**Title**: **Gas-Phase Formation of the Resonantly Stabilized 1-Indenyl (C9H7**•**) Radical in the Interstellar Medium**

**Short title**: **Interstellar Routes to 1-Indenyl**

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**Abstract**

The 1-indenyl (C9H7•) radical - a prototype aromatic and resonantly stabilized free radical (RSFR) carrying a six- and a five-membered ring - has emerged as a fundamental molecular building block of non-planar polycyclic aromatic hydrocarbons (PAHs) and carbonaceous nanostructures in deep space and combustion systems. However, the underlying formation mechanisms have remained elusive. Here, we reveal an unconventional low-temperature gas-phase formation of 1-indenyl via barrierless ring annulation involving reactions of atomic carbon (C(3P)) with styrene (C6H5C2H3) and propargyl (C3H3•) with phenyl (C6H5•). Macroscopic environments like molecular clouds act as natural low-tempe­rature laboratories, where rapid molecular mass growth to 1-indenyl and subsequently complex PAHs involving vinyl side-chained aromatics and aryl radicals can occur. These reactions may account for the formation of PAHs and their derivatives in the interstellar medium and carbonaceous chondrites and could close the gap of timescales of their production and destruction in our carbonaceous universe.

**Teaser**

The aromatic and resonantly stabilized free 1-indenyl radical is prepared in gas-phase under low-temperature conditions.

**Introduction**

For the last decade, resonantly stabilized free radicals (RSFRs) – organic open shell transients in which the unpaired electron is delocalized over the carbon skeleton – have emerged as fundamental molecular building blocks to polycyclic aromatic hydrocarbons (PAHs), and carbonaceous nanoparticles in combustion processes and in the interstellar medium (ISM) (*1-6*). Reaction pathways from RSFRs such as propargyl (C3H3•), cyclopentadienyl (C5H5•), benzyl (C7H7•), and 1-indenyl (C9H7•) (fig. S1A) to complex PAHs like pyrene (C16H10), fluoranthene (C16H10), chrysene (C18H12) have been investigated (*5, 6*). However, the presence of PAHs along with their derivatives such as ionized, hydrogenated, and side-chain substituted counter­parts in the ISM and carbonaceous chondrites such as Allende, Orgueil, and Murchison still represents a criti­cal paradox in our Universe (*7-9*). Time scales of PAH injection from carbon-rich circumstellar envelopes exceed a few 109 years, but the lifetimes of PAHs in deep space are limited by degradation through interstellar shocks, ultraviolet photons, and galactic cosmic rays to only a few 108 years (*10-12*). In essence, PAHs are destroyed faster than synthesized in carbon-rich Asymptotic Giant Branch (AGB) stars (*12*) along with planetary nebulae as their des­cen­dants (*13*). Hence, PAHs should not be observable via, e.g., unidentified infrared emissions (UIR) (*14*) – in the range from 3 to 14 µm – and diffuse interstellar bands (DIBs) discrete emission lines covering the visible (400 nm) to the near-infrared region (1.2 µm) (*15*) of the electromagnetic spectrum.

     Rapid molecular mass growth processes involving RSFRs signify a solution to this puzzle through the synthesis of PAHs in cold molecular clouds at temperatures as low as 10 K (*2, 8, 16*). Supported by recent observations of the propargyl radical in the Taurus Molecular Cloud (TMC-1) (*17, 18*), RSFRs can reach high fractional abundances of up to a few 10-8 with respect to molecular hydrogen. RSFRs hold lifetimes longer than non-resonantly stabilized hydro­car­bon radicals due to the delocalization of the unpaired electron over (part of) the carbon backbone (*19*), and can undergo rapid radical-radical recombination reactions (*20, 21*). However, whereas molecular beam experiments (*22, 23*) and astrochemical modeling (*17, 18*) provided compelling evidence on the forma­ti­on of the simplest RSFR in TMC-1 – propargyl (C3H3•) – via the bimo­lecular reaction of atomic carbon (C(3P)) with ethylene (C2H4), reaction pathways to more complex RSFRs are largely unknown (*24*). This knowledge is of particular importance for the 1-indenyl (C9H7•) radical (*25*). As a prototype of an aromatic *and* RSFR, the bicyclic, fused C5-C6 species represents the key building block of non-planar PAHs such as corannulene (C20H10), nanobowls (C40H10), and fullerenes (C60, C70) (fig. S1B) with the five-membered ring in the carbon backbone curving the carbon skeleton out of plane (*26, 27*). Therefore, an unraveling of the synthetic routes of 1-indenyl (C9H7•) radical is critical to constrain the population of PAHs delivered from reactions of RSFRs in our Universe.

     Herein, by exploiting molecular beams experiments (crossed molecular beams; chemical reactor) along with electronic structure calculations and astrochemical modeling, we provide persuasive evidence on the gas-phase formation of the 1-indenyl (C9H7•, X2A2) radical through the elementary reaction of atomic carbon (C, 3P) with styrene (C8H8, X1A') (reaction (1)) and via the radical-radical reaction of propargyl (C3H3•, X2B1) with phenyl (C6H5•, X2A1) (reaction (2)) (fig. S2). These bimolecular reactions are barrierless and exoergic with all transition states residing lower than the energies of the separated reactants, could proceed rapidly even at molecular cloud conditions of 10 K. These reactions may provide facile routes to 1-indenyl (C9H7•) via cyclization and aromatization reactions at astronomically observable fractional abundances of (6.1±3.5) ×10-11 with respect to molecular hydrogen in the TMC-1. As a prototype of an aromatic *and* RSFR, 1-indenyl can undergo mole­cu­lar mass growth processes leading to more complex aromatic structures such as naphthalene (C10H8) (*3*), phenanthrene (C14H10) (*4*), pyrene (C16H10) and fluoranthene (C16H10) (*5*). Whereas in low-temperature interstellar environ­ments, single collision conditions dominate (*28*), elevated pressures such as in hydrocarbon-rich atmospheres of planets and their moon like Titan facilitate three-body collisional stabilization of the reaction intermediate(s) with the buffer molecules like molecular nitrogen (N2) (*29, 30*). Thus, the route to indene (C9H8) formation is opened. These third-body stabi­li­za­tion processes also become increasing­ly important in high-pressure combustion settings with indene (C9H8) ubiquitously identified in hydrocarbon flames of, e.g. ethane (*31*), n-butane (*32*), and benzene (*33*). This investigation fills a critical gap in our knowledge of the underlying elementary mechanisms lead­ing to (aromatic) RSFRs in extreme environments by exploiting the 1-indenyl (C9H7•) radical as a benchmark. These reactions eventually lead to non-planar PAHs and carbo­na­ce­ous nanostructures (carbona­ce­ous grains) acting as molecular factories for biorelevant complex organics like amino acids and sugars in deep space (*16*) thus fundamentally enhancing our under­standing of the chemical evolution of carbonaceous matter in the Universe (*27*).

C (12 amu) + C8H8 (104 amu) → C9H7• (115 amu) + H• (1 amu) (1)

C3H3• (39 amu) + C6H5• (77 amu) → C9H7• (115 amu) + H• (1 amu) (2)

**Results**

**Carbon-Styrene System − Laboratory Frame**

     The crossed molecular beam studies of ground state atomic carbon (C; 12 amu) with styrene (C6H5C2H3; 104 amu) (Fig. 1A-B, reaction (1)) revealed reactive scattering signal at mass-to-charge (m/z) ratios of 116 (C9H8+/13CC8H7+), 115 (C9H7+/13CC8H6+), and 114 (C9H6+/13CC8H5+). Ion counts at m/z = 116 and 114 were collected at a level of 9 ± 2% and 78 ± 4% with respect to m/z = 115. Since the TOFs recorded at these m/z values are indistinguishable after scaling, we conclude the existence of a single H loss reaction channel (reaction (1)). Ion counts at m/z = 116 originate from naturally abundant 13CC8H6+, while m/z = 114 can be accounted for through dissociative electron impact ionization of the C9H7 neutral product in the electron impact ionizer to C9H6+. The laboratory angular distribution (LAD) was therefore collected at m/z 115 from 28° to 66° in 2.5° intervals. This distribution spans about 40° within the scattering plane as defined by both beams and displays a forward-backward symmetry with a maximum at the center-of-mass angle (CM) of 52.8 ± 0.6°. This finding suggests indirect reaction dynamics via long-lived C9H8 intermediate(s) (Fig. 1A-B). Since the hydrogen atom can be eliminated from the phenyl (C6H5•) group and/or from the vinyl moiety (C2H3•), crossed beam experiments were also conducted with D3- and D5-styrene, i.e., C6H5C2D3 and C6D5C2H3, respectively. These studies reveal that the atomic hydrogen loss can originate from both the vinyl moiety *and* the phenyl group (Methods).

**Center-of-Mass Frame**

     The interpretation of the laboratory data delivers conclusive evidence of the atomic hydrogen emission from both the vinyl moiety and the aromatic ring of styrene. It is our goal now to elucidate the underlying reaction mechanism(s) and to assign the C9H7 product isomer(s) formed in the bimolecular gas-phase reaction. This is accomplished by transforming the laboratory data into the CM frame (*34*) resulting in the CM translational energy distribution (*P(E*T*)*) and the angular distribution (*T(θ)*) (Fig. 1C-D). Best fits of the laboratory data are achieved by exploiting a single channel fit forming products with a mass combination of 115 amu (C9H7) and 1 amu (H). Crucial information on the reaction channel(s) and dynamics are derived through a detailed inspection of these CM functions. *First*, energy conservation dictates that the high energy cutoff of the *P(E*T*)* of 389 ± 24 kJ mol-1 presents the sum of the collision energy (35.4 ± 1.4 kJ mol-1, table S1) plus the reaction exoergicity for those molecules born without internal excitation. Therefore, a reaction energy of 353 ± 25 kJ mol-1 is revealed. This experimentally derived exoergicity agrees well with

the reaction exoergicity of 360 ± 8 kJ mol-1 to form the1-indenyl radical (C9H7•) plus atomic hydrogen. *Second*, the *P(E*T*)* displays a pronounced distribution maximum of 20 ± 2 kJ mol-1 revealing a tight exit transition state. *Third*, the *T(θ)* has intensity over the complete angular range and reveals a forward-backward symmetry with a maximum at 90° (sideway scattering); these findings support indirect reaction dynamics involving C9H8 complex(es) with lifetime longer than the rotational period, which undergoes unimolecular decomposition through atomic hydrogen loss nearly parallel to the total angular momentum vector (*34*).

**Propargyl-Phenyl System − Mass Spectra**

     The reaction of propargyl (C3H3•) with the phenyl radical (C6H5•) was conducted in a chemical microreactor (*3*). The microreactor consists of a heated silicon carbide (SiC) tube and is incorporated within the source chamber of a molecular beam apparatus equipped with a Wiley-McLaren reflectron time-of-flight mass spectrometer (Re-TOF-MS). Thermally labile propargyl bromide (C3H3Br) and nitrosobenzene (C6H5NO) precursor molecules were seeded in helium carrier gas and pyrolyzed *in situ* through cleavage of the weak carbon-bromine and carbon-nitrogen bonds, respectively, producing selectively helium-seeded propargyl (C3H3•) (*20*) and phenyl radicals (C6H5•) (*35*) at a reactor temperature of 1,373 ± 10 K (Methods). The reaction products were expanded supersonically and probed isomer-selectively via tunable vacuum ultraviolet light from a synchrotron (*3*). Control experiments of *only* helium-seeded nitrosobenzene and *only* propargyl bromide under identical experimental conditions were conducted (*35*) too (Fig. 2A) (“blank experiments”). Likewise, a representative mass spectrum recorded at a photon energy of 9.50 eV for the reaction of the phenyl (C6H5•) with propargyl (C3H3•) radical is displayed in Fig. 2B. A careful analysis of these mass spectra provides compelling evidence that the signal at m/z = 115 (C9H7+) and 116 (C9H8+/13CC8H7+) originates from the phenyl − propargyl radical – radical reaction but is absent in the control experiments. Accounting for the molecular weight of the reactants (C6H5•, 77 amu; C3H3•, 39 amu) and the products (C9H7, 115 amu; C9H8, 116 amu), molecules with the for­mula C9H7 are the reaction products of the reaction of propargyl (C3H3•) with phenyl (C6H5•) (reaction (2)) (fig. S2); the formation of C9H8 molecules can be linked to adducts and/or their isomerization products of the recombination of phenyl with propargyl radicals, which are then stabilized by a third body reaction with helium (*20*).

**Photoionization Efficiency Spectra**

     To unravel the nature of the isomer(s) formed, we turn to photoionization efficiency (PIE) curves, which report the intensity of a well-defined ion of a specific m/z ratio as a function of photon energy which is 7.50 to 10.0 eV in this case. The PIE curves for m/z = 116 (C9H8+/13CC8H7+) (Fig. 2C) and 115 (C9H7+) (Fig. 2D) can be reproduced via fitting with a linear combination of known reference curve(s) (*36*) of distinct isomer(s). *First*, the PIE curve at m/z = 116 can be replicated by the sum of four channels: 3-phenyl-1-propyne ((C6H5)CH2CCH), phenylallene ((C6H5)HCCCH2), indene (C9H8), and 13C-indenyl (13CC8H7+) (Fig. 2C); Second, the experi­mentally derived PIE curve at m/z *=* 115 (Fig. 2D, black) can be reproduced by a single contributor, the 1-indenyl radical (C9H7•, blue) (*37, 38*). 13C-indenyl ion counts contribute to a level of 9.9 % with respect to that of 1-indenyl as shown in Fig. 2D. Most important, the onset of the ion counts at 8.10 ± 0.05 eV correlates nicely with the NIST evaluated adiabatic ionization energy (IE) of indene at 8.14 ± 0.01 eV (*39*); the adiabatic ionization energy (IE) of 3-phenyl-1-propyne ((C6H5)H2CCCH) and phenylallene ((C6H5)HCCCH2) were determined to 8.75 ± 0.05 eV and 8.30 ± 0.05 eV, respectively (*40*). Therefore, we may conclude that within our error limits, 3-phenyl-1-propyne, phenylallene, indene, and 13C-indenyl contribute to signal at m/z = 116 with the branching ratios of the ion counts of 34 ± 2 %, 24 ± 3 %, 36 ± 2 %, and 6 ± 3 %, respectively. It is possible that 3-phenyl-1-propyne and phenylallene can undergo unimolecular decomposition via H-loss to form the corresponding C9H7 radicals (m/z = 115), namely 1-phenylpropargyl (1PPR, C6H5CHCCH) and 3-phenylpropargyl radicals (3PPR, C6H5CCCH2). From our fitting results, the match of the reference indenyl PIE with our experimental PIE curve of m/z = 115 demonstrate that indenyl should be the dominant product for m/z=115 at our high-temperature experimental condition of 1,373 ± 10 K. These results are supported by the recent kinetic calculations for the branching ratios for the C6H5 plus C3H3 reaction at different pressure and temperatures, which reveal that 1PPR and 3PPR are relatively minor products compared to 1-indenyl (*41*). Until now, there is very limited experimental PIE data for 1PPR and 3PPR (*37*). The comparison of available experimental PIE of each reference radical with our experimental PIE curve of 115 are shown in fig. S3. Since the experimental PIE of 1PPR and 3PPR are recorded in a very short range of photon energy (7.5 – 7.8 eV for 3PPR and 7.5 – 9.0 eV for 1PPR), it is not possible to precisely calculate the branching ratios for the indenyl, 1PPR and 3PPR.

**Electronic Structure Calculations and Reaction Mechanisms − Carbon-Styrene System**

     The electronic structure calculations of relative energies of local minima, transition states and products were conducted at an accuracy of ± 5 kJ mol-1 (Fig. 3) (*42, 43*) and reveal that the reaction of atomic carbon with styrene can be initiated on the triplet surface through a barrierless addition of the carbon atom to the π electron density of the carbon-carbon double bond of the vinyl moiety (C2H3). This addition leads to a phenyl-substituted triplet cyclopropylidene intermediate **i1** stabilized by 225 kJ mol-1 with respect to the separated reactants. In analogy to the reaction with the stem compound ethylene (C2H4) (*44, 45*), the compu­tations also predict that insertion of atomic carbon into any carbon-hydrogen bond of the vinyl or phenyl functional groups is closed. **i1** ring opens via a barrier of only 36 kJ mol-1 to the thermodynamically preferred triplet phenylallene (**i2**). Four reaction pathways are opened from **i2**: a hydrogen migration from the ortho position of the phenyl ring to the C2 of the side chain forming **i3,** a 1,2-H migration in the side chain tophenyl substituted triplet vinylmethylene (**i5**), and two unimolecular decompositions via H loss from the CH and CH2 moieties forming 3-phenylpropargyl (**p3**) and1-phenylpropargyl (**p2**) radicals via tight exit transition states. Commencing with **i3**, cis-trans isomerization of the side chain leads to **i4**; this is followed by hydrogen migration from the C1 carbon atom of the side chain to the *ortho* carbon atom of the aromatic ring yielding **i5**, which can further isomerize via *cis-trans* isomerization to **i6**. **i6** can unimolecularly decompose via atomic hydrogen elimination to 1-phenyl­propar­gyl (**p2**) or undergo cyclization to the bicyclic 3aH-indene intermediate (**i7**). This bicyclic intermediate can lose a hydrogen atom to form 1-indenyl (**p1**) or isomerize via hydrogen atom migration to triplet indene (**i8**) prior to hydrogen atom elimination from the CH2 moiety to 1-indenyl (**p1**). Both pathways involve tight exit transition states of 35 and 60 kJmol-1 with respect to the separated products with the **i7** → **i8** → **p1** + H pathway unfavorable compared to **i7** → **p1** + H due to the high barrier of 163 mol-1 for the hydrogen atom migration.

     How do these results compare to our experimental findings? *First*, the experimentally deter­mined reaction exoergicity for the hydrogen atom loss to C9H7 isomers of -353 ± 25kJ mol-1 agrees nicely with the computed data of -360± 5kJ mol-1 to yield 1-indenyl (**p1**) plus atomic hydrogen. Therefore, we can conclude that at least the indenyl radical (C9H7•, **p1**) is formed in the bimolecular reaction of atomic carbon with styrene. The presence of the theromodynamically less stable isomers 1-phenylpropargyl (**p2**, -217 ± 5kJ mol-1) and 3-phenylpropargyl (**p3**, -208± 5 kJ mol-1) can be masked in the low energy section of the CM translational energy distri­bution. This conclusion also gains support from statistical calculations with Rice-Rams­perger-Kassel-Marcus (RRKM) theory

(Methods) to predict branching ratios within the limits of complete energy randomization (*42*). This treatment predicts that 1-indenyl (**p1**) contri­butes to 54.9 % of all products, whereas 1-phenylpropargyl (**p2**) and 3-phenylpropargyl (**p3**) account for 41.6 % and 3.5 %, respectively. It shall be highlighted that alternative indenyl isomers, i.e. 2-indenyl (144 kJ mol-1), 3-indenyl (145 kJ mol-1), 4-indenyl (133 kJ mol-1), 5-indenyl (132 kJ mol-1), 6-indenyl (133 kJ mol-1), and 7-indenyl (132 kJ mol-1) are thermodynamically less stable than 1-indenyl with relative energies indicated in the parentheses (*46*). Therefore, the formation of 2- to 7-indenyl cannot account for the experimentally derived reaction energy.

*Second*, the *P(ET)* reveals a tight exit transition state in the decomposition of C9H8 reaction intermediate(s). The presence of a tight exit transition state is verified computationally for the pathways **i7** → **i8** → **p1** + H and **i7** → **p1** + H. The reverse reaction, i.e., the recombination of atomic hydrogen with 1-indenyl (**p1**), formally represents a radical – radical reaction and hence should proceed via atom – radical recom­bi­nation without an entrance barrier *if* this reaction proceeds on the singlet surface (*47, 48*). However, the experimental evidence of a tight exit transition state supports our computations that the reaction proceeds on the triplet surface without intersystem crossing to the singlet manifold.

*Third*, the sideway scattering is evident from the computed structure of the transition state associated with the fragmentation of **i7** to **p1** + H (Fig. 3) with the atomic hydrogen leaving nearly perpen­dicularly to the rotational plane of the decomposing **i7** interme­diate. Note that the RRKM calcu­la­tions also predict that 99 % of 1-indenyl (**p1**) originates from **i7** → **p1** + H and less than 1 % from **i7** → **i8** → **p1** + H.

*Finally*, we would like to address the experimental findings of the isotopic substi­tution studies in light of the computed surface (Fig. 3; figs. S4 and S5). Branching ratios of the four pathways i) **i2** → **p3** + H(3.5 %), ii) **i2** → **p2** + H(29.5 %), iii) **i6** → **p2** + H(12.1 %), and iv) **i7** → **p1** + H(54.7 %)along with the dominance of 1-indenyl (**p1**; 54.9 %) and 1-phenylpropargyl (**p2**; 41.6 %) are predicted via the RRKM calculations (table S2). Considering these pathways, the *predicted* ratio of the hydrogen atom loss from the phenyl group versus the vinyl moiety is 1.22 ± 0.03: 1. The isotopic experiments also determined the extent of the hydrogen loss in the C/C6H5C2D3 (from the phenyl group; fig. S4) and C/C6D5C2H3 systems (from the vinyl group; fig. S5) detected at m/z = 120 and 118, respectively to be 1.18 ± 0.02: 1 (Supplementary Materials). This result is in excellent agreement with the RRKM calculations suggesting that in order to eventually eliminate atomic hydrogen, the carbon atom preferentially attacks initially the vinyl moiety, but not the aromatic ring.

     Considering the larger cone of acceptance of the aromatic ring compared to the vinyl group, these findings seem counterintuitive. Further, atomic carbon was found to react with the benzene molecule (C6H6) (*49*) forming the cyclic1,2-didehydrocycloheptatrienyl radical (C7H5•) plus atomic hydrogen. This reaction has neither an entrance nor an exit barrier and is only weakly exoergic by 8 kJmol-1. In the present situation, the reaction of atomic carbon with the aromatic ring of styrene has two competing exit channels: a vinyl radical (C2H3•) loss forming the cyclic 1,2-didehydro­cycloheptatrienyl radical (C7H5•) (fig. S6, **p4**) as the heavy co fragment (reaction (3)) and an atomic hydrogen loss leading to three distinct vinyl-1,2-didehydrocycloheptatrienyl radicals (reaction (4)) (fig. S6, **p5**-**p7**). The reactions are only slightly exoergic, by 19 kJmol-1 (C7H5• plus C2H3•) and by 40, 6, and 15 kJmol-1 for the vinyl-1,2-didehydro­cyclo­heptatrienyl (C7H4C2H3•) plus atomic hydrogen channel depending on the position of the de-facto carbon atom insertion via addition – ring opening into the six-membered ring of styrene with respect to the vinyl group. Therefore, we may conclude that although reactions (3) and (4) are feasible, they are much less favorable thermodynamically than the formation of 1-indenyl (**p1**) and 1-/3-phenylpropargyl (**p2**/**p3**). Most important, reaction (4) cannot be responsible for the experi­mentally observed translational energy distribution.

C(3P) + C6H5C2H3 → C7H5• + C2H3• (3)

C(3P) + C6H5C2H3 → C7H4C2H3• + H• (4)

**Propargyl-Phenyl System**

     Having elucidated the formation of 1-indenyl (C9H7•) in the reaction of atomic carbon with styrene, we now turn our attention to the propargyl – phenyl system (Fig. 4). According to the previous calculations (*48*), the reac­ti­on is initiated by the barrierless addition of the propargyl with the CH2 or CH terminal moieties radical to the radical site of phenyl producing intermediates **i9** (3-phenyl-1-propyne) and **i10** (phenylallene), respectively. These isomers reside in deep potential energy wells and are stabilized by 381 and 400 kJ mol-1 with respect to the separated reactants. **i9** isomerizes via a hydrogen shift and ring closure forming the bicyclic intermediate **i11**. Two pathways are open from **i10**: i) isomerization to **i11** via hydrogen atom migration from the terminal carbon at the CH2 moiety and closure to a five-membered ring, and ii) isomerization to **i12** through atomic hydrogen shift from the phenyl ring to the side chain. Once formed, **i11** can further isomerize to indene (**i13**) via hydrogen migration or fragments to the 1-indenyl radical (**p8**) in an overall exoergic reaction. Alternatively, **i12** can undergo ring closure to indene (C9H8) with the latter ejecting an atomic hydrogen barrierlessly forming 1-indenyl radical (C9H7•). A close inspection of

the PES reveals five reaction sequences to 1-indenyl (C9H7•) with barriers located below the energy of the separated reactants. These pathways are in principle accessible even at ultralow temperatures of 10 K in the cold molecular cloud: **i9** → **i11** → **i13** → **p8 + H**, **i10** → **i11** → **i13** → **p8 + H**, **i9** → **i11** → **p8 + H**, **i10** → **i11** → **p8 + H**, and **i10** → **i12** → **i13** → **p8 + H**. It should be stressed that these calculations support the experimental identification of the 1-indenyl radical (C9H7•) and of three adducts 3-phenyl-1-propyne(**i9**), phenylallene (**i10**) and indene (**i13**) with three-body collisions with the buffer gas (helium) required to stabilize these initial collision complexes. Recently, Hansen et al. (*50*) and Selby et al. (*41*) studied the propargyl − phenyl reaction. Hansen et al. conducted the experiment in a continuous flow over the temeprature range of 800 to 1,600 K and pressures of 25 Torr (*50*). The authors detected ions attributable to C9H7+ and C9H8+. However, the electron impact ionization could neither reveal the source of C9H7+, i.e. nascent reaction product or dissociative electron impact ionization of C9H8, nor elucidate the nature of the structural isomers of C9H8.Selby et al. studied this reaction over 300 – 1000 K and 4 – 10 Torr utlizing time-resolved multiplexed photoionization mass spectrometry. The isomer-resolved branching ratios for the C9H8 products are reported from 300 to 1000 K. Based on their photoionization spectra, at 300 K and 4 torr, only the direct C9H8 adducts 3-phenyl-1-propargyl and phenylallene are observed with the branching ratios of 77 ± 5% and 23 ± 3%, respectively. As the temperature and pressure are increased to 1000 K and 10 torr, two additional C9H8 isomers, 1-phenyl-1-propyne and indene, along with the C9H7 + H channel are observed. The corresponding branching fractions of C9H8 isomers are 61 ± 6%, 18 ± 3%, 6 ± 1%, and 15 ± 5% for 3-phenyl-1-propargyl, phenylallene, 1-phenyl-1-propyne, and indene, respectively. It should be noted that the C9H7 isomer distributions are not determined experimentally although it supplies 16 ± 5% of total C9H8 signal at 1000 K. Here, our experiment is conducted at much higher temperature and pressure of 1373 ± 10 K and 200 ± 10 torr exploiting a chemical micro reactor and tunable synchrotron vacuum ultraviolet (VUV) light coupled with a Re-TOF-MS. Compared with the results from Selby et al. under lower temperature conditions, new insights into the high-temperature chemistry of C3H3 + C6H5 reaction are derived. Firstly, only three C9H8 isomers are observed at 116, namely 3-phenyl-1-propyne (34 ± 2%), phenylallene (24 ± 3%), and indene (36 ± 2%). Secondly, 1-indenyl (C9H7) is determined to be the dominant product at 115 with 1PPR and 3PPR possibly being the minor products.

**Astrochemical Modeling**

     The identification of the 1-indenyl radical (C9H7•) via the *barrierless* elementary reactions (1) and (2) lends to an opportunity of incorporating these findings into astrochemical models of cold molecular clouds. It is vital to underline that both reactions have no entrance barriers, all barriers of the isomerization processes are below the energy of the separate reactants, and the overall reactions are exoergic. These findings denote key prere­qui­sites for reactions to proceed in low-temperature environments such as in molecular clouds (10 K). To investigate the implications of our findings to the chemistry of 1-indenyl in cold molecular clouds, we untangled the viability of the formation of 1-indenyl through the neutral-neutral reactions (1) and (2) utilizing the University of Manchester Institute for Science and Technology (UMIST) Database (RATE2012) (*51*) operated with the two-step single-point time-dependent astrochemical model described in References (*52*) and (*53*). The physical parameters of the models were updated according to Markwick et al. (*54*) and McElroy et al. (*51*); reaction rate coefficients and (preexponential) factor α (table S3) are parameterized according to McElroy et al. (*51*). The physical parameters of the cold molecular cloud are triggered by a temperature of 10 K, a cosmic ray ionization rate of 1.3×10-17 s-1, a visual extinction of 10 Mag, and a number density of molecular hydrogen of 104 cm-3. The chemical network was also enhanced with recently explored barrierless and rapid reactions related to the formation of propargyl (C3H3) (*22*), benzene (C6H6) (*52*), and indene (C9H8) (*27*). The key bimolecular reactions and photodissociation processes newly incorporated into the astrochemical model leading to the formation of 1-indenyl are shown in Fig. 5 and the details are depicted in table S3. In the simulations, the fiducial gas-phase model was firstly operated until the chemistry evolved to the steady-state; then, the obtained molecular abundances at this point are employed as the initial conditions for the second-step model where the ice mantle species are injected into the gas phase until the model reaches the steady-state again. Finally, the predictive capabilities of the model are verified by comparing the relevant species observed with modeled fractional abundances.

     These modeling studies reveal captivating findings (Fig. 6; fig. S7). *First*, the exceptional performance of the astro­chemical model for TMC-1 can be nicely benchmarked for the propargyl (C3H3), cyano­benzene (C6H5CN), and indene (C9H8) recently detected at fractional abundances of 0.8×10-8 – 1.2×10-8 (*17, 18*), 2.4×10-11 – 1.2×10-10 (*55, 56*), and 7.6×10-10 – 1.0×10-9 (*57, 58*) toward TMC-1. Prepared principally via the barrierless reac­ti­ons of atomic carbon with ethylene (*22*) and of benzene with cyano radicals (*59*), the predicted peak fracti­onal abundances of propargyl and cyanobenzene at 1.3×105 and 7.9×104 years of 2.9×10-9 – 1.1×10-8 and 4.1×10-11 – 4.7×10-11 with respect to molecular hydrogen replicate the astronomical observations exceptionally well (Fig. 6). A match between the modelled (1.0×10-10 – 9.0×10-10) and observed fractional abundances (7.6×10-10 – 1.0×10-9) has also been achieved for indene (C9H8) with dominating formation routes involving the reactions of methylidyne (CH) with styrene (C8H8) (*27*) and *o*-benzyne (C6H4) with allyl (C3H5) (*60*). *Second*, barrierless molecular mass growth processes via ring annulation were predicted to form 1-indenyl (C9H7•) peaking at fractional abun­dances of 2.4×10-11 – 9.7×10-11 at 2.5×105 years; reaction (1) and reaction (2) contribute nearly equally with 55% and 45%, respectively. These fractional abundances suggest that the 1-indenyl radical (C9H7•) might be detectable by radio telescopes such as the Green Bank Observatory (*61*) and Yebes Radio Telescope (*17*).

**Discussion**

     Our combined experimental, computational, and astrochemical modeling study provided compelling evidence on the very first gas-phase preparation of the aromatic and resonantly stabilized 1-indenyl (C9H7•) radical via elementary reactions of atomic carbon (C(3P)) with styrene (C6H5C2H3) and of the propargyl radical (C3H3•) with the phenyl radical (C6H5•). These pathways provide unique access to 1-in­de­nyl via barrierless-entrance and exoergic reactions involving uncon­ventional isomeri­za­tion steps of the collision complexes via hydrogen shifts, ring closure/ openings, and aromati­zation. These prerequisites represent fundamental criteria for both reactions to operate in cold molecular clouds such as TMC-1 and offer an unusual source of 1-indenyl (C9H7•) as precursors to a low-temperature route of PAHs in deep space, which may assist in deciphering the “life-time-paradox” of PAHs in the ISM. These findings also suggest that upon reaction with atomic carbon and propargyl radicals, *any* vinyl side-chained six-membered aromatic ring or *any* aryl radical can be converted to a cyclopentadienyl moiety under low-temperature conditions (fig. S2) thus providing a facile and barrierless route of annulation of a benzene ring embedded in complex PAHs. These reaction routes are of particular importance as a critical sink of propargyl radicals detected with fractional abundances of (1.0 ± 0.2) × 10-8 in TMC-1, which are unreactive with closed shell hydrocarbons under cold molecular cloud con­ditions revealing barriers to addition between 31 and 60 kJmol-1 for, e.g. alkynes, alkenes, and aromatics (*62-64*). In low-temperature atmospheres of planets and their moons such as Titan and Triton, the outcome of these reactions is influenced by the atmospheric pressures. Whereas higher altitudes with pressures less than 10-3 Torr support bimolecular reactions leading to 1-indenyl (C9H7•), third body stabilization of the reaction intermediates in lower atmospheric layers leads to their stabilization and generation of distinct C9H8 isomers of 3-phenyl-1-propyne, phenylallene, and indene, which may act as fundamental molecular growth species in Titan’s organic aerosol layers (*65*). Overall, our investigations provide a very first step to systematically elucidate the funda­mental reaction pathways to RSFRs in low temperature environ­­ments as a critical prerequisite to their molecular mass growth processes to PAHs in extreme environments. Although the C2v symmetric 1-indenyl (C9H7•) has not been detected yet in TMC-1, its resonance stabilization might lead to substantial fractional abundances thus calling for new astronomical searches for 1-indenyl’s astronomical identification. Combined with our extended astrochemical model, this identification would provide critical constraints on the largely elusive low-temperature molecular mass growth processes to aromatics in TMC-1 and act as a catalyst initiating advanced RSFR triggered chain-propagating reactions eventually culminating in the rapid formation of carbonaceous nanostructures in deep space.

**Materials and Methods**

**Experimental Methods − Carbon-Styrene System**

     The gas phase reaction of ground-state atomic carbon (C; 3P) with styrene (C6H5C2H3; X1A') was carried out under single collision conditions utilizing a crossed molecular beam apparatus (*34*). The primary atomic carbon reactant was generated *in situ* via laser ablation of graphite exploiting the 266 nm output of an Nd:YAG laser at 8-10 mJ pulse-1, and seeding the ablated atoms in helium. A chopper wheel selected a part of the pulsed supersonic beam defined by the peak velocity vp of 2534 ± 61 m s-1 and a speed ratio S of 2.2 ± 0.3. Under these experimental conditions, the carbon atoms produced are only in the ground electronic state (3P) (*66*). The primary beam crossed a secondary beam of xenon-seeded (99.999%, Matheson) styrene (C8H8, >99%, TCI) defined by vp = 389 ± 6 m s-1 and S = 28.0 ± 0.4 with a seeding fraction of 1 % at a backing pressure of 550 Torr. This resulted in a CM angle of 52.8 ± 0.6° and a collision energy of 35.4 ± 1.4 kJ mol-1. The D3- and D5-styrene (CDN Isotopes, 98% D) were employed in the experiment to extract information on the position of the atomic hydrogen loss (table S1). After electron-impact ionization of the neutral products (80 eV, 2 mA), the ions were monitored using a quadrupole mass spectrometer (QMS) operating in the TOF mode under ultrahigh-vacuum conditions (6×10-12 Torr). After the normalization to CM angle and integration of the TOFs, the LAD distribution at well-defined m/z can be derived. A forward-convolution method based on Jacobian transformation is employed to convert the data collected in the laboratory frame (LAD, TOFs) into the CM frame (*28, 34*).

**Experimental Methods − Propargyl-Phenyl System**

     The experiments were conducted at the Chemical Dynamics Beamline (9.0.2.) of the Advanced Light Source (ALS) utilizing a high-temperature chemical micro reactor consisting of a resistively heated SiC tube of 20 mm heating length and 1 mm inner diameter. This device is located inside the source chamber of a molecular beam setup equipped with a Re-TOF-MS (*21*). The molecular beam apparatus is designed to study elementary chemical reactions ultimately leading to PAH growth *in situ*. In detail, phenyl (C6H5•) and propargyl (C3H3•) radials were prepared *in situ* via pyrolysis of nitrosobenzene (C6H5NO; 97 %; Sigma-Aldrich) (*35*) and propargyl bromide (C3H3Br; Sigma Aldrich, > 98%) (*20*) precursors, respectively. The reactants were seeded in helium carrier gas at total pressures of 200 ± 10 torr at the reactor inlet. The propargyl bromide precursor was kept in a stainless-steel bubbler at a temperature of 199 K obtained in a dry ice-ethanol bath; the nitrosobenzene precursor was stored in a Swagelok particulate filter (Swagelok: SS-6F-15) and cooled to 273 K via an ice bath. Both vessels were arranged in series: the helium carrier gas first passed through the liquid propargyl bromide sample; the resulting helium-seeded propargyl bromide gas mixture was then passed over the solid nitrosobenzene sample before entering the reactor. The temperature of the SiC tube was determined using a Type-C thermocouple to be 1,373 ± 10 K. The products formed in the reactor are entrained in a molecular beam, which passed a 2 mm skimmer located 10 mm downstream to the reactor; the beam then entered the main chamber, which houses the Re-TOF-MS. The neutral products within the supersonic molecular beam were photoionized in the extraction region of the mass spectrometer utilizing quasi-continuous tunable synchrotron vacuum ultraviolet (VUV) light. VUV single photon ionization represents essentially a fragment-free ionization technique and is a soft ionization method compared to the harsher conditions of electron impact ionization (*67*). The ions formed via soft photoionization were extracted and detected by a microchannel plate detector. Under our experimental condition, the residence time in the reactor tube is a few tens of microseconds (*68, 69*). PIE curves, which report ion counts as a function of photon energy with a step interval of 0.05 eV at a well-defined m/z, were produced by integrating the signal recorded at the specific m/z for the species of interest. Control experiments were also proceeded by expanding neat helium carrier gas with each precursor separately into the resistively heated silicon carbide tube, but neither indene nor indenyl was detected. Finally, reference PIE curves of helium-seeded 1-bromoindene (C9H7Br) (*46*), and 3-phenyl-1-propyne (C9H8, Sigma Aldrich, 97%) were recorded in the present work within the same experimental setup, respectively, whereas the PIE curve of phenylallene was provided by Hansen et al. (*40*).

**Computational Methods − Electronic Structure Calculations**

     Electronic structure calculations in the present work were carried out on the triplet C9H8 potential energy surface accessed by the carbon - styrene reaction. In particular, geometries of the reactants, products, intermediates, and transition states involved in this reaction were optimized at the density functional theory B3LYP/6-311G(d,p) level (table S4) (*70, 71*), with vibrational frequencies computed using the same theoretical approach. Single-point energies were further refined within the explicitly-correlated CCSD(T)-F12/cc-pVTZ-F12 method (*72, 73*), which normally provides the energetic parameters of local minima and transition states within ‘chemical accuracy’ of ~5 kJ mol-1 for hydrocarbons in terms of average absolute deviations (*42*). The GAUSSIAN 16(*74*) and MOLPRO 2021 (*75*)program packages were used for the ab initio calculations. Rice-Ramsperger-Kassel-Marcus (RRKM) theory together with the steady-stated approximation (*76, 77*) implemented in our Unimol code (*78*), were applied to compute energy-dependent rate constants of all unimolecular reaction steps on the C9H8 triplet surface after the addition of the atomic carbon to styrene and to assess product branching ratios at zero-pressure limit under single-collision conditions.

**Astrochemical Modeling**

     To explore the chemistry leading to the 1-indenyl radical in the cold molecular cloud TMC-1, we constructed the chemical model by expanding the RATE12 network (*51*) with barrierless neutral – neutral reactions forming the 1-indenyl radical and their precursors. First, a time-dependent gas-phase model was operated until the chemistry evolves to steady-state, i.e., after typically 107 years. Simulations were also conducted in a separate model with the ice mantle species injected into the gas phase through reactive desorption until it reaches the steady state; this strategy was exploited successfully to demonstrate the key role of neutral-neutral reactions in the formation of benzene in TMC-1 (*52*). These results were then benchmarked with astronomical observations for cyanobenzene (C6H5CN), propargyl (C3H3), and indene (C9H7) to verify the predictive capabilities of the chemical network (Supplementary Materials).

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**Supplementary Materials**

Supplementary results

Figs. S1 to S7

Tables S1 to S4

Figure captions

**Fig. 1.** **Results for the reaction of the atomic carbon (C) with styrene (C8H8)**.LAD (A), TOF spectra (B), CM translational energy (C), and angular flux distributions (D). Data are recorded at m/z = 115. The black circles with their error bars indicate the normalized experimental distribution; the open circles delineate the experimental data; the red lines represent the best fits obtained and the shaded areas depictthe error limits of the best fit.

**Fig. 2. Results for the phenyl (C6H5•) with propargyl (C3H3•) reaction**. Photoionization mass spectra recorded at a photon energy of 9.50 eV with masses of 107 (C6H5NO+), 108 (13CC5H5NO+), 118 (C3H379Br+), and 120 (C3H381Br+); the inserts highlight ion signal from m/z = 110 to 127 (A). Photoionization mass spectra recorded at 9.50 eV and 1,373 ± 10 K (B). Photoionization efficiency (PIE) curves recorded at 116 (C) and 115 (D) for products of interest formed at a reactor temperature of 1,373 ± 10 K. The black/blue/green/orange/magenta lines in (C) and (D) represent experimental and reference PIE curves and the red line resembles the overall fit. The error bars consist of two parts: ±10% based on the accuracy of the photodiode and a 1 σ error of the PIE curve averaged over the individual scans.

**Fig. 3.** **Potential energy surfaces (PES) of C−C8H8 reaction**. PES for the reaction of ground-state atomic carbon (C; 3P) with styrene (C8H8; X1A'). All energies are given in kJ mol-1 with respect to the energy of the separated reactants.

**Fig. 4.** **Potential energy surfaces (PES) of C6H5-C3H3 reaction**. Dominant reaction pathways for the phenyl (C6H5•) with propargyl (C3H3•) reaction extracted from Morozov et al. (*48*). The values on top/bottom of the arrows indicate the energies of the transition states. All energies are given in kJ mol-1 with respect to the energy of the separated reactants.

**Fig. 5.** **Reaction network forming 1-indenyl**. Compilation of key bimolecular reactions and photodissociation processes newly incorporated into the astrochemical model leading to the formation of 1-indeny.

**Fig. 6.** **Results of the astrochemical model for TMC-1.** The fractional abundances of the gas-phase cyanobenzene (C6H5CN), indene (C9H8), propargyl (C3H3), and 1-indenyl (C9H7) are plotted as a function of time after the injection event. Astronomically observed fractional abundances, along with the uncertainties of cyanobenzene, indene, and propargyl, are visualized by the green, blue, and pink-colored horizontal bar.