THE JOURNAL OF CHEMICAL PHYSICS **128**, 084315 (2008)

Formation of the diphenyl molecule in the crossed beam reaction of phenyl radicals with benzene

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(Received 21 November 2007; accepted 18 December 2007; published online 29 February 2008)

The chemical dynamics to form the D5-diphenyl molecule, $C_6H_5C_6D_5$, via the neutral-neutral reaction of phenyl radicals (C_6H_5) with D6-benzene (C_6D_6), was investigated in a crossed molecular beams experiment at a collision energy of 185 kJ mol^{-1}. The laboratory angular distribution and time-of-flight spectra of the $C_6H_5C_6D_5$ product were recorded at mass to charge m/z of 159. Forward-convolution fitting of our data reveals that the reaction dynamics are governed by an initial addition of the phenyl radical to the π electron density of the D6-benzene molecule yielding a short-lived $C_6H_5C_6D_6$ collision complex. The latter undergoes atomic deuterium elimination via a tight exit transition state located about 30 kJ mol^{-1} above the separated reactants; the overall reaction to form D5-diphenyl from phenyl and D6-benzene was found to be weakly exoergic. The explicit identification of the D5-biphenyl molecules suggests that in high temperature combustion flames, a diphenyl molecule can be formed via a single collision event between a phenyl radical and a benzene molecule. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2834221]

I. INTRODUCTION

During the last decades, the aromatic diphenyl molecule ($C_6H_5C_6H_5$) has attracted substantial interest from the combustion[1,2] and astrochemistry[3] communities as a precursor to form polycyclic aromatic hydrocarbons[4,5] (PAHs) and carbonaceous nanoparticles in circumstellar envelopes of carbon stars and in the combustion of fossil fuel.[6] Here, carbonaceous nanoparticles—often referred to as soot—are emitted to the atmosphere with an average global emission rate of anthropogenic carbon from fossil fuel combustion as high as 2.4×10^{10} kg/year.[7] Once liberated into the ambient environment, soot particles in respirable size of 10–100 nm can be transferred into the lungs by inhalation[8] and are strongly implicated in the degradation of human health,[9] particularly due to their high carcinogenic risk potential. PAHs and carbonaceous nanoparticles are also serious water pollutants of marine ecosystems[10] and bioaccumulate in the fatty tissue of living organisms.[11] Together with leafy vegetables, where PAHs and soot deposit easily, they have been further linked to soil contamination,[12] food poisoning, liver lesions, and tumor growth. Therefore, on Earth, PAHs are considered as unwanted, toxic by-products in combustion processes. In the interstellar medium, however, PAHs-like species account for up to 10% of the cosmic carbon budget.[13] They have been implicated as carriers of the unidentified infrared emission bands[14] and of diffuse interstellar bands.[15] A quantitative understanding of the formation of PAHs is therefore essential to develop clean combustion devices and to understand the astrochemical evolution of the interstellar medium.

However, despite this crucial importance of PAHs, even the formation route of the very first binuclear PAH, diphenyl ($C_6H_5C_6H_5$), which is considered as a building block to form anthracene and more complex PAHs, is unknown. Reaction networks modeling PAH formation in the interstellar medium[16] and in combustion flames[17,18] strongly indicate that ground state phenyl radicals ($C_6H_5, X\,^2A_1$) present the most important transient species to initiate the growth of PAHs.[19] A crucial step in these reaction models is thought to be hydrogen abstraction and phenyl radical addition reactions. Nevertheless, an investigation of the products of the simplest phenyl radical reaction with an aromatic molecule, benzene ($C_6H_6, X\,^1A_{1g}$) has remained elusive for the last century. Consequently, the reaction products of this elementary reaction have not been assigned. To shed light on this fundamental question, we conducted a crossed molecular beam study of the gas phase reaction of the phenyl radical, C_6H_5, with D6-benzene, C_6D_6, to synthesize the D5-diphenyl molecule, $C_6H_5C_6D_5$, [reaction (1)] under single collision conditions.

$$C_6H_5(X\,^2A_1) + C_6D_6(X\,^1A_{1g}) \rightarrow C_6H_5C_6D_5(X\,^1A) + D(^2S_{1/2}). \quad (1)$$

This system presents the prototype reaction of an aromatic radical (phenyl)[20] with ubiquitous benzene molecules to form diphenyl molecules via a single radical–neutral collision in the interstellar medium and in combustion flames. Benzene has been observed, for instance, toward the carbon-rich planetary nebula CRL 618.[21] The increasing photon flux from the central star can also photodissociate the benzene molecule to form the phenyl radical plus atomic hydrogen. Upon reaction with benzene, diphenyl is expected to be synthesized. This reaction is also interesting from the viewpoint of a physical-organic chemist as it represents a benchmark system of an aromatic radical-substitution reaction initiated by a polyatomic organic radical R [reaction (2)].[22] In prin-

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ciple, if R is an aromatic radical, the coupling of two aromatic rings can take place via an addition-elimination reaction as depicted in Eq. (2). This pathway is similar to a nucleophilic aromatic substitution in which the nucleophile reactant attacks the aromatic ring. Nevertheless, the related free-radical-substitution reaction involving the simplest aryl radical, phenyl, and benzene has not been studied in the gas phase to date.

$$R + C_6H_6 \rightarrow [RC_6H_6] \rightarrow C_6H_5R + H. \tag{2}$$

Here, we present the first account on the chemical dynamics of the reaction of ground state phenyl radicals ($C_6H_5(X\,^2A_1)$) with D6-benzene ($C_6D_6(X\,^1A_{1g})$). An investigation at the molecular level, i.e., in a collision free environment where it is possible to observe the consequences of a single reactive event, can provide a direct insight into the mechanism of reactions (1) and (2).[23,24] The crossed molecular beam method with mass spectrometric detection is particularly suitable for investigating reactions giving polyatomic products whose spectroscopic properties are unknown. This work provides conclusive evidence of the synthesis of the D5-diphenyl molecule ($C_6H_5C_6D_5$) as the primary reaction product under single collision conditions. The results are compared with related mechanisms involved in the reactions of the cyano radical ($CN(X\,^2\Sigma^+)$) (Ref. 25) and of flourine ($F(^2P)$) (Ref. 26) with benzene. This allows us not only to critically evaluate generalized concepts of prototype free-radial-substitution reactions involving the aromatic benzene molecule and its D6-isotopologue in the gas phase, but also to untangle the role of the title reaction in the formation of diphenyl molecules in combustion flames and in the interstellar medium via a single neutral-neutral reaction.

II. EXPERIMENTAL

The reaction was studied under single collision conditions at a collision energy of 185 ± 3 kJ mol^{-1} using a crossed molecular beam machine.[27] A pulsed supersonic phenyl radical beam was generated via a *quantitative* flash pyrolysis of helium-seeded nitroso benzene (C_6H_5NO) at seeding fractions of less than 0.1% by expanding this mixture through a resistively heated silicon carbide tube.[28] A chopper wheel, located after the skimmer, selected a component of the phenyl radical beam of a peak velocity of 2800 ± 15 m s^{-1} and speed ratio of 7.5 ± 0.2 before it intersected a pulsed, helium-seeded D6-benzene beam at 90° in the interaction region of the scattering chamber.[29] The peak velocity and speed ratio of the D6-benzene beam were determined to be 1170 ± 15 m s^{-1} and 13.0 ± 0.5, respectively. We have chosen D6-benzene instead of benzene so that it became feasible to discriminate the atomic hydrogen from the atomic deuterium loss pathway, which could originate from the phenyl radical and from the D6-benzene reactant, respectively. The reaction products are detected after electron impact ionization at 80 eV via a quadrupole mass spectrometer housed in a rotatable ultrahigh-vacuum chamber (10^{-11} torr) by recording time-of-flight (TOF) spectra at different laboratory scattering angles for distinct mass-to-charge ratios (m/z) of the ionized products. Information on the reaction dynamics was then gained by fitting the laboratory data using a forward-convolution routine. This yielded the angular flux distribution $T(\theta)$ and the translational energy flux distribution $P(E)$ in the center-of-mass (CM) system.[30]

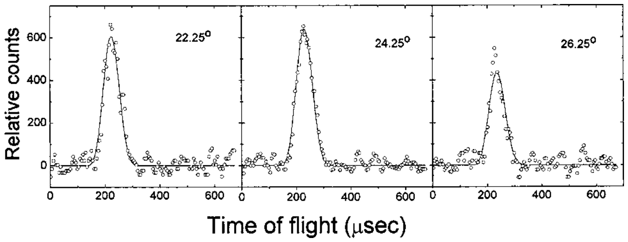

FIG. 1. Time-of-flight data of the D5-diphenyl molecule recorded at $m/z = 159$ ($C_{12}H_5D_5^+$) at selected laboratory angles; open circles represent experimental data, the solid line the fit.

III. RESULTS

A. Laboratory data

The reaction of D6-benzene (C_6D_6) with phenyl radicals (C_6H_5) could release either a hydrogen or a deuterium atom forming products of the generic formula $C_{12}H_4D_6$ and $C_{12}H_5D_5$, respectively. Upon electron impact ionization, the corresponding parent molecules would be detectable at mass-to-charge ratios m/z of $m/z = 160$ and $m/z = 159$, respectively. However, in our experiments, we could not detect any signal at $m/z = 160$, but only at $m/z = 159$. This finding alone suggests that in the reaction of phenyl radicals with D6-benzene, only a deuterium atom is emitted. This results in the formation of a product of the gross formula $C_{12}H_5D_5$. Representative TOF spectra recorded at $m/z = 159$ are compiled in Fig. 1. The corresponding laboratory angular distribution, which is obtained by integrating the TOF spectra at different angles, are depicted in Fig. 2. In principle, we should expect a small signal at $m/z = 160$; this should arise from the ^{13}C isotopologue, $^{13}CC_{11}H_5D_5$. However, an inspection of the signal counts of the TOFs recorded at $m/z = 159$ suggests that a maximum signal of about 12% of the counts at $m/z = 159$ arising from the 1.1% natural ^{13}C abundance and the number of carbon atoms in $C_{12}H_5D_5$ is within the noise limits of the experiments. We also investigated a possible deuterium abstraction channel leading to D1-benzene ($m/z = 79$) plus D5-phenyl radicals. However, within the detection limits, no reactive scattering signal was observable for this channel. Summarized, the reactive scattering signal and the TOF spectra alone demonstrate that the reaction of D6-benzene with phenyl radicals [reaction (1)] is dictated by a phenyl radical versus deuterium exchange pathway.

B. Center-of-mass functions

Having identified a reaction product of the generic formula $C_{12}H_5D_5$, we are investigating now the reaction dynamics and the nature of the product isomer. Here, quantitative information on the dynamics of the reaction is obtained by moving from the laboratory coordinate system to the CM reference frame and analyzing the product angular $T(\theta)$ and translational energy $P(E_T)$ distributions. Here, the CM func-

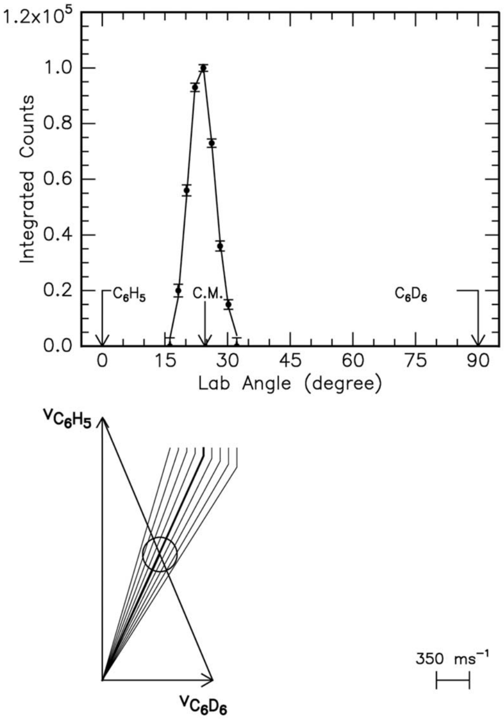

FIG. 2. Upper: Laboratory angular distribution of the D5-diphenyl molecule recorded at $m/z=159$ ($C_{12}H_5D_5^+$). Circles and 1σ error bars indicate experimental data, the solid lines the calculated distribution, and CM the center-of-mass angle. Lower: Newton diagram for the reaction of phenyl radicals with D6-benzene. The circle stands for the maximum center-of-mass recoil velocity of the D5-diphenyl product.

tions are derived by a forward-convolution fit of the product laboratory angular and TOF distributions. The solid lines superimposed on the experimental results in Figs. 1 and 2 are the calculated curves utilizing the best-fit center-of-mass functions, the circles the experimental data. The translational energy distributions aid in gaining valuable information on the reaction dynamics (Fig. 3). The distribution depicts a maximum around 30 kJ mol^{-1}; this finding suggests a tight exit transition state of a decomposing reaction intermediate ($C_{12}H_5D_6$) to form atomic deuterium plus $C_{12}H_5D_5$. Consequently, the reversed reaction, i.e., the addition of the deuterium atom to the $C_{12}H_5D_5$ molecule is anticipated to have an entrance barrier on the order of 30 kJ mol^{-1}. In addition, the high energy cutoff of the translational energy distribution presents the sum of the absolute value of the reaction exoergicity plus the relative collision energy. By subtracting the collision energy (185 kJ mol^{-1}) from the high energy cutoff of 220 ± 15 kJ mol^{-1}, we can derive a reaction exoergicity of 35 ± 15 kJ mol^{-1}. This reaction energy correlates well with computed values of 22 ± 8 (Ref. 31) and 18 ± 8 kJ mol^{-1} (Ref. 32) to form the D5-diphenyl isomer plus atomic deuterium. The formation of the acenapthene isomer plus atomic hydrogen is exoergic by 95 ± 5 kJ mol^{-1} and can be clearly ruled out. Based on these considerations, the average available energy channeled into the translational degrees of freedom of the products is calculated to be 60 ± 5 kJ mol^{-1}, i.e., a fraction of about $28 \pm 3\%$. This order of magnitude suggests that the reaction proceeds via indirect scattering dynamics involving a reaction intermediate ($C_{12}H_5D_6$).[23,24]

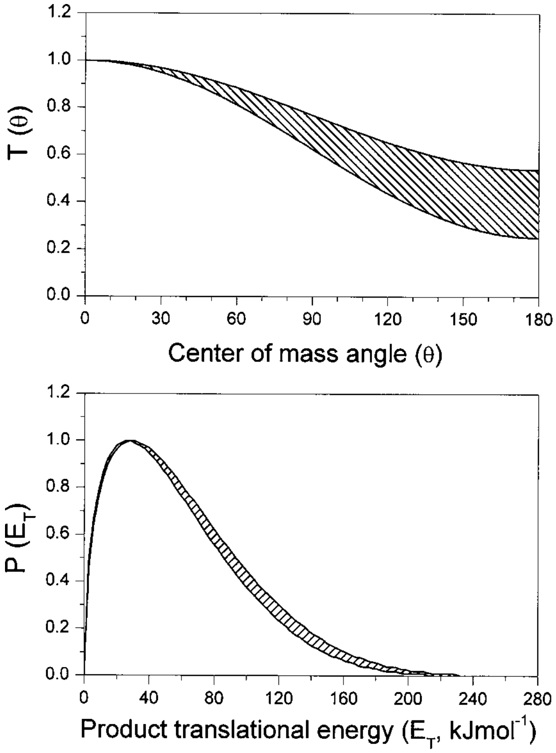

FIG. 3. Center-of-mass angular flux distribution (upper) and center-of-mass translational energy flux distribution (lower) for the reaction of phenyl radicals with D6-benzene to form atomic deuterium plus the D5-biphenyl molecule.

An inspection of the center-of-mass angular distribution (Fig. 3) supports these conclusions and helps to collect additional information on the scattering dynamics. First, the center-of-mass angular distribution portrays flux over the complete range from 0° to 180°. This finding alone suggests that the reaction dynamics are indirect and involve the formation of a $C_{12}H_5D_6$ intermediate prior to the decomposition of the latter via atomic deuterium loss. Secondly, the $T(\theta)$ depicts a marked forward scattering, i.e., the flux at 0° is enhanced compared to 180°. The intensity ratio of the poles, $I(0°)/I(180°)$, is calculated to be 2.5 ± 0.7. This result implies that the lifetime of the decomposing reaction intermediate is shorter than the rotational period (osculating complex).[33] Based on this intensity ratio and the osculating complex model we can estimate that the lifetime of the reaction intermediate is about 0.54 ± 0.12 of the rotational period of the decomposing complex.

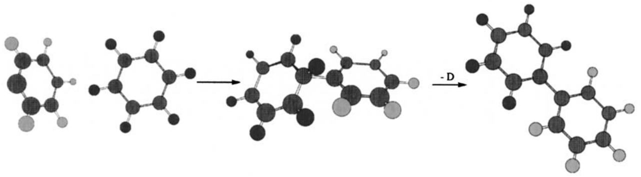

FIG. 4. Schematic representation of the reaction mechanism of phenyl radicals with D6-benzene leading to D5-diphenyl plus atomic deuterium (right) via a doublet radical intermediate (center). Carbon, hydrogen, and deuterium atoms are depicted in black, dark blue, and light blue, respectively.

IV. DISCUSSION

Having analyzed the laboratory data (TOF spectra, laboratory angular distribution) and the center-of-mass translational energy and angular distributions, we are merging now these information and attempt to elucidate the reaction mechanism. The results suggest that the phenyl radical adds with its radical center to the π-electron density of the aromatic D6-benzene to yield a $[C_6H_5-C_6D_6]$ doublet radical intermediate (indirect scattering dynamics via complex formation) whose lifetime is about half of its rotational period (Fig. 4). The outcome of our fits are relatively insensitive to the entrance barrier in the range of 0–40 kJ mol^{-1}. The rovibrationally excited collision complex was found to fragment via atomic deuterium atom loss to form the D5-biphenyl molecule ($C_6H_5C_6D_5$) through a tight exit transition state located about 30 kJ mol^{-1} above the separated products. This final step leads to a rearomatization from the intermediate to the D5-diphenyl product. The overall reaction was deduced to be exoergic by 35 ± 15 kJ mol^{-1}. Our experimental data correlate well with a theoretical study of the reaction of phenyl radicals with benzene.[31] The authors proposed that the entrance barrier to addition is about 11 kJ mol^{-1}. This process forms a reaction intermediate which is stabilized by only about 95 kJ mol^{-1}. The weak potential energy well can explain the relatively short lifetime of the decomposing $[C_6H_5-C_6D_6]$ reaction intermediate. Also, the computed exit barrier of about 20 kJ mol^{-1} agrees reasonable well with the experimentally derived order of magnitude of 30 kJ mol^{-1}. Finally, the crossed beam experiments verify the dominance of the atomic deuterium replacement channel and the absence—within less than 5% of the exchange pathway—of the deuterium abstraction mechanism as postulated from kinetics studies of this reaction;[34] the latter also determined a classical activation energy of reaction of about 20–40 kJ mol^{-1}.[35,36] Note that the related reactions of cyano radical ($CN(X\,^2\Sigma^+)$) (Ref. 25) and of fluorine atoms ($F(^2P)$) (Ref. 26) with benzene follow a similar radical addition—hydrogen/deuterium elimination pathways involving intermediates, which reside in shallow potential energy wells of less than 170 kJ mol^{-1}, and exit barriers of the atomic hydrogen/deuterium elimination of 29–35 kJ mol^{-1}. However, due to the energetics and separation of the π and π^* orbitals of the cyanoradical, the latter adds without entrance barrier to the benzene molecule. Finally, we would like to comment on a pronounced difference between the reaction of the phenyl radical with benzene on one hand, and the reaction of benzene with atomic fluorine and the cyanoradical on the other hand. Both latter systems depicted a forward-backward symmetric center-of-mass angular distribution and a pronounced peaking at 90° (sideways scattering). This pattern was attributed to geometrical constraint in the exit channel where the hydrogen/deuterium atoms are ejected almost parallel to the total angular momentum vector and nearly perpendicularly to the plane of the former benzene molecule.[25,26] However, the present study does not show a distribution maximum at 90°, although the electronic structure calculations predicted that the hydrogen atom is released at an angle of 94°, i.e., almost perpendicularly, to the rotational plane. How can this be explained? We have to consider that both the reactions of atomic fluorine and the cyanoradical with benzene were conducted at collision energies of 10.7 and 19.5–34.4 kJ mol^{-1}, much lower than the present study of 185 kJ mol^{-1}. Due to this enhanced collision energy, it is likely that the hydrogen emission shows less geometrical constraints than in those systems at lower collision energy. In other words, the reversed reaction of a hydrogen/deuterium atom addition to the phenylacetylene molecule can follow a larger range of impact parameters than those in the fluorine-benzene and cyanobenzene systems. This trend was also observed in the crossed beam reaction of cyanoradicals with acetylene;[37] here, at lower collision energies, the distribution showed sideways scattering; however, as the collision energy was increased, no characteristic sideway scattering was observable anymore.

V. SUMMARY

Summarized, the crossed beam studies identified the D5-diphenyl molecule as the sole reaction product in the radical-neutral reaction of the phenyl radicals with D6-benzene under collision-free conditions. The inferred reaction dynamics indicate the existence of a short-lived reaction intermediate. Under single collision conditions as provided in crossed beam experiments, the latter decomposed via loss of a deuterium atom. However, in low temperature and high pressure combustion flames, this intermediate may be stabilized or may react with another molecule if the time between collisions is sufficiently short. We should stress that in cold molecular clouds, the title reaction is closed due to its inherent entrance barrier. However, in planetary nebulae such as CRL 618 and in combustion systems, the translational temperature of the reactants can reach a few 1000 K, and the entrance barrier can be overcome. Therefore, in planetary nebulae and in high temperature combustion flames, the diphenyl radical can be formed via a single radical-neutral encounter under gas phase single collision conditions.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Basic Energy Sciences (DE-FG02-3ER15411).

[1] A. M. Lipanov, M. A. Korepanov, and Z. A. Tukhvatullin, *Proceedings of the NATO Advanced Research Workshop on Ecological Risks Associated with the Destruction of Chemical Weapons* 22–26 October 2003 (unpublished), p. 57.
[2] S. Sidhu, B. Gullett, J. Klosterman, R. Striebich, J. Ryan, P. Lemieux, and M. De Vito, Organohalogen Compd. **56**, 69 (2002).
[3] K. Mimura, Geochim. Cosmochim. Acta **59**, 579 (1995).
[4] M. Frenklach, Phys. Chem. Chem. Phys. **4**, 2028 (2002).
[5] H. Richter and J. B. Howard, Prog. Energy Combust. Sci. **26**, 565 (2000).
[6] A. Ergut Y. A. Levendis, H. Richter, and J. Carlson, *Fourth Joint Meeting of the U.S. Sections of the Combustion Institute: Western States, Central States, Eastern States, Philadelphia, PA, United States*, 20–23 March 2005 (unpublished), Paper No. A05/1
[7] D. G. Aubin and J. P. Abbatt, J. Phys. Chem. A **107**, 11030 (2003).
[8] L. D. Sabin, K. Kozawa, E. Behrentz, A. M. Winer, D. R. Fitz, D. V. Pankratz, S. D. Colome, and S. A. Fruin, Atmos. Environ. **39**, 5243 (2005).
[9] B. J. Finlayson-Pitts and J. N. Pitts, Jr., Science **276**, 1045 (1997).
[10] K. Hylland, J. Toxicol. Environ. Health **69**, 109 (2006).

[11] S. Shantakumar, M. D. Gammon, S. M. Eng, S. K. Sagiv, M. M. Gaudet, S. L. Teitelbaum, J. A. Britton, M. B. Terry, A. Paykin, T. L. Young, L. W. Wang, Q. Wang, S. D. Stellman, J. Beyea, M. Hatch, D. Camann, B. Prokopczyk, G. C. Kabat, B. Levin, A. I. Neugut, and R. M. Santella, J. Expo Anal Environ. Epidemiol. **15**, 482 (2005).

[12] P. Oleszczuk and S. Baran, J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. **40**, 2085 (2005).

[13] Y. J. Pendleton and L. J. Allamandola, Astrophys. J., Suppl. Ser. **138**, 75 (2002).

[14] E. Peeters, A. L. Mattioda, D. M. Hudgins, and L. J. Allamandola, Astrophys. J. **617**, L65 (2004).

[15] W. W. Duley, Faraday Discuss. **133**, 415 (2006).

[16] M. Frenklach and E. D. Feigelson, Astrophys. J. **341**, 372 (1989).

[17] J. Appel, H. Bockhorn, and M. Frenklach, Combust. Flame **121**, 122 (2000).

[18] H. Richter and J. B. Howard, Phys. Chem. Chem. Phys. **4**, 2038 (2002).

[19] R. J. McMahon, M. C. McCarthy, C. A. Gottlieb, J. B. Dudek, J. F. Stanton, and P. Thaddeus, Astrophys. J. **590**, L61 (2003).

[20] P. v. R. Schleyer, Chem. Rev. (Washington, D.C.) **101**, 1115 (2001).

[21] J. Cernicharo, A. M. Heras, A. G. G. M. Tielens, J. R. Pardo, F. Herpin, M. Guelin, and L. B. F. M. Waters, Astrophys. J. **546**, L123 (2001).

[22] J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed. (Wiley, New York, 1992).

[23] R. I. Kaiser, Chem. Rev. (Washington, D.C.) **102**, 1309 (2002).

[24] P. Casavecchia, Rep. Prog. Phys. **63**, 355 (2000).

[25] N. Balucani, O. Asvany, A. H. H. Chang, S. H. Lin, Y. T. Lee, R. I. Kaiser, H. F. Bettinger, P. v. R. Schleyer, and H. F. Schaefer III, J. Chem. Phys. **111**, 7457 (1999).

[26] K. Shobatake, J. M. Parson, Y. T. Lee, and S. A. Rice, J. Chem. Phys. **59**, 1427 (1973).

[27] X. Gu, Y. Guo, F. Zhang, A. M. Mebel, and R. I. Kaiser, Faraday Discuss. **133**, 245 (2006).

[28] R. I. Kaiser, O. Asvany, Y. T. Lee, H. F. Bettinger, P. v. R. Schleyer, and H. F. Schaefer III, J. Chem. Phys. **112**, 4994 (2000).

[29] The peak velocities of the phenyl radical, a., and D_2-acetylene beam were determined to be 2541 (low collision energy), 3047 (high collision energy), 925, and 920 m s^{-1}.

[30] R. I. Kaiser, C. Ochsenfeld, D. Stranges, M. Head-Gordon, and Y. T. Lee, Faraday Discuss. **109**, 183 (1998).

[31] J. Park, S. Burova, A. S. Rodgers, and M. C. Lin, J. Phys. Chem. A **103**, 9036 (1999).

[32] P. J. Linstrom and W. G. Mallard, *NIST Standard Reference Database Number 69*, National Institute of Standards and Technology, Gaithersburg, MD, June 2005.

[33] W. B. Miller, S. A. Safron, and D. R. Herschbach, Proc. Phys. Soc. London **44**, 108 (1967).

[34] A. Fahr and S. E. Stein, Sym. (Int.) Combust., [Proc.] **22**, 1023 (1989).

[35] A. Fahr, W. G. Mallard, and S. E. Stein, Sym. (Int.) Combust., [Proc.] **21**, 825 (1988).

[36] J. C. Scaiano and L. C. Stewart, J. Am. Chem. Soc. **105**, 3609 (1983).

[37] N. Balucani, O. Asvany, L. C. L. Huang, Y. T. Lee, R. I. Kaiser, Y. Osamura, and H. F. Bettinger, Astrophys. J. **545**, 892 (2000).