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 (C10H8)—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 exergonic reaction between the phenyl radical (C6H5) and vinylacetylene (CH2=CH-C≡CH) involving a van-der-Waals complex and a 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.

Results

Crossed Molecular Beams Studies—Laboratory Frame. The gas phase reactions of the phenyl and of the D5-phenyl radical with vinylacetylene (C6H5CH2=CH-C≡CH) has remained an open question. Here, we report the results of the crossed molecular beam reactions of phenyl [C6H5CH2A] and D5-phenyl [C6D5CH2A] radicals with vinylacetylene [CH2=CH-C≡CH(CH=CH2)] 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 as potential “molecular nurseries” of PAH synthesis.


The authors declare no conflict of interest.

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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 ± 1.0 kJ mol⁻¹ and 48.4 ± 1.0 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 \( m/z = 128 \) (C₁₀H₅⁻) (Fig. 1); signal at \( m/z = 129 \) originated from the ionized, \(^{13}\)C-substituted product (\(^{13}\)CC₅H₄⁻), and within the detection limits not from a C₁₀H₆ adduct. These raw data alone indicate that the reaction of the phenyl radical (C₁₀H₅⁻) with vinylacetylene (CH₂ = CH-C ≡ CH; C₅H₃⁻) leads to the synthesis of a hydrocarbon molecule with the molecular formula C₁₀H₅ 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 \( m/z = 133 \) (C₁₀H₅D₅⁻) indicating that in the reaction of D₅-phenyl (CD₅⁻) with vinylacetylene (C₅H₃⁻), 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 C₁₀H₅ 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(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 (C₁₀H₅) plus 1 (H) and 133 (C₁₀H₅D₅) 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 C₁₀H₆ and C₁₀H₅D₅ 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 ± 30 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 exergic by 268 ± 30 kJ mol⁻¹. This value is in excellent agreement with the computed \((−265 ± 5 \text{ kJ mol}^{-1})\) and literature data \((−276 ± 18 \text{ kJ mol}^{-1})\) (34) to form naphthalene plus atomic hydrogen. The 1-phenyl-vinylacetylene isomer is less stable by 223 ± 5 kJ mol⁻¹ and cannot account for the experimentally derived reaction energy. Note that the \( P(E_T) \) depicts a pronounced distribution maximum of 30–40 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 C₁₀H₆ and C₁₀H₅D₅ complexes with life times longer than their rotational periods (35). Most importantly, the \( T(\theta) \) depicts a pronounced distribution maximum at 90° with ratios of the flux intensities at the respective maxima and minima of the distribution, \( I(90°)/I(0°) \), of 1.3 ± 0.2 to form C₁₀H₆/C₁₀H₅D₅ plus atomic hydrogen; this “sideways” scattering exposes geometrical constraints of the fragmenting C₁₀H₆/C₁₀H₅D₅ 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](https://www.pnas.org/cgi/doi/10.1073/pnas.1113827108)
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 C10H8 intermediates [1], [2], and [3] bound by 154 to 208 kJ mol\(^{-1}\). Most importantly, when the phenyl radical 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 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 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 kJ mol\(^{-1}\) and 10 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 7.7 Å\(^3\), which correlates with greater attractive long range dispersion forces between the phenyl radical and vinylacetylene compared to phenyl and acetylene (3.48 Å\(^3\)) or ethylene (4.15 Å\(^3\)), 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
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 $5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ 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 I.E. – E.A. = 8.48 eV (27) and our computed phenyl to vinylacetylene (at C1) addition rate constant being $1.5 \times 10^{-11}$ and $2.5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 and 100 K, respectively* (39). For comparison, it is important to note that reactions of the cyano (C≡N) and ethynyl (C≡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 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 kJ mol$^{-1}$, respectively. The resulting doublet radicals [3] and [2] undergo either a hydrogen shift followed by cyclization and naphthalene formation (Eq. [7]→[6]) or 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 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 sp$^3$ hybridized C1 carbon atom of the CH$_3$ 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 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 monomeric products cis-1-phenyl-vinylacetylene, 4-phenyl-vinylacetylene, and trans-1-phenyl-vinylacetylene are accessible; these isomers, however, are more than 200 kJ mol$^{-1}$ less stable than naphthalene. At zero pressure and collision energies lower than 5 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 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 C$_2$H$_2$ 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-C$_3$H$_4$ and n-C$_3$H$_4$, respectively. These reactions are exergonic by 46 and 3 kJ mol$^{-1}$, but involve abstraction barriers of 21 and 37 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 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 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°, as predicted based on the center-of-mass angular distribution peaking at 90°. Note that our experiment was conducted at a collision energy of 47 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...
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% (C9H6), (40, 41) reactions of the latter with vinylacetylene might propagate PAH extension to systems with three fused benzene rings: anthracene and phenanthrene (C14H10). 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, and dissociative recombination (47, 48). On the other hand, photolysis of (deuterated) chlorobenzene (C6D6Cl) (∼99.9%; Fluuka) 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 μJ per pulse 1 mm downstream of the nozzle prior to the skimmer at fractions of ∼90%. The metered beam containing the (deuterated) phenyl radical passed a skimmer and a four-slot collision wheel, which selected segments of the pulsed (deuterated) phenyl radical (C6D6, X2A1) beam of well defined peak velocities (vp) and speed ratios (S) (SI Materials and Methods). The phenyl radical beam bisected a pulsed molecular beam of vinylacetylene seeded in argon (Airgas, 99.999999%) 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/Ze 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(E½) and the angular distribution T(θ) 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(E½) and T(θ) were iteratively optimized until the best fit was reached.

Electronic Structure Calculations. Geometries of all intermediates and transition states on the C6H5 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

\[ E(\text{G3}) = E(\text{MP2,CC}) + [E(\text{CCSD(T)})/6-311G^*(d,p)] + \Delta E(\text{ZPE}) + \Delta E(\text{MP2} - \text{G3}) - \Delta E(\text{MP2} - \text{G3})^* \]

where \( E(\text{G3}) \) is the basis set correction and \( E(\text{ZPE}) \) is the zero-point energy. \( E(\text{ZPE}) \) is a spin-orbit correction, and \( E(\text{HLZ}) \), 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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Supporting Information

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SI Materials and Methods

Electronic Structure Calculations. Relative yields of various products of the reaction of phenyl radicals with vinylacetylene under single-collision conditions were evaluated by Rice-Ramsperger-Kassel-Marcus calculations (1–3) of energy-dependent rate constants for individual unimolecular steps and of branching ratios of different channels. The computational procedure for these calculations has been described in detail in our previous works (4). We calculated rate constants as functions of available internal energy of each intermediate or transition state; the internal energy was taken as a sum of the energy of chemical activation in the reaction of phenyl radicals with vinylacetylene and the collision energy, assuming that a dominant fraction of the latter is converted to internal vibrational energy. Only a single total-energy level was considered throughout, as for single-collision conditions (zero-pressure limit). The harmonic approximation was used in calculations of numbers and densities of states needed to evaluate the rate constants. With all rate constants in hand, we computed product branching ratios by solving first-order kinetic equations for unimolecular branching intermediates formed as a result of the addition of phenyl to various carbon atoms in vinylacetylene. We employed the steady-state approximation to compute the branching ratios.

The entrance channel for the phenyl radical addition to C1 in vinylacetylene required special attention. Earlier G2MP2/B3LYP/6-311G** calculations by Moriarty and Frenklach (13) gave a low barrier of 4 kJ mol⁻¹ for this channel. Although we were able to reproduce the addition transition state structure at B3LYP, its refined single-point energy computed at the present G3(MP2,CC) level of theory appeared to be lower than that of the separated reactants. This result indicated that a careful potential energy surface (PES) scan for the phenyl addition to C1 is necessary. IRCMax/G3(MP2,CC) calculations (5) where single-point energies are evaluated along the minimal energy reaction path (MEP) obtained from the intrinsic reaction coordinate (IRC) B3LYP calculations, appeared to be unsuccessful due to an unstable behavior of the RCCSD(T)/6-311G** energies along this path; the coupled cluster calculations also exhibited high T1 diagnostics (6) values indicating a strong multiconfigurational character of the wavefunction in this area of the PES. Therefore, we performed the PES scan using multireference methods of quantum chemistry. In particular, we performed partial geometry optimization along the MEP (with the C-C distance for the forming bond fixed at different values between 2 and 4 Å and all other geometric parameters being optimized) at the complete active space self-consistent-field (CASSCF) level (7) with the 6-311G** basis set. The CASSCF active space consisted of nine electrons distributed on nine orbitals, (9, 9); typically, occupied orbitals with population numbers below 1.98 and vacant orbitals with population numbers above 0.02 were included. Vibrational frequencies for the partially optimized structures along the MEP were computed at the same CASSCF(9,9)/6-311G** level. The CASSCF calculations were carried out using the DALTON 02 program package (8). Next, dynamic correlation was taken into account via single-point multireference perturbation theory (9) (CASPT2/6-311G**) calculations for each optimized structure along the path using MOLPRO 2006. A (7,7) active space was utilized in the CASPT2 calculations; all 25 occupied valence orbitals were included in single and double excitations. The resulting CASPT2(7,7)/6-311G**//CASSCF(9,9)/6-311G** + ZPE (CASSCF(9,9)/6-311G**) potential energy curve along the MEP illustrated in Fig. 4 of the main text shows an attractive character with a van-der-Waals complex [0] at around 3 Å followed by a submerged barrier at ~2.5 Å and a further decent to [1].

Thermal rate constants for the barrierless addition of the phenyl radical to the C1 channel were computed using the canonical variational transition state theory (10–12) and utilizing the CASPT2(7,7)/6-311G**//CASSCF(9,9)/6-311G** + ZPE (CASSCF(9,9)/6-311G**) potential energy MEP curve. The standard rigid-rotor, harmonic-oscillator approximation was used to estimate the partition functions needed for rate constants computations, except low-frequency torsions about single bonds, which were treated as free internal rotors.

Fig. S1. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C1 atom in vinylacetylene. Relative energies are given in units of kJ mol$^{-1}$ relative to phenyl and vinylacetylene.
Fig. S2. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C4 atom in vinylacetylene. Relative energies are given in units of kJ mol$^{-1}$ relative to phenyl with vinylacetylene.
Fig. S3. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C3 atom in vinylacetylene. Relative energies are given in units of kJ mol$^{-1}$ relative to phenyl plus vinylacetylene.

Fig. S4. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C2 atom in vinylacetylene. Relative energies are given in units of kJ mol$^{-1}$ relative to phenyl plus vinylacetylene.
Fig. S5. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the direct hydrogen atom abstraction channels leading to benzene plus isomers of C$_4$H$_3$. Relative energies are given in units of kJ mol$^{-1}$ relative to phenyl plus vinylacetylene.

Other Supporting Information Files
Table S1 (DOC)
Table S2 (DOC)