

Supporting Information

Parker et al. 10.1073/pnas.1113827108

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 isomerization and fragmentation steps of initial reaction 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 descent 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.

1. Eyring H, Lin SH, Lin SM (1980) *Basic Chemical Kinetics* (Wiley, New York) pp 512.
2. Robinson PJ, Holbrook KA (1972) *Unimolecular Reactions* (Wiley, New York) pp 400.
3. Steinfeld J, Francisco J, Hase W (1982) *Chemical Kinetics and Dynamics* (Prentice Hall, Englewood Cliffs, NJ).
4. Kislov VV, Nguyen TL, Mebel AM, Lin SH, Smith SC (2004) Photodissociation of benzene under collision-free conditions: An ab initio/Rice-Ramsperger-Kassel-Marcus study. *J Chem Phys* 120:7008–7017.
5. Malick DK, Petersson GA, Montgomery JA, Jr. (1998) Transition states for chemical reactions I. Geometry and classical barrier height. *J Chem Phys* 108:5704–5713.
6. Lee TJ, Taylor PR (1989) A diagnostic for determining the quality of single-reference electron correlation methods. *Int J Quant Chem Symp* 23:199–207.
7. Jensen HJ, Agren H, Olsen J (1991) SIRIUS: a general-purpose direct second-order MCSCF program, in E. Clementi, Ed., *Modern Techniques in Computational Chemistry*, (Springer, New York), pp 1269.
8. Angeli C, et al. (2005) *Dalton, a molecular electronic structure program* Release 2.0: see <http://www.kjemi.uio.no/software/dalton/dalton.html>.
9. Werner HJ (1996) Third-order multiconfiguration reference perturbation theory: the CASPT3 method. *Mol Phys* 89:645–661.
10. Truhlar DG, Garrett BC (1984) Variational transition state theory. *Annu Rev Phys Chem* 35:159–189.
11. Truhlar DG, Isaacson AD, Garrett BC (1985) *Theory of Chemical Reaction Dynamics*, ed Baer M, (CRC Press, Boca Raton, FL) pp 4:65.
12. Wigner E (1937) Calculation of the rate of elementary association reactions. *J Chem Phys* 5:720–725.
13. Moriarty NW, Frenklach M (2000) Ab initio study of naphthalene formation by addition of vinylacetylene to phenyl. *Proc Combust Inst* 28:2563–2568.

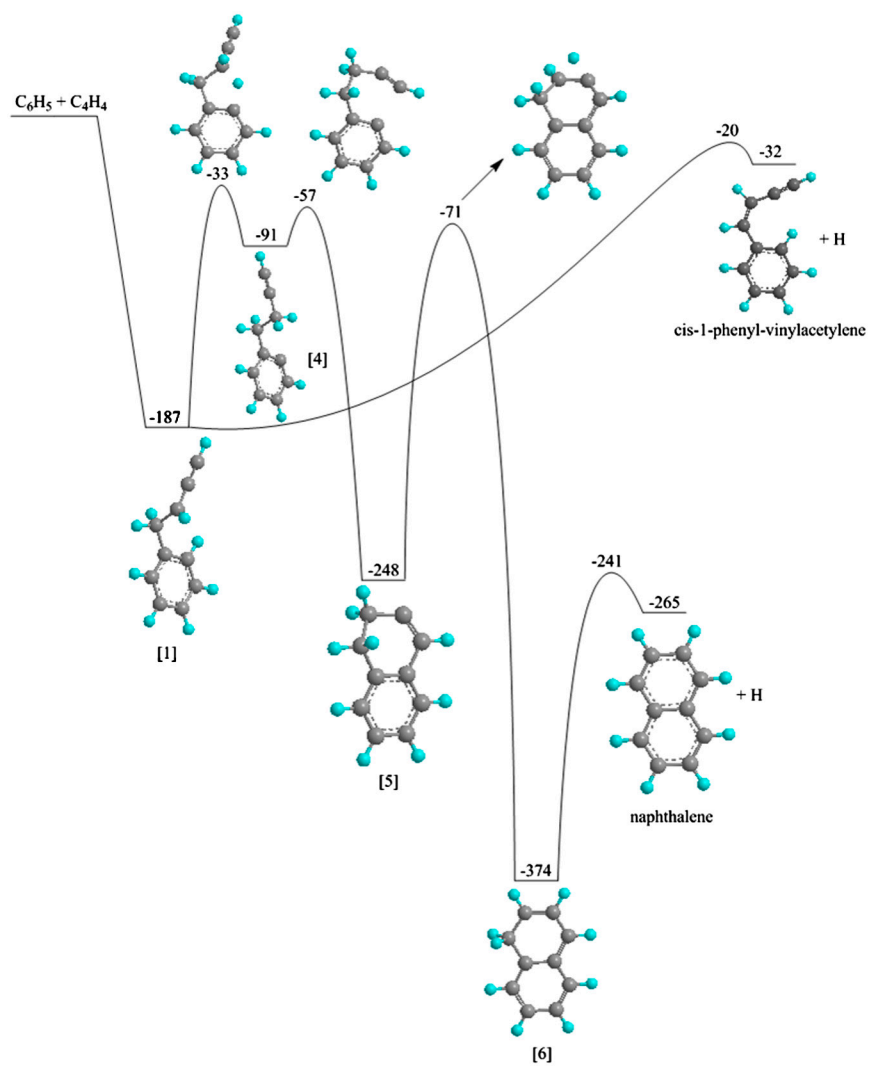


Fig. S1. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C1 atom in vinylacetylene. Relative energies are given in units of kJ mol^{-1} relative to phenyl and vinylacetylene.

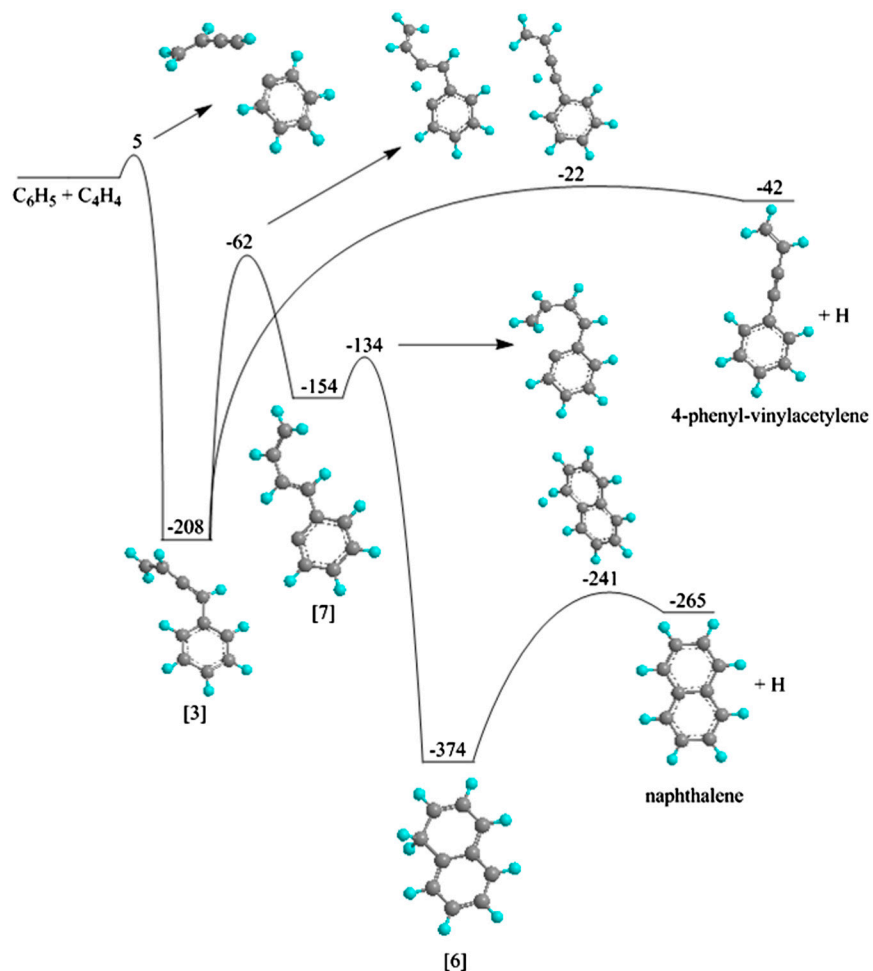


Fig. S2. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C4 atom in vinylacetylene. Relative energies are given in units of kJ mol^{-1} relative to phenyl with vinylacetylene.

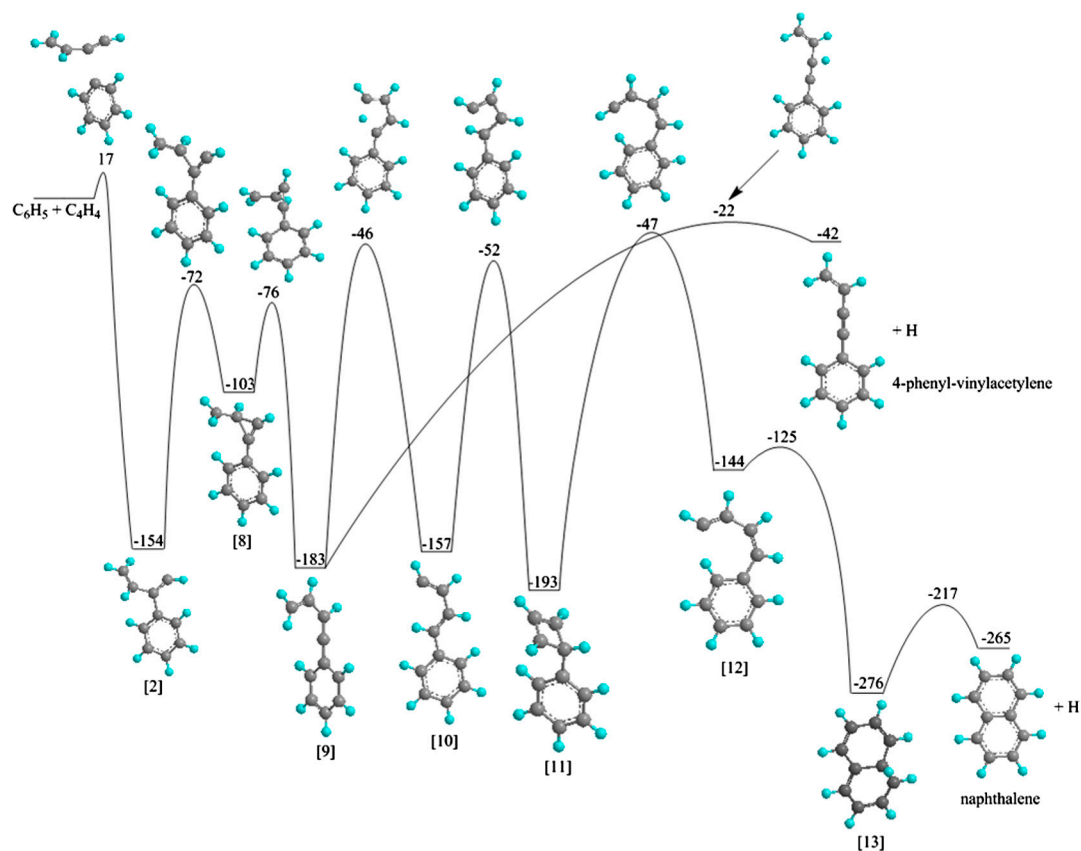


Fig. S3. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C3 atom in vinylacetylene. Relative energies are given in units of kJ mol^{-1} relative to phenyl plus vinylacetylene.

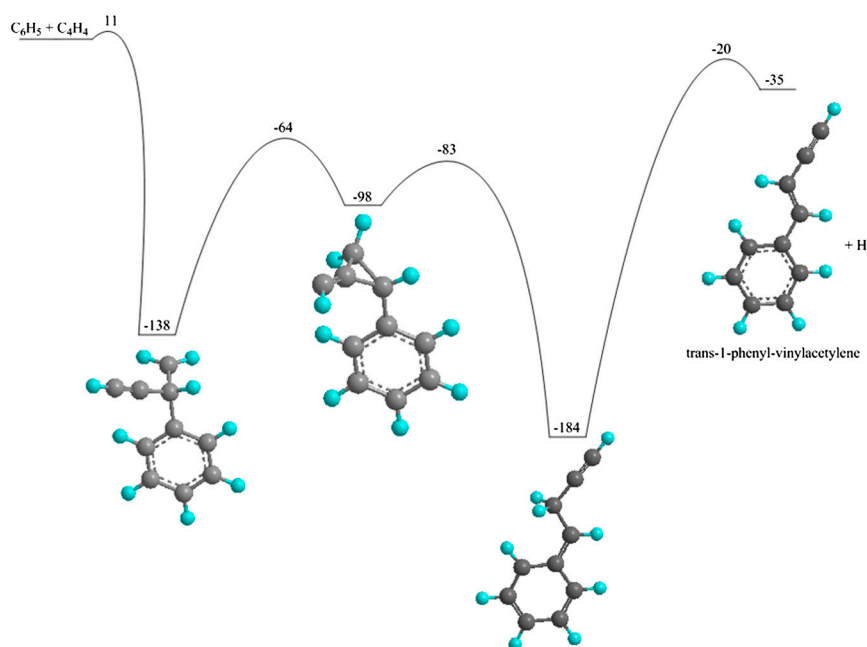


Fig. S4. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the channel initiating with phenyl addition to the C2 atom in vinylacetylene. Relative energies are given in units of kJ mol^{-1} relative to phenyl plus vinylacetylene.

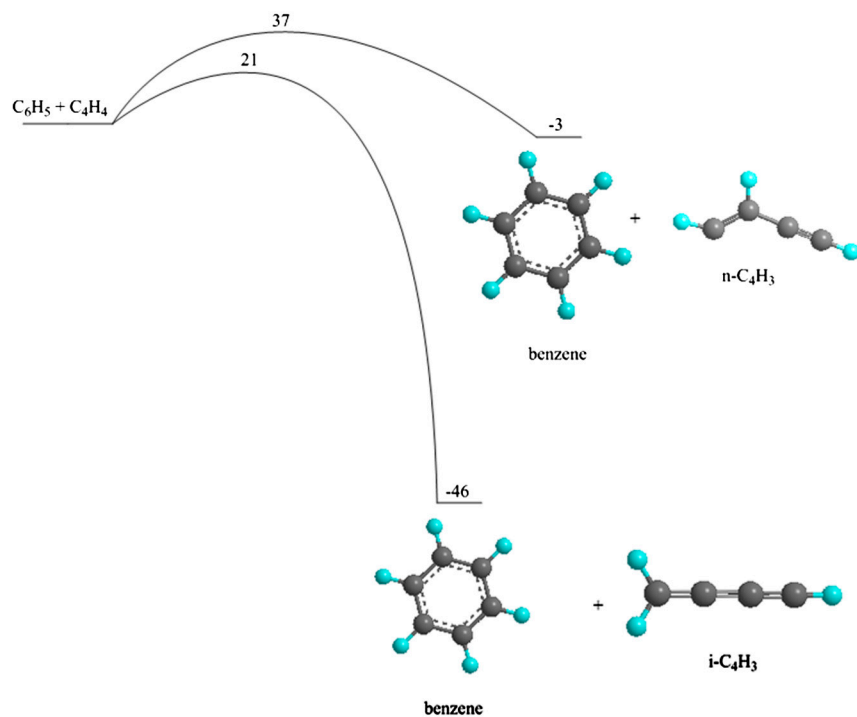


Fig. S5. Potential energy surface of the reaction of phenyl radical with vinylacetylene for the direct hydrogen atom abstraction channels leading to benzene plus isomers of C_4H_3 . Relative energies are given in units of kJ mol^{-1} relative to phenyl plus vinylacetylene.

Other Supporting Information Files

[Table S1 \(DOC\)](#)

[Table S2 \(DOC\)](#)