Formation of benzene in the interstellar medium

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Polycyclic aromatic hydrocarbons and related species have been suggested to play a key role in the astrochemical evolution of the interstellar medium, but the formation mechanism of even their simplest building block—the aromatic benzene molecule—has remained elusive for decades. Here we demonstrate in crossed molecular beam experiments combined with electronic structure and statistical calculations that benzene (C_6H_6) can be synthesized via the barrierless, exoergic reaction of the ethynyl radical and 1,3-butadiene, $C_2H + H_2CCHCHCH_2 \rightarrow C_6H_6 + H$, under single collision conditions. This reaction portrays the simplest representative of a reaction class in which aromatic molecules with a benzene core can be formed from acyclic precursors via barrierless reactions of ethynyl radicals with substituted 1,3-butadiene molecules. Unique gas-grain astrochemical models imply that this low-temperature route controls the synthesis of the very first aromatic ring from acyclic precursors in cold molecular clouds, such as in the Taurus Molecular Cloud. Rapid, subsequent barrierless reactions of benzene with ethynyl radicals can lead to naphthalene-like structures thus effectively propagating the ethynyl-radical mediated formation of aromatic molecules in the interstellar medium.

astrochemistry | polycyclic aromatic hyrdrocarbons | reaction dynamics | bimolecular reaction

Polycyclic aromatic hydrocarbons (PAHs) and related species such as (de)hydrogenated, ionized, and substituted PAHs are presumed to be omnipresent in the interstellar medium (ISM) (1, 2). PAH-like species are suggested to account for up to 30% of the galactic interstellar carbon (2), have been implicated in the astrobiological evolution of the ISM (3), and provide nucleation sites for the formation of carbonaceous dust particles (4). They have been also linked to the unidentified infrared (UIR) emission bands observed in the range of 3–14 μm (3,300–700 cm⁻¹) (5) and to the diffuse interstellar bands (DIBs) (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 μm). UIR bands have also been observed toward the Cigar Galaxy M82; DIBs are widespread in the ISM of the Local Group and into the distant universe (7). Current astrochemical models propose that the synthesis of the simplest building block of PAHs—the aromatic benzene molecule $[C_6H_6(X^1A_{1g})]$—is driven by ion–molecule reactions (8) of methane (CH_4), ethylene (C_2H_4), and propargyl (C_3H_3) with $C_5H_2^+$ and $C_4H_2^+$ ions and involves $C_6H_5^+$ ions of unknown structures. However, the validity of these processes remains conjecture because they have neither been verified computationally nor experimentally. Therefore, the formation mechanisms of the simplest building block of PAH species in interstellar space—the aromatic benzene molecule as detected toward the planetary nebula CRL 618 (9)—have remained elusive to date.

In this article, we present the results of crossed molecular beam reactions of D1-substituted ethynyl radicals $[C_2D; X^2\Sigma^+]$ with 1,3-butadiene $[H_2CCHCHCH_2; X^1A_g]$ and its D2- and D4-substituted counterparts, i.e., $[H_2CCDCDCH_2]$ and $[D_2CCHCHCD_2]$. By combining these data with electronic structure calculations and astrochemical models, we provide compelling evidence that the aromatic benzene molecule $[C_6H_6(X^1A_{1g})]$ together with its acyc-

lic 1,3-hexadien-5-yne isomer $[HCCCHCHCHCH_2; X^1A']$ can be formed via a barrierless, single collision event involving the reaction of two neutral molecules: 1,3-butadiene and the ethynyl radical. This reaction presents the simplest representative of a reaction class in which aromatic molecules with a benzene core can be formed from acyclic precursors via barrierless reactions of the ethynyl radicals with substituted 1,3-butadiene molecules in the ISM such as in cold molecular clouds like the Taurus Molecular Cloud (TMC-1).

Results

Electronic Structure Calculations. Our electronic structure calculations indicate that the reaction proceeds without an entrance barrier (Fig. 1). Details of the calculations are compiled in *Materials and Methods*. Reaction pathways to two isomers were identified: formation of the aromatic benzene molecule and synthesis of the thermodynamically less stable, acyclic 1,3-hexadien-5-yne isomer. An initial addition of the ethynylic radical center to one of the terminal carbon atoms of the 1,3-butadiene molecule leads to an acyclic reaction intermediate [i1], which is stabilized by 282 kJ mol⁻¹ with respect to the reactants. From here, this collision complex can undergo unimolecular decomposition by emitting a hydrogen atom via a tight exit transition state forming an acyclic C_6H_6 isomer: 1,3-hexadien-5-yne. The overall reaction was computed to be exoergic by 116 kJ mol⁻¹. Alternatively, intermediate [i1] can isomerize to the cyclic structure [i4]. This molecule represents a singly hydrogenated benzene molecule and can be formed from [i1] via an initial ring closure to [i2] followed by a hydrogen shift or through an initial hydrogen shift forming [i3] followed by cyclization to [i4]. A comparison of the height of transition states involved in the initial steps of the reaction sequence [i1] → [i2] → [i4] versus [i1] → [i3] → [i4] suggests that [i1] preferentially undergoes ring closure followed by hydrogen migration. Which of both pathways is the dominating route of benzene formation? Our statistical calculations reveal that, over a range of collision energies from 0 to 50 kJ mol⁻¹, near 99% of all the benzene molecules are formed through the reaction sequence [i1] → [i2] → [i4], whereas only 1% of the benzene molecules are synthesized via the route involving [i1] → [i3] → [i4]. Once formed, the cyclic intermediate [i4] emits a hydrogen atom via a tight exit transition state located 13 kJ mol⁻¹ above the separated products forming the aromatic benzene molecule; this barrier correlates well with an experimentally determined activation energy of 18.0 ± 1.1 kJ mol⁻¹ for the reversed reaction of an addition of a hydrogen atom to benzene as determined over a temperature range of 298–400 K (10). Our calculations suggest
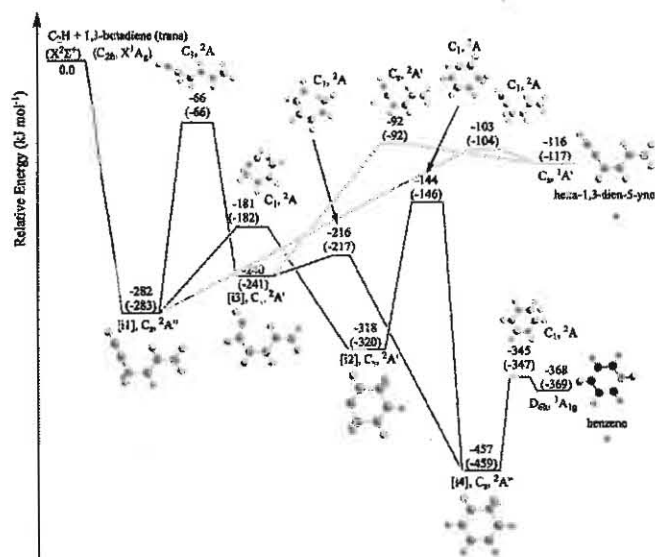
Fig. 1. Potential energy surface for the reaction of ground state ethynyl radicals $[C_2H(X^2\Sigma)^+]$ with 1,3-butadiene $[CH_2CHCHCH_2(X^1A_g)]$. Relative energies are given in units of kilojoules per mole. Energies in parenthesis refer to the energetics of the reaction with the D1-ethynyl radicals. Also indicated are electronic wave functions and point groups of the reactants, intermediates, and transition states. Red and blue lines indicate the reaction pathways to the acyclic and benzene isomers, respectively. Optimized Cartesian coordinates for all structures are given in the *SI Text*.

further that the overall reaction yielding benzene is strongly exoergic by 368 kJ mol⁻¹.

Crossed Molecular Beam Studies—Laboratory Frame. The reaction was also studied experimentally under single collision conditions in the gas phase utilizing a molecular beam machine by crossing a supersonic beam of D1-ethynyl radicals $[C_2D(X^2\Sigma)^+)]$ with a supersonic 1,3-butadiene beam perpendicularly in the interaction region at a collision energy of 45.4 ± 2.1 kJ mol⁻¹ (*Materials and Methods*). The neutral reaction products were first ionized via electron impact at 80 eV and then mass and velocity analyzed by a triply differentially pumped quadrupole mass spectrometer held on the order of 10⁻¹¹ torr while recording TOF spectra of the ionized neutral molecules. We detected reactive scattering signal at $m/z = 79$ ($C_6H_5D^+$). These data suggest that a molecule of the empirical formula C_6H_5D plus atomic hydrogen is formed. The TOF spectra and the laboratory angular distribution are shown in Fig. 2. Although we have provided evidence of the existence of a D1-ethynyl radical versus atomic hydrogen replacement pathway, in which the hydrogen atoms originates from the 1,3-butadiene molecule, we have not resolved the question whether the hydrogen atom is released from the terminal C1/C4 and/or central C2/C3 position. Therefore, we also conducted experiments of the D1-ethynyl radical with 1,1,4,4-D4-1,3-butadiene and 2,3-D2-1,3-butadiene at the center-of-mass angle. For reaction with 1,1,4,4-D4-1,3-butadiene (hydrogen atoms at the C2/C3 positions), no signal of the atomic hydrogen loss channel was observed at $m/z = 83$ ($C_6D_5H^+$). Therefore, we can conclude that no C_6D_5H isomer is formed; we only detected signal at $m/z = 82$ for the atomic deuterium loss ($C_6D_4H_2^+$). However, in the reaction with 2,3-D2-1,3-butadiene (hydrogen atoms at the terminal C1/C4 positions), we clearly observed signal at $m/z = 81$ ($C_6D_3H_4^+$) (*SI Text*). These experiments demonstrate that the hydrogen atom is emitted from the terminal carbon atoms of the 1,3-butadiene molecule.

Crossed Molecular Beam Studies—Center-of-Mass Frame. Having identified product(s) with the empirical formula C_6H_5D and

characterized the terminal carbon atoms of 1,3-butadiene releasing the hydrogen atom, we are focusing our attention now on the identification of the structural isomer(s) formed. The identification procedure of the isomers requires elucidating the chemical dynamics of the reaction by transforming the experimental data from the laboratory to the center-of-mass reference frame (11). The simulated distributions are overlaid in Fig. 2 with the corresponding center-of-mass functions visualized in Fig. 3. Let us turn our attention first to the derived center-of-mass translational energy distribution, $P(E_T)$. For those molecules formed without internal excitation, the high-energy cutoff of the $P(E_T)$ resembles the sum of the absolute of the reaction exoergicity and the collision energy; this algebraic quantity is clearly dictated by the law of energy conservation. An adequate simulation of the laboratory data could not be achieved with only a single channel leading exclusively to the 1,3-hexadien-5-yne isomer or benzene. With only one channel pertaining to the acyclic isomer, the simulated TOF spectra were too slow, and the laboratory angular distribution was found to be too narrow. On the other hand, a one-channel fit accounting solely for the reaction energy to form the D1-benzene molecule yielded TOF spectra that were too fast and a laboratory angular distribution that was significantly broader than the data. However, we could successfully replicate the experimental data by utilizing a two-channel fit with the center-of-mass functions depicted in Fig. 3. Let us have a closer look at the $P(E_T)$s. It is important to note that the high-energy cutoffs of 150 ± 20 and 380 ± 20 kJ mol⁻¹ are in excellent agreement with the computed reaction energies to form the acyclic and the benzene isomer plus the collision energy, i.e., 161 and 413 kJ mol⁻¹. Likewise, the $P(E_T)$s hold distribution maxima of about 15–25 kJ mol⁻¹. This pattern likely suggests that the reaction intermediates decompose via rather tight exit transition states. The indirect nature of the reaction pathways is also verified by the center-of-mass angular distributions, $T(\theta)$s, because both graphs depict intensity over the complete angular range (12). Further, both channels are forward–backward symmetric with respect to 90°. The symmetry indicates that the intermediates have a significantly longer lifetime than the rotational period. Also, ratios of the flux intensities at the respective maxima and minima of the distribution, $I(90°)/I(0°)$, were found to be 1.9 ± 0.3 and 1.3 ± 0.3 to form 1,3-hexadiene-5-yne and benzene, respectively. This "sideways" scattering reveals the constraints of the decaying intermediates: Here, for each channel, the hydrogen atom is ejected perpendicularly to the molecular plane of the rotating, decomposing complex almost parallel to the total angular momentum vector (13).

Discussion

Reaction Pathways to Benzene and the 1,3-Hexadien-5-yne Isomer. Combining the results from the electronic structure calculations (Fig. 1) with those obtained from the interpretation of the center-of-mass functions (Fig. 3) and the laboratory data (Fig. 2 and *SI Text*), we are able to unravel the underlying reaction mechanisms. First and foremost, the computations verify the experimental results of an indirect reaction mechanism involving C_6H_6D reaction intermediate(s). The reaction is triggered via an addition of the D1-ethynyl radical with its radical center to one of the terminal carbon atoms of 1,3-butadiene without entrance barrier. We would like to stress that, in our computations, the barrierless addition was verified by a careful examination of the potential energy surface in the entrance channel (intrinsic reaction coordinate calculations), which indicates that the potential energy of the system steadily and monotonically decreases as the D1-ethynyl radical approaches 1,3-butadiene. The barrierless nature of this reaction is also supported by Nizamov and Leone's low-temperature kinetics studies in the range from 104 to 296 K, which suggest rate coefficients within gas kinetics limits of a few 10⁻¹⁰ cm³ s⁻¹ (14); however, these experiments did not determine the nature of the reaction products. In the bimolecular crossed beam reaction,

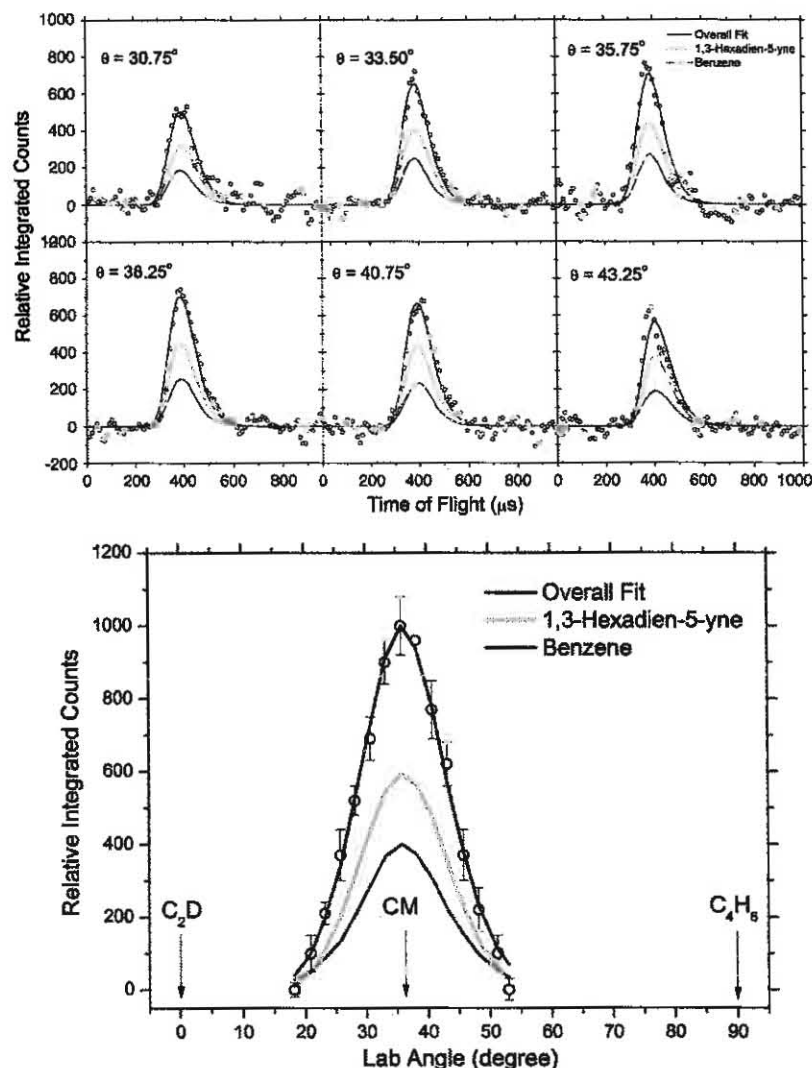**Fig. 2.** (*Top*) Time-of-flight data for the reaction of the D1-ethynyl radical [$C_2D(X^2\Sigma^+)$] with 1,3-butadiene monitored at $m/z = 79$. (*Bottom*) Corresponding laboratory angular distribution of the $C_6H_5D^+$ ions recorded at $m/z = 79$. Open circles signify the experimental data, red and blue lines represent the calculated distribution for the 1,3-hexadien-5-yne and benzene isomers, respectively, and the black line the sum. CM designates the center-of-mass angle.
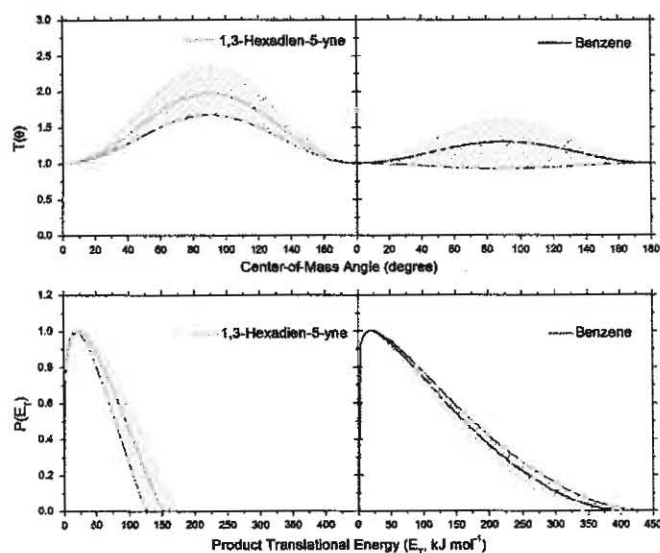

Fig. 3. Center-of-mass angular (*Upper*) and translational energy flux distributions (*Lower*) leading to the formation of the 1,3-hexadien-5-yne (red) and benzene molecule (blue). Hatched areas indicate the acceptable upper and lower error limits of the fits. The solid line defines the best-fit functions.

the resulting doublet radical intermediate [i1] was found to either decompose forming the 1,3-hexadien-5-yne isomer or to undergo ring closure followed by hydrogen shift yielding ultimately the singly hydrogenated benzene molecule [i4], which then loses a hydrogen atom forming D1-benzene. As proven experimentally based on the off-zero peaking of the center-of-mass translational energy distributions and also theoretically, both exit transition states are rather tight and located about 13–23 kJ mol^{-1} above the separated products. The tight transition state can be easily understood because the reversed reactions involve the addition of a hydrogen atom to a closed shell hydrocarbon, which is associated with an entrance barrier. Considering the computed structures of the exit transition states, the hydrogen atom leaves the decomposing complex almost perpendicular to the molecular plane, i.e., 101° and 102° for the hydrogen atom loss from [i1] and [i4], respectively, as predicted from the center-of-mass angular distributions. The derived mechanism also gains support from the experiments with partially deuterated 1,3-butadienes. Recall that these studies provided evidence that the ejected hydrogen atom in [i4] originates from the terminal position of the 1,3-butadiene molecule.
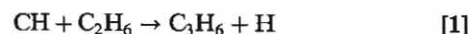
Branching Ratios of Benzene and the 1,3-Hexadien-5-yne Isomer. It is also important to discuss the branching ratios of the two isomers

formed because these ratios are crucial to transfer our findings to real interstellar environments. Note that our experiment was conducted at a collision energy of about 45 kJ mol^{-1}, which is equivalent to a thermal energy of about 5,400 K, which is comparable with temperatures in the circumstellar envelopes of carbon-rich stars and protoplanetary nebulae like CRL 618—where benzene was detected—close to the photosphere, that reach up to a few thousand kelvin (15). However, these temperatures are significantly higher than the average translational temperature in cold molecular clouds (10 K). If two competing products are formed in a chemical reaction, the branching ratios of these two channels may depend on the collision energy. Our computations suggest that this is the case. At the limit of zero pressure and zero collision energy, which resembles conditions in cold molecular clouds, our statistical calculations indicate that about 40% of the products are benzene. As the collision energy rises to 45 kJ mol^{-1}, this fraction drops monotonically to about 20%. This fluctuation can be rationalized in terms of the reduced lifetime (which is still higher than its rotational period) of the initial addition intermediate [i1] and hence less favorable cyclization step to [i2] versus a decomposition to form the acyclic isomer. In our experiment, we find benzene fractions of about 30 ± 10%, in good agreement with the computational predictions, which demonstrates that our calculations are conducted at a level high enough to replicate our experimental findings. Finally, we would like to address briefly a competing reaction pathway at elevated collision energies and temperatures: the hydrogen abstraction forming acetylene and resonantly stabilized n-C_4H_5 radicals. Here, the direct hydrogen abstraction from the terminal and central carbon atoms of 1,3-butadiene involve barriers of about 4 and 7 kJ mol^{-1}. Hence, in low-temperature interstellar clouds, these pathways are closed, but might be relevant in interstellar environments with elevated temperatures.

Interstellar Reaction Models. Having verified the formation of the aromatic benzene molecule under single collision conditions, we now apply these findings to the "real" ISM. Most importantly, our studies indicate that the reaction has no entrance barrier, all barriers involved in the formation of benzene are below the energy of the separated reactants, and the overall reaction to form benzene is exoergic. These findings represent a crucial prerequisite for this reaction to be important in low-temperature molecular clouds. If any barrier lies above the energy of the separated reactants or if the reaction is endoergic, the low temperatures of the molecular clouds such as TMC-1 would typically inhibit the formation of benzene. In constructing a chemical reaction network for the gas-phase formation of benzene in interstellar clouds, two input parameters are crucial: the reaction products (benzene and its acyclic isomer) and the rate constants. In our network, we implemented a rate constant of $3.0 \pm 0.9 \times 10^{-10}$ cm^3 s^{-1} and accounted for the branching fractions of benzene versus the 1,3-hexadien-5-yne isomer as elucidated in our present study. We recognize that Nizamov and Leone's data were recorded at temperatures between 104 and 296 K (14). However, an analysis of ethynyl-radical reactions with unsaturated hydrocarbons shows that their rate constants are almost invariant with temperature (16). Therefore, a rate constant of $3.0 \pm 0.9 \times 10^{-10}$ cm^3 s^{-1} for cold interstellar clouds with a benzene fraction of 40% versus 60% for the 1,3-hexadien-5-yne isomer presents a sensible input parameter.

Formation of Benzene in the ISM—Qualitative Considerations. The results of our astrochemical models (*Materials and Methods*) for dark clouds like TMC-1 have important implications. We objectively investigated the effects of ion–molecule reactions versus neutral–neutral chemistry leading to benzene. With respect to benzene, the reaction sequence was found to start with the fast reaction of methylidyne radicals (CH) with ethane (C_2H_6) (17, 18), which leads to propene (C_3H_6) plus atomic hydrogen (reac-

tion 1); the latter reacts rapidly with another methylidyne radical forming then 1,3-butadiene (C_4H_6) (19–21) (reaction 2). Hereafter, the ethynyl radical can react with 1,3-butadiene to form —besides the acyclic isomer—benzene plus atomic hydrogen. Our models suggest further that ethane—the primary starting point for the neutral–neutral benzene synthesis—is not likely to be formed via gas-phase chemistry, but is preferentially synthesized on dust grains inside ice mantles by successive hydrogen atom addition to acetylene (C_2H_2) (22) or by reactions between the methyl radical (CH_3) fragments produced by irradiation of methane (CH_4) on the interstellar grains (23). In a similar way, 1,3-butadiene can be also formed by recombination of two vinyl radicals (C_2H_3). Cometary ices are also known to be rich in ethane (24), where the observed abundances are comparable to that of methane. It is therefore plausible that large quantities of ethane can be released into the gas phase in interstellar clouds following events that result in ice mantle sublimation via grain-grain collisions (25) or shocking of the ISM (26). This situation is very different from the hot core model, where a newly formed star thermally heats the grains thus leading to a thermal sublimation of the molecules from the grain (27).

$$CH + C_2H_6 \rightarrow C_3H_6 + H \qquad [1]$$

$$CH + C_3H_6 \rightarrow 1,3\text{-}C_4H_6 + H \qquad [2]$$

$$1,3\text{-}C_4H_6 + C_2H \rightarrow c\text{-}C_6H_6 + H \qquad [3]$$

Formation of Benzene in the ISM—Quantitative Considerations. How does the unique neutral–neutral reaction scheme compare quantitatively with the previously proposed ion–molecule reaction network? First, if benzene is formed only by ion–molecule reactions, peak fractional abundances of benzene of 1×10^{-10} are expected. Secondly, recall that the ion–molecule reactions incorporated into these previous astrochemical models leading to benzene via the $C_6H_5^+$ bottleneck have neither been investigated theoretically nor experimentally (28). Upon removal of the guessed ion–molecule reactions, the peak abundance of $C_6H_5^+$ drops by over 3 orders of magnitude resulting in a similar reduction of benzene formed via ion–molecule reactions to fractional abundances of *less than* 10^{-13}. Third, the incorporation of the neutral–neutral reaction sequences leading to benzene via the reaction of 1,3-butadiene plus ethynyl clearly shows that this pathway presents the most important route to synthesize benzene in cold molecular clouds such as TMC-1. Fig. 4 displays the quantitative results of a gas-grain chemical model for TMC-1 (25). After about 6×10^4 y
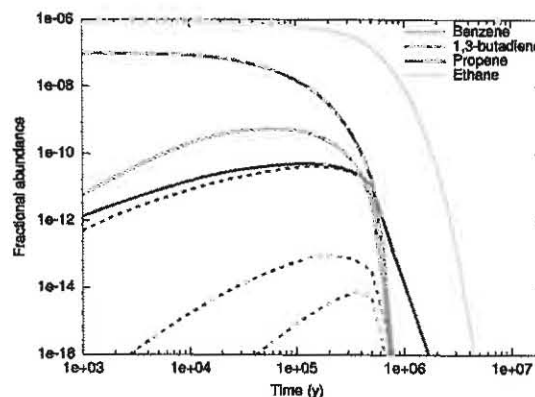

Fig. 4. Results from the chemical model for TMC-1 in which oxygen is depleted and ice mantles are injected into the gas. The abundances of gas-phase molecular species are plotted as a function of time after the injection event (solid lines). Dashed lines are from the same model but without the injection of 1,3-butadiene from the dust.

of chemical evolution, benzene formed by neutral–neutral chemistry reaches a peak fractional abundance of about 5×10^{-10} with respect to molecular hydrogen—a factor of 5 higher than the benzene abundances reached in reaction schemes based on "guessed" ion–molecule reactions. A detailed sensitivity analysis suggests that the fractional abundances of benzene formed via the neutral–neutral scheme vary with $\pm 2 \times 10^{-10}$ within the error limits of the rate constant of the ethynyl–1,3-butadiene reaction and the uncertainties of the hydrogen production rates in reactions 1 and 2. Note that the benzene fraction of 5×10^{-10} is of a similar magnitude to the ubiquitous interstellar cyclopropenylidene molecule (c-C_3H_2) (29). Therefore, we can conclude that the formation of benzene via the neutral–neutral reaction of the ethynyl radical and 1,3-butadiene is the dominating process in cold clouds like TMC-1 where the gas-phase oxygen is depleted on dust grains; the "freeze out" of oxygen on the grains is a direct consequence of astronomical observations and required to account for the low abundances of molecular oxygen as observed in molecular clouds (30).

Interstellar Versus Combustion Chemistry. We would like to stress that alternative neutral–neutral reactions to form benzene in the ISM have been "borrowed" from the high-temperature, combustion chemistry community and incorporated in previous interstellar chemistry models. These bimolecular processes involve, for instance, reactions of resonantly stabilized free radicals such as n-C_4H_3 and n-C_4H_5 with acetylene (C_2H_2) (31). However, these reactions have significant entrance barriers of about 20–31 (32, 33) to 23 kJ mol^{-1} (34), respectively, which cannot be overcome at molecular cloud temperatures of 10 K. Likewise, the self-recombination of the propargyl radical (C_3H_3) followed by isomerization and stabilization of the benzene intermediate via a third-body collision has been discussed to form benzene in flames (35, 36). In cold molecular clouds, the collision complex formed in the self-recombination of two propargyl radicals cannot be stabilized by a third-body collision. Although this reaction has no entrance barrier, third-body collisions are on the order of magnitude of one every 10^9 y for interstellar clouds with typical number densities of 10^2–10^4 cm^{-3}; this time scale is much larger than the typical lifetime of these cold molecular clouds of typically 10^6 y (37). Consequently, three body processes such as the self-reaction of propargyl and collisional stabilization of the C_6H_6 intermediate(s) are unimportant in cold molecular clouds. Another possibility might be radiative stabilization of the C_6H_6 intermediate(s) via emission of an infrared photon. Radiative association is known to be a plausible channel for some ion–molecule reactions (38) and hence a similar process might, in principle, produce benzene. To be efficient, the rate of radiative stabilization of the energized benzene intermediate has to be faster than that for its dissociation. This difference in rates is not the case for the energized benzene formed by recombination of two propargyl radical. Its radiative stabilization rate constant, computed using the theoretical approach by Klippenstein et al. (38) for the average temperature corresponding to the available internal energy of 611 kJ mol^{-1}, i.e., the exothermicity of the self-recombination of two propargyl radicals yielding ultimately the benzene (36), is in the range of 50 s^{-1}. This reaction exothermicity is several orders of magnitude lower than the dissociation rate constant of the energized benzene to form atomic hydrogen plus a phenyl radical, 10^5 s^{-1} (39). In principle, benzene can be formed via hydrogen abstraction by the phenyl radical from any hydrogen-carrying molecules such as ubiquitous molecular hydrogen. However, this reaction has a classical activation energy of 33–35 kJ mol^{-1} (40) and hence cannot proceed in cold molecular clouds like TMC-1. Therefore, reactions which may lead to the formation of benzene under combustion relevant conditions do not yield benzene under those low-temperature and pressure conditions in cold molecular clouds. However, the newly investigated ethynyl-radical mediated formation of benzene overcomes these problems, and the aromatic benzene molecule can be formed via a single collision of two neutral particles under bimolecular conditions without entrance barrier in interstellar space.

Conclusion

We have demonstrated that the aromatic benzene molecule—the central building block of polycyclic aromatic hydrocarbons—can be formed under single collision conditions via the gas-phase reaction of ethynyl radicals with 1,3-butadiene. The formation of an aromatic, closed shell molecule via a rapid neutral–neutral reaction presents a first step toward a systematic understanding of how complex PAHs and related molecules might be formed in the ISM via neutral–neutral reactions involving benzene. Because the hydrogen atoms in 1,3-butadiene can be replaced by organic side groups, the reaction of ethynyl with 1,3-butadiene presents the simplest representative of a reaction class in which aromatic molecules with a benzene core can be formed from acyclic precursors via barrierless reactions of the ethynyl radicals with substituted 1,3-butadiene molecules. Electronic structure calculations predicted further that the phenylacetylene molecule (C_6H_5CCH), synthesized from exoergic, barrierless reactions of benzene with the ethynyl radical (41, 42), can even react with a second ethynyl radical to form 1,2-diethynylbenzene [$C_6H_4(C_2H)_2$] plus a hydrogen atom. The reaction of 1,2-diethynylbenzene with a third ethynyl radical in turn produces an intermediate, which isomerizes via ring closure and emits atomic hydrogen to yield a dehydrogenated, aromatic, and bicyclic naphthalene core. Therefore, successive neutral–neutral reactions of aromatic molecules such as benzene and naphthalene with ethynyl radicals present a versatile, hitherto overlooked reaction class to yield complex, PAH (like) structures via ring expansions at temperatures as low as 10 K, as present in cold molecular clouds. Although benzene has no permanent dipole moment and hence cannot be observed via its rotational spectrum, the reaction of benzene with ubiquitous cyano radicals can lead to benzonitrile (C_6H_5CN) (43) holding a large dipole moment of 4.18 D. Therefore, the hitherto unobserved benzonitrile molecule could act as a tracer for benzene in cold molecular clouds (44). We anticipate that our combined experimental, theoretical, and modeling study will act as a role model to initiate further investigations of the formation and chemistry of polycyclic aromatic molecules in low-temperature interstellar environments. A link of the laboratory and modeling data with prospective astronomical searches utilizing the Atacama Large Millimeter Array are expected to provide a comprehensive picture of the processes involved in the formation of aromatic molecules in the ISM.

Materials and Methods

Electronic Structure Calculations. Our electronic structure calculations were conducted at the CCSD(T)/CBS level of theory (see *SI Text* for details) to predict relative energies of the intermediates [i1–i4], the transition states, and products of the reactions of the ethynyl and D1-ethynyl radical with 1,3-butadiene to an accuracy of about 5 kJ mol^{-1}. Stationary points were optimized at the hybrid density functional B3LYP level with the 6-311G** basis set using the Gaussian 98 program package (45). Vibrational frequencies and zero-point vibrational energy corrections were calculated using the same B3LYP/6-11G** method.

Experimental. The crossed beam reaction of the deuterated ethynyl radical, $C_2D(X^2\Sigma^+)$, with 1,3-butadiene, $CH_2CHCHCH_2(X^1A_g)$, was conducted with a universal crossed molecular beam apparatus (46) at a collision energy of 45.4 ± 2.1 kJ mol^{-1} by crossing a pulsed beam of D1-ethynyl radicals perpendicularly with a pulsed beam of 1,3-butadiene molecules. The products were monitored using a triply differentially pumped quadrupole mass spectrometer in the TOF mode after electron-impact ionization of the neutral molecules. To collect information on the scattering dynamics, the laboratory data (TOF, angular distribution) were transformed into the center-of-mass reference frame utilizing a forward-convolution routine. This iterative method initially assumes the angular flux distribution, $T(\theta)$, and the translational

energy flux distribution, $P(E_T)$ in the center-of-mass system. Laboratory TOF spectra and the laboratory angular distributions were then calculated from the $T(\theta)$ and $P(E_T)$ function and were averaged over a grid of Newton diagrams to account for the apparatus functions and also for the angular and velocity spreads of both reactant beams.

Astrochemical Modeling. We examined the viability of the formation of benzene via neutral–neutral reactions using chemical models based on the dipole-enhanced University of Manchester Institute for Science and Technology Rate06 reaction database (47) updated with rate constants relating to the formation of benzene and its 1,3-butadiene precursor as compiled in the *SI Text*, which also includes uncertainties of the rate constants of the

methylidyne radical reactions and in the experimental uncertainties of the hydrogen atom yields given by the kinetics studies as cited above.

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