of (deuterated) chlorobenzene ( $C_6H_5Cl$  99.9%;  $C_6D_5Cl$  99%; Fluka) in the primary source. The gas mixture was introduced by a piezoelectric pulsed valve (Proch-Trickl), operated at 120 Hz and with a backing pressure of about 1.5 atm. The (deuterated) chlorobenzene was photolyzed by focusing the 193 nm excimer laser output operating at 60 Hz and 10 mJ per pulse 1 mm downstream of the nozzle prior to the skimmer at fractions of ~90%. The molecular beam entraining the (deuterated) phenyl radical passed a skimmer and a four-slot chopper wheel, which selected segments of the pulsed (deuterated) phenyl radical ( $C_6D_5$ ,  $X^2A_1$ ) beam of well defined peak velocities ( $v_p$ ) and speed ratios ( $S$ ) (SI Materials and Methods). The phenyl radical beam bisected a pulsed molecular beam of vinylacetylene seeded in argon (Airgas, 99.9999%) at fractions of 5%. Vinylacetylene was synthesized according to ref. 49. The reaction products were monitored using a triply differentially pumped quadrupole mass spectrometer in the TOF mode after electron-impact ionization of the neutral molecules at 80 eV. The ions were separated according to their mass-to-charge ratio by a quadrupole mass spectrometer; only ions with the desired mass-to-charge,  $m/z$ , value passed through and were accelerated toward a high voltage (–22.5 kV) stainless steel target coated with an aluminum layer. The ions hit the surface and initiated an electron cascade that was accelerated by the potential until they reached an aluminum coated organic scintillator whose photon cascade was detected by a photomultiplier tube. The signal from the photomultiplier tube was then filtered prior to feeding into a multichannel scaler to record time-of-flight spectra. The TOF spectra recorded at each angle and the product angular distribution in the laboratory frame were fit with Legendre polynomials using a forward-convolution routine. This method uses an initial choice of the product translational energy  $P(E_T)$  and the angular distribution  $T(\theta)$  in the center-of-mass reference frame to reproduce TOF spectra and a product angular distribution. The TOF spectra and product angular distribution obtained from the fit were then compared to the experimental data. The parameters of the  $P(E_T)$  and  $T(\theta)$  were iteratively optimized until the best fit was reached.

**Electronic Structure Calculations.** Geometries of all intermediates and transition states on the  $C_{10}H_8$  potential energy surface accessed via the reaction of phenyl radicals with vinylacetylene as well as the reaction reactants and products were optimized using the hybrid density functional B3LYP method (50, 51) with the 6-311G\*\* basis set. The same method was used to obtain vibrational frequencies, molecular structural parameters, zero-point energy (ZPE) corrections, and to characterize the stationary points as minima or first-order saddle points. To obtain more accurate energies, we applied the G3(MP2,CC)//B3LYP modification (52, 53) of the original Gaussian 3 (G3) scheme (54) for high-level single-point energy calculations. The final energies at 0 K were obtained using the B3LYP optimized geometries and ZPE corrections according to the following formula  $E_0[G3(MP2,CC)] = E[CCSD(T)/6-311G(d,p)] + \Delta E_{MP2} + E(ZPE)$ , where  $\Delta E_{MP2} = E[MP2/G3large] - E[MP2/6-311G(d,p)]$  is the basis set correction and  $E(ZPE)$  is the zero-point energy.  $\Delta E(SO)$ , a spin-orbit correction, and  $\Delta E(HLC)$ , a higher level correction, from the original G3 scheme were not included in our calculations, as they are not expected to make significant contributions into relative energies. We applied the Gaussian 98 (55) program package to carry out B3LYP and MP2 calculations, and the MOLPRO 2006 (56) program package to perform calculations of spin-restricted coupled cluster RCCSD(T) energies. Polarizabilities were computed at the B3LYP/aug-cc-pVTZ level of theory using the Gaussian 09 package (57).

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