INTRODUCTION

Since Léger’s and Puget’s very first hypothesis of polycyclic aromatic hydrocarbons (PAHs)—organic molecules composed of fused benzene rings—as the missing link between small carbon molecules and carbonaceous nanoparticles (interstellar grains) (1), PAHs (2) along with their (de)hydrogenated (3), alkylated (4, 5), protonated (6), and ionized (7) counterparts have been associated with the diffuse interstellar bands (DIBs) (8)—discrete absorption features superimposed on the interstellar extinction curve ranging from the visible (400 nm) to the near-infrared (1.2 μm)—and the unidentified infrared (UIR) emission bands (9, 10) in the 3- to 14-μm range. Encompassing up to 20% of the carbon budget in our galaxy (11, 12), the identification of PAHs in carbonaceous chondrites such as Murchison, Allende, and Orgueil (13, 14) along with 13C/12C and D/H isotopic analyses (15) advocates a circumstellar origin of aromatics in carbon-rich asymptotic giant branch (AGB) stars and planetary nebulae as the descen- dants of AGB stars at elevated temperatures of a few 1000 K through molecular mass growth processes involving hydrogen abstraction–carbon addition (HACA) sequences (16).

Micelotta et al. (17, 18) revealed that, once formed, interstellar PAHs are swiftly destroyed by galactic cosmic rays, photolysis, and shock waves, causing lifetimes of only a few 10^8 years. These time scales are substantially shorter than those for the injection of PAHs from carbon-rich circumstellar envelopes into the interstellar medium of 2 × 10^9 years (19–22). Consequently, PAHs should exist neither in the interstellar medium nor in meteorites, and the ubiquitous presence of PAHs represents a key paradox in astrophysics. This inconsistency could be resolved by inferring the existence of hitherto elusive low-temperature routes to a rapid growth of PAHs in the interstellar medium to offset their destruction (23). An identification of these low-temperature pathways is of particular importance to untangle the origin of PAHs carrying five-membered rings such as indene, which represents an essential molecular building block of nonplanar PAHs like corannulene (C_{20}H_{10}) along with fullerenes (C_{60}, C_{70}), thus offering a new concept on the low-temperature chemistry of carbon in our galaxy.

Polycyclic aromatic hydrocarbons (PAHs) are fundamental molecular building blocks of fullerenes and carbonaceous nanostructures in the interstellar medium and in combustion systems. However, an understanding of the formation of aromatic molecules carrying five-membered rings—the essential building block of nonplanar PAHs—is still in its infancy. Exploiting crossed molecular beam experiments augmented by electronic structure calculations and astrochemical modeling, we reveal an unusual pathway leading to the formation of indene (C_{9}H_{8})—the prototype aromatic molecule with a five-membered ring—via a barrierless bimolecular reaction involving the simplest organic radical—methylidyne (CH)—and styrene (C_{6}H_{5}C_{2}H_{3}) through the hitherto elusive methylidyne addition–cyclization–aromatization (MACA) mechanism. Through extensive structural reorganization of the carbon backbone, the incorporation of a five-membered ring may eventually lead to three-dimensional PAHs such as corannulene (C_{20}H_{10}) along with fullerenes (C_{60}, C_{70}), thus offering a new concept on the low-temperature chemistry of carbon in our galaxy.
medium carrying a five-membered ring: indene. The carbon backbone of indene—the simplest representative of an aromatic molecule carrying a six-membered benzene ring fused with a five-membered cyclopentadiene moiety—represents a fundamental molecular building block of nonplanar PAHs like corannulene (C20H10) and may signify an essential reaction intermediate in the molecular mass growth processes, leading ultimately to interstellar fullerenes (C60, C70) (24, 25).

RESULTS

Crossed molecular beam studies—Laboratory frame

The reactive scattering experiments were carried out exploiting a crossed molecular beam apparatus (Materials and Methods). For the reaction of the methylidyne radical [CH; 13 atomic mass units (amu)] with styrene (C8H8; 104 amu), reactively scattered products were observed at mass/charge ratio (m/z) of 117 (C9H8+), 116 (C9H8+), and 115 (C9H7+) with relative intensities of 10 ± 2%, 100%, and 200 ± 10%, respectively. The scattering signal was relatively weak; hence, at each angle, up to 5 × 10^6 time-of-flight (TOF) spectra had to be averaged over 50 hours to obtain reasonable signal-to-noise ratios. After scaling, the TOF spectra at all m/z values were found to be superimposable. These findings propose that signal at m/z = 116 arises from the hydrogen atom loss channel accompanied by the formation of a molecule with the molecular formula C9H8 formed via the reaction CH (13 amu) + C8H8 (104 amu) → C9H8 (116 amu) + H (1 amu). Signal at m/z = 117 (13C C8H8+) arises from the natural abundance of 13C isotope of carbon, whereas ion counts at m/z = 115 are connected to dissociative electron impact ionization of the neutral reaction products in the detector. Therefore, having evidenced the formation of molecule(s) with the formula C9H8, TOF spectra of the nascent C9H8 reaction product were collected at m/z = 116 at distinct laboratory angles from 36° to 66° in 5° intervals. The TOFs were then normalized with respect to the TOF at the center of mass (ΩCM) and integrated to yield the laboratory angular distribution (LAD) (Fig. 2). Notable features of the LAD of the C9H8 product(s) are the symmetry around the CM angle and the angular spread of at least 30° in the scattering plane, suggesting indirect scattering dynamics via the formation of C9H9 complexes.

Crossed molecular beam studies—CM frame

To unravel the underlying reaction mechanism(s) along with the nature of the C9H8 isomer(s), the experimental data were transformed from the laboratory to the CM reference frame (29, 30). This forward convolution approach yields the CM translational P(E) and angular flux T(θ) distribution as depicted in Fig. 3. Best fits of the laboratory
This value agrees nicely with the National Institute of Standards and Technology (NIST) reaction energy of $-364 \pm 12 \text{ kJ mol}^{-1}$. The subtraction of the collision energy $E_C (20.6 \pm 0.2 \text{ kJ mol}^{-1})$ from the sum of the absolute value of the reaction exoergicity plus the collision energy $E_C (20.6 \pm 0.2 \text{ kJ mol}^{-1})$ provides information on the pertinent reaction channel(s) and dynamics. First, $P(E_T)$ assists in the identification of the product isomer(s). Accounting for the conservation of energy, those products formed without internal excitation, the high-energy cutoff of $376 \pm 38 \text{ kJ mol}^{-1}$ denotes the sum of the absolute value of the reaction exoergicity plus the collision energy $E_C (20.6 \pm 0.2 \text{ kJ mol}^{-1})$. The subtraction of the collision energy reveals that the reaction is highly exoergic by $-355 \pm 25 \pm 3 \text{ kJ mol}^{-1}$, indicating a tight exit transition state. Last, the $T(\theta)$ distribution depicts flux over the complete angular range along with a forward-backward symmetry. This finding proposes indirect scattering dynamics via the formation of $C_9H_9$ complex(es) having a lifetime(s) longer than the(ir) rotational period. The pronounced distribution maximum at $90^\circ$ suggests geometrical constraints of the decomposing complex(es), i.e., a preferential emission of the hydrogen atom in the exit transition state perpendicular to the rotational plane of the decomposing intermediate nearly parallel to the total angular momentum vector ($\hat{L}$).

**Electronic structure calculations and formation mechanism**

The present study reveals that at least the indene molecule—the prototype aromatic molecule carrying one five- and one six-membered ring—can be formed via the elementary reactions of the methylidyne radical with styrene in the gas phase. We are combining these findings with computational and statistical results to propose the underlying reaction mechanism(s) (Fig. 4 and fig. S1). The computations reveal that the methylidyne radical can add barrierlessly either to the \( \pi \) electron density of the carbon-carbon double bond of the vinyl moiety (C$_2$H$_5$) (Fig. 4A) or to the aromatic ring (Fig. 4, B and C). In analogy to the stem compounds ethylene (C$_2$H$_4$) (34) and benzene (C$_6$H$_6$) (35), methylidyne is unlikely to insert into any carbon-hydrogen bond of the phenyl or vinyl functional groups. The addition of methylidyne to the vinyl moiety leads to a phenyl-substituted cyclopropenyl intermediate (i1), which opens to the thermodynamically preferred phenyl-substituted allylic radical intermediate (i2). The latter undergoes cis-trans isomerization to i3 followed by cyclization to i4; this reaction sequence is terminated by a hydrogen atom emission from the bridging C4 carbon atom accompanied by aromatization and formation of indene (p1) in an overall exoergic ($-356 \pm 8 \text{ kJ mol}^{-1}$) reaction through a tight exit transition state.

The addition of methylidyne to the benzene moiety is more complex because six chemically nonequivalent “aromatic” carbon-carbon bonds exist. The barrierless addition leading to intermediate i5, which undergoes a facile ring opening via a barrier of only 8 kJ mol$^{-1}$ to the vinyl-tropyl radical intermediate i6, is exemplified in Fig. 4 (B and C). Note that the addition process to any aromatic carbon-carbon bond followed by ring opening results in the formation of the doublet radical intermediate i6 (fig. S2). This intermediate isomerizes via ring contraction to the bicyclic intermediate (i7) followed by the four-membered ring opening to an open-shell substituted cyclopentadiene derivative (i8). Three distinct reaction pathways lead ultimately to the 1H-inden-6-yl-1,5-dihydro intermediate (i11), which eventually fragments via a hydrogen atom loss from the CH$_2$ moiety located at the six-membered ring complemented by aromatization and synthesis of indene (p1) once again via a tight exit transition state. These isomerization sequences involve rotations of the side chains—one of them representing the vinyl side chain of the indene.
Fig. 4. Potential energy surface. The potential energy surface for the reaction of the methylidyne radical with styrene including reaction pathways energetically accessible in the crossed molecular beam experiments via addition to the vinyl (path A) and benzene moiety (paths B and C). The route in red highlights the reaction pathway leading to the formation of indene plus atomic hydrogen. Relative energies are given in units of kJ mol\(^{-1}\). Atoms are color-coded in gray (carbon) and white (hydrogen).
styrene reactant—around the C–C bonds connecting them with the five-membered ring (i8 → i9, i8 → i15 → i16, or i12 → i13 → i14), which may be preceded by hydrogen migration in the five-membered ring (i8 → i12). The rotations are followed by ring closures (i9 → i10 or i14 → i11), in which the six-membered ring is reformed from two exocyclic C2 moieties; the bicyclic intermediate i10 is linked to i11 via H migration in the five-membered ring. Alternatively, intermediate i6 could isomerize in one or two steps involving (multiple) hydrogen migration steps leading to i18, followed by a sequence of ring contraction (i19) – hydrogen shift (i20) – ring opening (i21) – and cyclization (i22). The 1-indanyl radical represents the global minimum of the C9H9 potential energy surface and undergoes unimolecular decomposition via a loss of atomic hydrogen from the methylidyne moiety at the C2 carbon through a tight exit transition state accompanied by aromatization and formation of indene (p1).

Having identified six feasible reaction pathways leading eventually to indene plus atomic hydrogen, we are exploiting now a Rice-Ramsperger-Kassel-Marcus (RRKM) master equation analysis (Materials and Methods) to predict the dominating reaction pathway(s) to indene. First, according to RRKM calculations of product branching ratios at the experimental collision energy, the addition to the side chain near-ly exclusively produces indene via hydrogen atom loss from the benzene ring (96 ± 2% versus 4 ± 2%; p2). Alternatively, methylidyne addition to the benzene ring is predicted to result in the production of 63 ± 6% indene (by hydrogen atom loss from the vinyl chain), 33 ± 6% vinylcyclopentadienyl plus acetylene (p5), and 5 ± 3% other C9H8 isomers with the indene core (p3 and p4; fig. S1), which might be formed to 300 K (36, 37) and 2 × 10⁻¹⁰ to 3 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ for 300 to 700 K (38). While for the methylidyne-benzene system experimental kinetic data are available for 25 K (2.7 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹) (39) and from 297 to 674 K (40) with nearly temperature-independent rates of 4 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (36), our present variable reaction coordinate transition state theory (VRC-TST) calculations of methylidyne addition to the aromatic ring in benzene and to the double C=C bond in ethylene revealed that the rate constants for the former are by a factor of typically 1.5 higher than those for the latter in the same temperature interval (Supplementary Materials). The temperature dependence of the calculated rate constant for methylidyne-benzene is similar to that for the experimental rate constant for methylidyne-ethylene, and the computed values for both reactions reproduce the experimental measurements within 20% or better. On the basis of this comparison, we can anticipate that methylidyne addition to the benzene ring should be approximately 1.5 times more likely than methylidyne addition to the vinyl side chain. Next, according to RRKM calculations of product branching ratios at the experimental collision energy, the addition to the side chain nearly exclusively produces indene via hydrogen atom loss from the benzene ring (96 ± 2% versus 4 ± 2%; p2). Alternatively, methylidyne addition to the benzene ring is predicted to result in the production of 63 ± 6% indene (by hydrogen atom loss from the vinyl chain), 33 ± 6% vinylcyclopentadienyl plus acetylene (p5), and 5 ± 3% other C9H8 isomers with the indene core (p3 and p4; fig. S1), which might be formed
via hydrogen atom losses from both the ring and the vinyl chain. Note that the error bars in the computed branching ratios were assessed by varying the heights of the critical barriers for different product channels by ±4 kJ mol⁻¹, which is the typical expected accuracy for relative energies computed in this study. Neglecting the small contribution from the alternative C₉H₈ isomers p₃ and p₄, we evaluate the relative yields of hydrogen atom losses from the side chain and the benzene ring as 1.5 × 0.63/1 or nearly 1:1. Thus, the pathways to indene initiating with methylidyne addition to the ring, predominantly via intermediates i₆, i₇, i₈, and i₁₁, are as likely as the i₁ → i₂ → i₃ → i₄ → p₁ route initiating with methylidyne addition to the side chain. According to the predicted reaction mechanism, indene cannot be formed by elimination of the hydrogen atom originating from the methylidyne reactant.

**Astrochemical modeling**

Having provided compelling evidence on the formation of indene under single collision conditions via the MACA mechanism, we are examining through astrochemical modeling how these findings can be transferred from the laboratory to the interstellar medium. This is central because crossed molecular beam experiments along with computations cannot simulate the chemical complexity in molecular clouds. The computations predict that the elementary reaction of methylidyne with styrene has no entrance barrier to addition, all barriers implicated in the formation of indene are situated below the energy of the separated reactants, and the overall reaction to indene is exoergic. These findings signify vital criteria for this reaction to be open in low-temperature environments such as in molecular clouds, which have temperatures as low as 10 K. Any barrier would block these reactions in low-temperature interstellar environments. Therefore, our results can be applied to any cold environment in deep space such as molecular clouds, where both the methylidyne and styrene reactants exist. Methylidyne radicals can be generated in the gas-phase photolysis of methane (CH₄) by Lyman α even present within the internal ultraviolet (UV) photon field deep inside molecular clouds (42). Styrene can be formed either via the barrierless, bimolecular reaction of a methylidyne radical with toluene (C₆H₅CH₃) [fig. S3 (43)] or via UV- and galactic cosmic ray–induced (reactive) desorption along with grain-grain collisions and removal of ice mantles of grains containing styrene (44, 45). Toluene itself can be produced barrierlessly from acyclic species in bimolecular ethynyl (C₂H) plus isoprene (C₅H₈) (46) and 1-propynyl (CH₃CC) plus 1,3-butadiene (C₄H₆) (47) reactions. To explore the overall efficiency of MACA on the formation of indene in the interstellar medium, astrochemical simulations were run for the cold molecular cloud TMC-1 using the Nautilus v1.1 code (48). Most of the physical parameters and initial fractional abundances of the reactive species were adopted from Hincelin et al. (49) and are described in more detail in the Supplementary Materials. This reaction network was updated to include chemistries leading eventually to the indene molecule as elucidated in the present work.
These modeling studies reveal exciting findings (Fig. 5). The left-hand panel shows the results of the simulation with the standard cosmic ray ionization rate of $\zeta = 1.3 \times 10^{-17}$ s$^{-1}$, while the right-hand panel depicts results using a value of $\zeta = 1.3 \times 10^{-18}$ s$^{-1}$, which is in line with data recently derived by Ilyev et al. (50) for L1544, another source in Taurus. The astrochemical models disclose significant amounts of indene formed via MACA in the gas phase at fractional abundances of up to a few $10^{-12}$. The dipole moment of indene (C$_9$H$_8$) of 0.50 D is slightly higher than the dipole moment of propylene (C$_3$H$_6$), which has been detected recently in TMC-1, of 0.36 D (51), suggesting that an astronomical detection of indene toward TMC-1 is challenging, but technologically feasible in the context of a high–spectral resolution, high-sensitivity survey using, e.g., the Robert C. Byrd 100 m Green Bank Telescope (GBT) or the Atacama Large Millimeter/submillimeter Array (ALMA). Cyanoin- dene isomers (C$_9$H$_7$CN; fig. S5), which may form via rapid, barrierless neutral-neutral reactions of indene with the cyano radical (CN) (52), hold significantly higher dipole moments between 4.03 and 5.70 D, thus classifying “cyano-tagged” indene viable candidates to be searched for. This strategy has been exploited successfully by Chin et al. (53) and Lovas et al. (54) along with McGuire et al. (55) to detect cyanoallene [H$_2$CCCH(CN)] and cyanobenzene (C$_6$H$_5$CN) formed via bimolecular gas-phase reactions of CNs with microwave inactive allene (H$_2$CCCH$_2$) (56) and benzene (C$_6$H$_6$) (57), respectively. Our astrochemical models predict cyanoindene isomers to be present with fractional abundances of up to $10^{-11}$ with respect to molecular hydrogen—levels that are comfortably in the realm of the GBT or ALMA—with the larger value of $\zeta$ revealing an even stronger effect on the abundances of cyanoindene compared to indene.

**DISCUSSION AND CONCLUSIONS**

Our combined crossed molecular beams, electronic structure, and astrochemical modeling study reveals that indene may form not only in hot circumstellar envelopes of carbon-rich stars together with planetary nebulae as thought previously but also in cold molecular clouds via facile, barrierless reactions involving the simplest organic radical (methylidyne) with styrene. Because indene carries a five-membered ring, the low-temperature pathway may deliver a population of indene, which could provide a structural motif for the generation of nonplanar PAHs such as coronulene and even fullerences (Fig. 1). These five-membered rings are critical to bent PAHs out of plane; as evident form kinetic Monte Carlo models of graphene-edge growth, the exclusion of reactions creating five-membered rings from the simulation leads only to planar PAHs (23, 58). It is worth mentioning that PAH formation might also involve nucleation, where reactive surfaces provided by seed particles such as silicon carbides initiate grain growth processes through deposition of aromatic molecules. After ejection to the interstellar medium, the upper layers of these grains, which may contain aromatic molecules, might be desorbed by UV radiation, sputtering, or shattering by grain-grain collision (59). Furthermore, in solar nebula, the abstraction of a hydrogen atom followed by the addition of acetylene molecules may form significant quantities of PAHs by considering the higher initial concentration based on the astronomical observational results; these processes involve entrance barriers and only operate at elevated temperatures of typically 1000 K and beyond (60). Thus, the present investigation of barrierless, low-temperature pathways to indene may bring us closer to unraveling the paradox of the injection and destruction time scales of aromatics.

The work reported here represents an important step toward a systematic understanding of the fundamental chemical processes leading to the formation of indene and nonplanar PAHs in low-temperature environments in deep space. Whereas indene has been shown to be the product in high-temperature processes involving reactions of phenyl radicals (C$_6$H$_5$) with allene (H$_2$CCCH$_2$) and methylacetylene (CH$_3$CCH) (61, 62) along with the benzyl radical (C$_7$H$_7$)–acyclicene (C$_6$H$_8$) system (63), the MACA mechanism operates at low temperatures such as in molecular clouds. The only other barrierless reaction, which has been recently shown to form indene, is o-benzene (C$_6$H$_5$) plus allyl (C$_3$H$_4$) (64), but it involves two unstable species not detected in deep space. MACA has the potential to convert any vinyl group (C$_2$H$_3$) linked to an aromatic, six-membered ring eventually to a cyclopen- tadiene moiety via reaction of a methylidyne radical (Fig. 6). MACA can compete with the ethynyl addition mechanism (EAM) (65, 66), which is predicted to convert the vinyl group attached to a PAH molecule to a six-membered ring. Whereas the carbon backbone of the benzene ring stays intact as long as the methylidyne radical adds to the vinyl moiety (Fig. 7), an addition to the benzene ring leads to a complete structural reorganization of the benzene moiety, leading to a newly formed six-membered ring incorporating the vinyl functional group. The complete reorganization of the carbon skeleton of a “stable” aromatic system even at temperatures as low as 10 K leads to a complete “loss of memory” of the molecular structure and is rather unprecedented, as traditional molecular mass growth processes to aromatic systems merely “add” rings to an existing aromatic structure. Considering the crucial role of nonplanar PAHs in the formation of fullerences and carbonaceous dust particles—commonly referred to as interstellar grains—and in the chemical evolution of the universe, with grains acting as vital molecular factories to synthesize biorelevant organics like amino acids and sugars, the elucidation of the elementary steps leading to dust particles in our galaxy is fundamental to enhance our knowledge of the chemistry of car- bonaceous matter in our galaxy.

**MATERIALS AND METHODS**

**Crossed molecular beam experiments**

The reaction of the methylidyne (CH; X$	ext{^3}$Σ) radical with styrene (C$_6$H$_5$: X$^1$A$^+$) was performed in gas phase under single collision conditions exploiting a crossed molecular beam machine (67). A pulsed supersonic beam of methylidyne radicals was produced by photodissociation of helium (99.9999%; Air Gas)–seeded bromoform (CHBr$_3$: ≥ 99%; Aldrich Chemistry) held in a stainless steel bubbler at a stagnation pressure of 2.2 atm and 283 K. This mixture was introduced into a pulsed piezoelectric valve operating at a repetition rate of 60 Hz, pulse widths of 80 µs, and a peak voltage of −400 V. The 248-nm output of excimer laser (30 Hz; COMPex 110, Coherent Inc.) intersected molecular beam 1 mm downstream of the nozzle (68). A chopper wheel rotating at 120 Hz selected a section of the pulse defined by a peak velocity of 1850 ± 11 ms$^{-1}$ and speed ratio of 11.7 ± 0.7. The rotational temperature was characterized by laser-induced fluorescence to be 14 ± 1 K (69). This segment crossed a pulsed supersonic beam of styrene (C$_6$H$_8$: >99.0%; TCI America) seeded in xenon (99.999%; Matheson) at a fraction of 1% at 570 torr perpendicularly. The section of the supersonic styrene beam crossing the methylidyne radical beam has a peak velocity and speed ratio of...
386 ± 4 ms⁻¹ and 28.0 ± 0.4, respectively, resulting in a collision energy of 20.6 ± 0.2 kJ mol⁻¹ and CM angle 59.1 ± 0.3°. The beam characteristics are defined in table S1. The reactive-scattering products were ionized by an electron-impact ionizer operating at 80 eV and 2-mA emission current, before they entered a quadrupole mass spectrometer (QMS, Extrel 150-QC) operating in the TOF mode (70, 71). The designated ion species filtered by the QMS at a specific m/z traveled toward a stainless steel target coated with a thin layer of aluminum biased at −22.5 kV, and a cascade-of-electron pulse was initiated upon impact. The electrons were then expelled from the stainless steel target and flew toward an organic scintillator to generate a photon pulse, before being detected by a Burle photomultiplier tube (model 8850) operating at −1.35 kV. The signal was filtered by a discriminator (Advanced Research Instruments, model F-100TD) at a level of 1.6 mV and fed into a Stanford Research System SR430 multichannel scaler. The rotatable detector allows the collection of angular resolved TOF spectra at discrete angles, integrate and normalize them with respect to the intensity at the CM angle, and then derive the product LAD at a specific m/z. To obtain information on the reaction dynamics, we used a forward-convolution routine to convert the data from the laboratory frame into the CM reference frame (29, 30). Considering the barrierless reaction, the collision energy (Eₜ) dependence of the cross-section σ was obtained from the line-of-center model as σ ~ Eₜ⁻¹/₃ (32). The flux contour map, I(θ, υ) = P(υ) × T(θ), which presents the flux of the reactively scattered products as a function of the CM scattering angle (θ) and product velocity (υ), contains all information of the reactive scattering process.

Electronic structure and RRKM calculations

Geometries of the reactants, products, intermediates, and transition states involved in the methylidyne-styrene reaction on the C₉H₈ potential energy surface were optimized at the B3LYP/6-311G(d,p) level of theory (72, 73) with vibrational frequencies computed using the same method. Single-point energies were further improved using the composite G3(MP2,CC) model chemistry scheme (74–76). The G3(MP2,CC)/B3LYP theoretical approach is capable of providing the energetic parameters with “chemical accuracy” within 3 to 6 kJ mol⁻¹ for hydrocarbons in terms of average absolute deviations. The Gaussian 09 (77) and MOLPRO 2010 (78) program packages were used for the ab initio calculations. RRKM theory (79–82) was used to compute energy-dependent rate constants of all unimolecular reaction steps on the C₉H₈ surface following the initial addition of the methylidyne radical to styrene and to obtain product branching ratios under single-collision conditions using our in-house UNIMOL code (83).

VRC-TST calculations of rate constants for methylidyne addition to C₉H₈ and C₇H₆

Rate constants for the barierless CH + benzene and CH + ethylene addition reactions were computed using VRC-TST (84–86). A multifaceted spherical dividing surface (84) used in the calculations was built as the equidistant surface between the pivot points assigned to the associating/dissociating fragments. At short-range distances (less than 5 Å), the pivot point placement was varied along the symmetry axis of the orbitals of benzene/ethylene. The centers of mass of the reacting fragments served as the pivot points at long-range distances (84). A complex of interacting fragments on a dividing surface was generated using the geometries of CH and benzene/ethylene optimized as separate fragments at the B3LYP/6-311G(d,p) (72, 73) level of theory. The notation “rigid” is used here to denote the lack of geometrical relaxation in a complex on a dividing surface. The single-point energies of rigid structures were probed at the CCSD(T)/cc-pVDZ (87) level of theory. The single-point energies of the rigid structures were further amended with the one-dimensional geometry relaxation correction (84) and the complete basis set (CBS) correction (88). The one-dimensional geometry relaxation correction was calculated for the minimum energy path (MEP) rigid structures relaxed using B3LYP/6-311G(d,p) geometry optimization. The CBS correction was calculated using the CCSD(T)/cc-pVnZ (n = D, T, Q) energies of the rigid MEP structures. To summarize, in the VRC-TST reactive flux calculations, the energies of the rigid structures sampled on a dividing surface were first probed at the CCSD(T)/cc-pVDZ level of theory followed by the ad hoc one-dimensional relaxation and CBS corrections

\[ E = E_{\text{rigid}} \left[ \text{CCSD(T)/cc-pVDZ}\right] + \Delta E[\text{geom}]+ \Delta E[\text{CBS}] \]

where \( E_{\text{rigid}} \) is the single-point energy of the interacting rigid fragments and \( \Delta E[\text{geom}] \) is the geometry relaxation correction computed as the difference of CCSD(T)/cc-pVDZ energy of the optimized MEP structure corresponding to a particular value of the \( R_{CC} \) distance and the rigid structure at the same \( R_{CC}[\text{CBS}] \) was calculated as follows

\[ \Delta E[\text{pVTZ}] = E_{\text{rigid}} \left[ \text{CCSD(T)/cc-VTZ}\right] - E_{\text{rigid}} \left[ \text{CCSD(T)/cc-pVTZ}\right] \]

\[ \Delta E[\text{pVQZ}] = E_{\text{rigid}} \left[ \text{CCSD(T)/cc-VQZ}\right] - E_{\text{rigid}} \left[ \text{CCSD(T)/cc-VTZ}\right] \]

\[ \Delta E[\text{CBS}] = \Delta E[\text{pVQZ}] + 0.69377 \times (\Delta E[\text{pVQZ}] - \Delta E[\text{pVTZ}]) \]

The temperature-dependent high-pressure limit rate constants for the CH + benzene and CH + ethylene addition reactions are shown in fig. S4, and the computed ratios of these rate constants at different temperatures are presented in table S3.

Astrochemical modeling

For this work, the three-phase astrochemical code, Nautilus v1.1, was used (48). In addition to running models using the standard cosmic ray ionization rate of \( \dot{\zeta} = 1.3 \times 10^{-17} \) s⁻¹, we carried out additional simulations with a value of \( \dot{\zeta} = 1.3 \times 10^{-16} \) s⁻¹. This latter value is based on the recent study by Ivlev and coworkers (50) of gas and dust temperatures toward L1544, which is another source in Taurus fairly close to TMC-1. It has previously been suggested in a number of recent works that the cosmic ray ionization is higher than the standard value toward the Galactic Center (89–91); however, the study by Ivlev and coworkers is remarkable, in part, because it similarly suggests that the standard value is too low even for regions outside the Galactic Center. To account for cosmic ray–driven reactions, the method of Shingledecker and Herbst (92) and Shingledecker et al. (93) is exploited. The physical conditions and elemental abundances appropriate for TMC-1 are listed in tables S5 and S6; an initial carbon-to-oxygen ratio of 1.2 was used (49). Our chemical network is based on that used by Shingledecker et al. (94). To it, we added reactions related to the formation of indene (C₅H₄) and similar polycyclic species. New gas-phase reactions are given in table S7, with rates taken from the literature where available or computed via Eqs. 2 and 3; \( \dot{\zeta} \) is the cosmic ray ionization rate, and
\( \alpha \) describes the efficiency of photodissociation by internally generated UV photons.

\[
k_3 = \alpha \left( \frac{T}{300 \, \text{K}} \right)^\beta e^{-\gamma} \quad (1)
\]

\[
k_2 = \alpha \zeta \quad (2)
\]

To objectively explore the effects of the formation of indene on the icy grains followed by desorption into the gas phase, we also explored (i) neutral-neutral reactions between ground-state species, (ii) the cosmic ray–driven radiolysis of the new species, and (iii) reactions involving one ground-state species and one suprathermal species in a higher electronic state. Suprathermal reactions occur quickly (95, 96), with rate coefficients incorporated based on the attempt frequency (94). Whenever experimental production rates in the ices were not available, we computed the rate coefficients using expression (3) where \( \alpha \) is the branching fraction and \( \gamma \) is the G value of formation, which gives the number of molecules produced per 100 eV deposited in the system.

\[
k_{\text{rad}} = \alpha \left( \frac{S}{100 \, \text{eV}} \right) \gamma \left( \Phi \frac{\zeta}{10^{-17} \, \text{s}^{-1}} \right) \quad (3)
\]

Although we have included this grain-surface analog system of the MACA route in our network, it contributes to the overall abundance of gas-phase indene was found to be negligible at levels of less than 1%. The main destruction routes for indene include recombination reactions and with CNs thereafter. Depletion onto the 10 K grains represents 95% in involving one ground-state species and one suprathermal species in a gas phase pyrene cation: Support for a polycyclic aromatic hydrocarbon origin of the unidentified infrared emission bands. Phys. Rev. Lett. 86, 5691–5694 (2001).


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