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On the formation of nitrogen-substituted polycyclic aromatic hydrocarbons (NPAHs) in circumstellar and interstellar environments

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The chemical evolution of extraterrestrial environments leads to the formation of polycyclic aromatic hydrocarbons (PAHs) *via* gas phase radical mediated aromatization reactions. We review that these *de facto* barrierless reactions are capable of forming prebiotic molecules such as nitrogen substituted PAHs (NPAHs), which represent the missing link between nitrogen bearing acyclic molecules and prebiotic nucleobases along with vitamins found in meteorites. Crucial routes leading to the incorporation of nitrogen atoms into the aromatic ring have been exposed. Pyridine can be formed from the reaction of abundant vinyl cyanide and its radical or *via* cyano radicals reacting with 1,3-butadiene. The NPAHs 1,4-dihydro(iso)quinoline and (iso)quinoline can be synthesized through reaction of pyridyl radicals with 1,3-butadiene or sequentially with two acetylene molecules, respectively. The inclusion of nitrogen into an aromatic system and their growth can fill the mechanistic gaps missing leading from acyclic nitrogenbearing molecules *via* pyridine to NPAH-type molecules in the interstellar medium.

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1. Introduction

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During the last decade, considerable progress has been made

in untangling the elementary reactions leading to the gas phase

formation of polycyclic aromatic hydrocarbons (PAHs) - organic

Dorian S. N. Parker

molecules carrying fused benzene rings¹⁻¹¹ – along with their hvdrogen-deficient aromatic (AR)¹²⁻¹⁶ and resonance stabilized free radical (RSFR)¹⁷⁻³⁰ precursors under single collision conditions in the laboratory and in the interstellar medium. Today, PAH-like molecules are proposed to be omnipresent in the interstellar medium (ISM), account for up to 30% of the galactic interstellar carbon,^{31,32} and provide critical nucleation sites for the formation of carbonaceous dust particles.^{33,34} PAH-like species have been also attributed as carriers of the unidentified infrared (UIR) emission bands observed at 3.3, 6.2, 7.7, 11.2, and 12.7 µm resulting from ultraviolet pumped infrared fluorescence of PAHs with an excess of 50 carbon atoms.^{35,36} The 6.2 μ m band has been linked to protonated PAHs,^{35,37} but could also originate from of nitrogen-substituted PAHs.³⁸ Further, PAHs likely contribute to the diffuse interstellar bands (DIBs)^{39,40} – discrete absorption features superimposed on the interstellar extinction curve ranging from the blue part of the visible (400 nm) to the nearinfrared $(1.2 \text{ }\mu\text{m})$. The detection of the simplest PAH naphthalene (C10H8) along with more complex PAHs such as anthracene/ phenanthrene $(C_{14}H_{10})$ and pyrene/fluoranthrene $(C_{16}H_{10})$ in at least 20 carbonaceous chondrites strongly implies an interstellar origin.^{41,42} Spatial distribution of PAHs⁴³ and isotope (D, ¹³C) enrichment⁴⁴ validate an interstellar source and propose inner envelopes of carbon-rich asymptotic giant branch (AGB) stars such as of IRC + 10216, where temperatures reach up to a few 1000 K, as the key breeding grounds.

Considering the combustion-relevant temperatures of circumstellar envelopes (CSEs) close to the central star, the most promising routes to synthesize circumstellar PAHs have been 'lent' from the combustion chemistry community. These pathways have been suggested to involve molecular weight growth processes through sequential reactions of aromatic (AR) and resonance stabilized free radicals (RSFR) such as the phenyl (C_6H_5) and the propargyl radicals (C_3H_3), respectively, eventually leading via PAHs to carbonaceous nanoparticles (carbon-rich grains).^{31,32,45-47} Together with acetylene (C₂H₂) and methylacetylene (CH₃CCH), these pathways have been the backbone of the hydrogen abstraction-acetylene addition (HACA),⁴⁸⁻⁵¹ phenyl addition-cyclization (PAC),^{52,53} and ethynyl addition (EA) pathways¹¹ leading to naphthalene $(C_{10}H_8)^{47}$ and also indene (C_9H_8) .^{5,54} However, in recent years it has become clear that interstellar PAHs are faster destroyed by photolysis, interstellar shocks, and cosmic ray bombardment than they can be formed, suggesting life times of PAHs in the order of a few 10^8 years.^{55–58} These timescales are much shorter than the timescale for the injection of PAHs into the interstellar medium by carbon-rich AGB stars and potentially carbon-rich planetary nebulae as their offspring: 2×10^9 years.^{46,59} Most importantly, a recent computational study by Mebel et al. revealed that the HACA mechanism - the central backbone in contemporary PAH synthesis in circumstellar envelopes of carbon rich AGB stars essentially terminates with the formation of naphthalene ($C_{10}H_8$) and acenaphthalene (C12H8).60 Parker et al. confirmed this prediction experimentally by demonstrating that the reaction of acetylene (C_2H_2) with 1- and 2-naphthyl radicals $(C_{10}H_7)$ under combustion like conditions leads only to 1- and 2-ethynylnaphthalene

along with acenaphthalene ($C_{12}H_8$), but neither forms anthracene ($C_{14}H_{10}$) nor phenanthrene ($C_{14}H_{10}$).⁶¹ Therefore, the ubiquitous presence of PAHs in the interstellar medium and in carbonaceous chondrites implies a crucial, hitherto unexplained route to a fast mass growth of PAHs in cold environments of the interstellar medium at temperatures as low as 10 K.^{4,62}

In recent years, results from crossed molecular beam studies and electronic structure calculations imply that barrier-less, rapid neutral-neutral reactions involving overall excergic reactions of dicarbon $(C_2)^{12}$ and ethynyl radicals $(C_2H)^{63}$ with 1,3-butadiene (C_4H_6) represent a prominent route to synthesize aromatic structures – the phenyl radical (C_6H_5) and the benzene molecule (C_6H_6) – from acyclic precursor molecules in the gas phase in cold molecular clouds like TMC-1 holding temperatures as low as 10 K (Fig. 1). Crossed beam studies also provided compelling evidence of a facile formation of (methylsubstituted) PAHs, which can be formally derived from naphthalene $(C_{10}H_8)^4$ and 1,4-dihydronaphthalene $(C_{10}H_{10})$,¹ upon reaction of phenyltype radicals with vinylacetylene $(C_4H_4; H_2C=CH-CCH)$ and (methylsubstituted^{2,10}) 1,3-butadiene $(C_4H_6; H_2C=CH-CH=CH_2)$.



Fig. 1 Synthetic routes building up monocyclic and bicyclic aromatic molecules. Pathways without entrance barriers are highlighted in blue, whereas reactions involving entrance barriers are color coded in red; the latter are only open in circumstellar envelopes of dying carbon stars holding temperatures of a few 1000 K close to the photosphere.

The underlying reaction dynamics were found to involve a *de facto* barrier-less addition of the phenyl-type radical within an initial van-der-Waals complex through a submerged barrier to a vinyl-type moiety (H_2CCR (R=H, CH₃)) yielding a resonance stabilized free radical intermediate (RSFR).⁶⁴ The latter then isomerize forming ultimately a cyclic intermediate, which then undergoes aromatization and PAH formation *via* atomic hydrogen loss (Fig. 2). In cold molecular clouds, these *de facto* barrier-less elementary reactions can synthesize naphthalene-and 1,4-dihydronaphthalene-based PAHs demonstrating the unique

link between resonance stabilized radical (RSFR) intermediates and the formation of polycyclic aromatic hydrocarbons (PAHs) in molecular clouds such as TMC-1 and OMC-1.

However, whereas well-defined low-temperature (cold molecular clouds; TMC-1) and high-temperature routes (circumstellar envelopes; IRC + 10216) to PAH formation in interstellar and circumstellar environments have begun to emerge, surprisingly little is known about the synthesis of their nitrogen-substituted counterparts (NPAHs), which can be formally derived from PAHs by replacing a methylidyne (CH) moiety by an isoelectronic



Fig. 2 Top: Relevant sections of the potential energy surface of the reaction of the phenyl radical (C_6H_5) with vinylacetylene (C_4H_4) leading to naphthalene ($C_{10}H_8$) under single collision conditions. The pathway forming naphthalene in cold molecular clouds is highlighted in red. Reproduced from ref. 4 with permission from the PNAS, copyright 2011. Bottom: Relevant sections of the potential energy surface of the reaction of the phenyl radical (C_6H_5) with 1,3-butadiene (C_4H_6) forming 1,4-dihydronaphthalene ($C_{10}H_{10}$) under single collision conditions. The pathway forming 1,4-dihydronaphthalene in cold molecular clouds is highlighted in red. Relative energies are given in units of kJ mol⁻¹. Reproduced from ref. 1 with permission from the *J. Am. Chem. Soc.*, copyright 2012.

nitrogen atom (N), together with their hydrogen deficient aromatic building blocks such as pyridine (C5H5N) in the interstellar medium. This lack of information is quite surprising taking into account that NPAHs are - considering their molecular structures - contemplated as precursors to biorelevant molecules such as nucleobases - key building blocks in ribonucleic acid (RNA).65 The astrophysical relevance of nitrogen-substituted aromatic molecules is well documented since the discovery of biorelevant molecules such as vitamin B3 (niacin)⁶⁶ and nucleobases (pyrimidines, purines)^{67,68} in carbonaceous chondrites like Murchison.⁴⁴ The detection of terrestrially rare nucleobases 2,6-diaminopurine and 6,8-diaminopurine in Murchison^{67,69} along with an ¹⁵N/¹⁴N isotope enrichment suggest an extraterrestrial source.⁷⁰ Nevertheless, discrete formation mechanisms of NPAHs such as (iso)quinoline along with their key building block pyridine (C5H5N) are still unknown. Recent astrochemical models have proposed that the synthesis of pyridine is driven by radical mediated reactions of hydrogen cyanide (HCN) with acetylene (C₂H₂).⁷¹ A latest study proposed pyridine formation via methylidyne radical (CH) insertion into pyrrole (C_4H_5N) ,⁷² but pyrrole has never been detected in the interstellar medium. Hence, even the formation of interstellar pyridine has remained elusive to date.

This Review is based on the novel concept of aromatization reactions via neutral-neutral reactions from monocyclic systems to polycyclic aromatic hydrocarbons (PAHs) (Fig. 1) and expands these investigations to the synthesis of nitrogen-substituted polycyclic aromatic hydrocarbons (NPAHs) along with their pyridine (C₅H₅N) building block (Fig. 3). These processes can take place in 'cold' molecular clouds like TMC-1 down to 10 K and also in 'hot' circumstellar envelopes of dying carbon stars such as of IRC + 10216 holding a few 1000 K as simulated in the laboratory via 'crossed molecular beam reactions' (2.1.) and in a 'chemical reactor' (2.2.). Considering that nitrogen (N) represents the fourth most abundant element being isoelectronic with the methylidyne (CH) moiety in aromatic molecules, this review also discusses similarities and striking differences in the formation of two prototype classes of aromatic molecules: benzene and pyridine as the building blocks of PAHs and NPAHs, respectively, along with (1,4-dihydro)naphthalene and (1,4-dihydro)(iso)quinoline as typical representatives of PAHs and NPAHs carrying two six-membered rings.

2. Experimental

2.1. The crossed molecular beam setup

The crossed molecular beam technique provides a unique approach to explore the outcome of a reaction of two neutral molecules, radicals, and/or atoms in the single collision environment without wall effects or third body collisions.^{17,73–76} This is achieved by generating supersonic beams of the reactants in separate side chambers and crossing them in the main reaction chamber (Fig. 4). The pulsed radical beams of pyridyl (C_5H_4N) and cyano (CN) are generated *in situ* either *via* photolysis of helium-seeded precursor molecules (chloropyridine; C_5H_4ClN)



Fig. 3 Synthetic routes building up monocyclic and bicyclic nitrogenbearing aromatic molecules. Pathways without entrance barriers are highlighted in blue, whereas reactions involving entrance barriers are color coded in red; the latter are only open in circumstellar envelopes of dying carbon stars holding temperatures of a few 1000 K close to the photosphere.

at 193 nm⁷⁷ or through laser ablation of a solid rod of carbon at 266 nm and subsequent co-reaction of the ablated species with the nitrogen reactant gas, which acts as a seeding gas as well.^{78,79} A chopper wheel is exploited to select a well-defined velocity of the pulsed radical beam, which in turn affords a precise collision energy between the primary and secondary beams. The secondary reactants - the hydrocarbons - were introduced via the secondary source chamber. The reaction products were monitored by a rotatable triply differentially pumped mass spectroscopic detector within the plane of the primary and secondary beams. The neutral products are universally electron impact ionized at 80 eV before being mass selected at a specific mass-to-charge ratio (m/z) and detected under ultra-high vacuum conditions as low as 3×10^{-12} Torr. The reactive scattering signal at a well-defined mass-to-charge ratio is recorded at multiple angles exploiting the time-of-flight (TOF) technique by recording the flight time versus the ion counts of an ion of the selected mass-to-charge ratio (m/z); the collision between the radical and the hydrocarbon molecule defines the 'time zero' in each experiment. At each angle, the TOFs are integrated providing a laboratory angular distribution, which reports the integrated ion counts at a defined mass-to-charge ratio versus the laboratory angle. These laboratory data (laboratory angular distribution, TOF spectra) are then transformed into the center-of-mass



Fig. 4 Schematic top view of the crossed molecular beams machine. Both pulsed beam source chambers are defined as source I and source II, respectively. The doublet radicals are generated in source I *via* reactive laser ablation (cyano, CN) and photolysis (pyridyl, C_5H_4N). The chopper wheel selects the appropriate primary beam velocity. The hydrocarbon reactants are introduced *via* source II.

reference frame exploiting a forward deconvolution technique.^{80,81} This yields two crucial functions, which allow us to extract the reaction dynamics and underlying reaction mechanisms: the center-of-mass angular distribution ($T(\theta)$) and the product translational energy distribution ($P(E_T)$). The final result is the generation of a product flux contour map, $I(\theta, u) = P(u) \times T(\theta)$, which reports the flux of the reactively scattered products (I) as a function of the center-of-mass scattering angle (θ) and product velocity (u). This map can be seen as the image of the chemical reaction and contains all the information on the scattering process.

2.2. The pyrolytic reactor

The 'high temperature' experiments simulating the outflow of carbon rich stars such as IRC + 10216 were carried out at the Advanced Light Source (ALS) at the Chemical Dynamics Beamline (9.0.2.) utilizing a 'pyrolytic reactor', which consists of a resistively heated silicon carbide nozzle operated at temperatures of typically 1000 K (Fig. 5).82 The radicals - pyridyl (C5H4N) and cyanovinyl (HC=CH-CN) - were generated in situ via pyrolysis of acetylene-seeded iodopyridine (C₅H₄IN) and through hydrogen abstraction from helium-seeded vinyl cyanide (C_2H_3CN) by phenyl radicals (C_6H_5) . After exiting the pyrolytic reactor, the molecular beam passes a skimmer and enters a detection chamber containing a Wiley-McLaren Reflectron Time-of-Flight (ReTOF) mass spectrometer. The products were photoionized in the extraction region of the spectrometer by exploiting quasi continuous tunable vacuum ultraviolet (VUV) light from the Chemical Dynamics Beamline 9.0.2 of the Advanced Light Source and detected with a microchannel plate (MCP) detector. Typically 10^{13} photons s⁻¹ are available at this



Fig. 5 Schematic presentation of the chemical reactor and the molecular beam machine at the Chemical Dynamics Beamline together with the VUV beam path. (1) Microchannel plate detectors, (2) reflector mirror, (3) molecular beam expansion, (4) ion optics.

terminal. The photoionization region is situated 12 cm downstream from the pyrolysis region. As the synchrotron light is quasi-continuous (500 MHz), a start pulse for the time-of-flight (TOF) ion packet is provided by pulsing the repeller plate (the lowest electrode in the Wiley-McLaren ion optics) of the time-of-flight ion optics. The ions hit a microchannel plate (MCP) detector; the signal from these ions were collected with a multichannel-scalar card (NCS; FAST Comtec 7886) triggered by the repeller plate pulse. Time-of flight spectra, which report the flight time of the ion versus the intensity of the ion counts, are recorded for the photoionization energy range between 8.0 eV and 10.0 eV. The typical step size used for these experiments is 50 meV. The energy resolving power $(E/\Delta E)$ is 1650 for 50 μ m slits. The photoionization efficiency (PIE) curves of a well-defined ion of a mass-to-charge ratio (m/z) can be obtained by plotting the integrated ion signal at the mass-to-charge versus the photoionization energy between 8.0 eV and 10.0 eV, normalized by the photon flux and the number of laser shots. The synchrotron VUV photon flux is measured by a calibrated silicon photodiode. Each PIE curve at a well-defined mass-to-charge ratio can then be fit by a linear combination of known PIE curves of all structural isomers. Since the absolute photoionization cross sections of these isomers are known quantitative information such as branching ratios of the structural isomers can be determined.

3. Results & discussion

Guided by Fig. 3, we present potential 'bottom up' synthetic pathways to bicyclic NPAHs (iso)quinoline (C_9H_7N) along with their doubly hydrogenated counterpart 1,4-dihydro(iso)quinoline (C_9H_9N) *via* the key building block: the pyridine molecule (C_5H_5N). The synthesis of pyridine might involve two possible pathways *via* the entrance-barrierless elementary reactions of

vinyl cyanide (C₂H₃CN) with cyanovinyl (HC=CH-CN)⁸² (Fig. 3, right) and of the cyano radical (CN) with 1,3-butadiene (C_4H_6) (Fig. 3, left).^{83,84} Vinyl cyanide (C₂H₃CN) itself can be formed *via* the entrance barrier-less bimolecular reaction of the cyano radical (CN) plus ethylene (C₂H₄),⁸⁵ with the latter resulting as the major product of the barrier-less reaction of methane (CH₄) with the methylidyne radical (CH).⁸⁶ On the other hand, 1.3-butadiene (C_4H_6) resembles a product of the elementary reaction of propylene (C₃H₆) with the methylidyne radical (CH)⁸⁷ with propylene being the heavy reaction product of the reaction of ethane (C_2H_6) with the methylidyne radical (CH).⁸⁸ Therefore, efficient barrier-less reactions of the methylidyne radical (CH) represent a crucial prerequisite to synthesize eventually both the 1,3-butadiene (C_4H_6) and the ethylene (C_2H_4) reactants. All reactions involved in the 1,3-butadiene routes to pyridine are exoergic and have no entrance barrier and hence can proceed in cold molecular clouds as well as in circumstellar envelopes. On the other hand, the pathways involving vinyl cyanide require the formation of the cyanovinyl radical (HC=CH-CN). Hydrogen abstraction pathways from vinyl cyanide (C₂H₃CN) involve a barrier thus blocking this reaction in cold molecular clouds; on the other hand, ultraviolet photolysis of vinyl cyanide (C₂H₃CN) from the internal ultraviolet field present even deep inside molecular clouds might open a pathway to the cyanovinyl radical (HC=CH-CN). Likewise, the elevated temperature in circumstellar envelopes opens up the vinyl cyanide (C₂H₃CN) route. Therefore, the aforementioned pathways provide synthetic routes to pyridine in cold molecular clouds via 1,3-butadiene and through vinyl cyanide (if the latter can be photolyzed to the cyanovinyl radical) and also in circumstellar envelopes involving the 1,3-butadiene and/or vinyl cyanide routes. In a similar pathway as benzene in losing a hydrogen atom upon photolysis,^{63,89,90} the exposure of pyridine to ultraviolet photons from the circumstellar or interstellar radiation field is predicted to form the pyridyl radical (C_5H_4N). Since the hydrogen atoms, however, are not chemically equivalent, the ortho (o), meta (m), and/or para (p) pyridyl radical can be formed.⁷⁷ These aromatic radicals, which are isoelectronic to the phenyl radical, can drive the formation of bicyclic NPAHs as elucidated below.

3.1. Pyridine

3.1.1. Crossed molecular beam studies. The reaction of the cyano (CN) radical with 1,3-butadiene (C_4H_6) is initiated by the barrier-less addition of the cyano radical with its radical center located on the carbon atom of the CH₂ moiety forming a doublet radical intermediate [1] (Fig. 6).^{83,84} With respect to pyridine formation, this collision complex isomerizes *via* a hydrogen shift from the CH₂ group to the carbon atom of the cyano moiety yielding intermediate [2] followed by cyclization to [3]. The latter could emit a hydrogen atom from the CH₂ moiety adjacent to the nitrogen atom thus yielding the pyridine molecule in an overall exoergic reaction ($\Delta_R G = -195$ kJ mol⁻¹). It is important to note that although pyridine can be formed *via* a barrierless and exoergic process through the bimolecular reaction of the cyano radical with 1,3-butadiene, the overall



Fig. 6 Section of the potential energy surface involved in the formation of pyridine (C_5H_5N) *via* the reaction of the cyano (CN) radical with 1,3-butadiene (C_4H_6). Reproduced from ref. 84 with permission from the *J. Am. Chem. Soc.*, copyright 2014.

branching ratio reaches only the one per cent level at most. This is because the intermediates [1] and [2] rather emit atomic hydrogen to form 1-cyano-1,3-butadiene (H₂C=CH-CH=CH(CN)) through transition states which are lower than the competing transition state required to be overcome in the cyclization of [2] to [3]. Therefore, the thermodynamically less stable 1-cyano-1,3butadiene product ($\Delta_{\rm R}G = -96 \text{ kJ mol}^{-1}$) represents the dominant product with pyridine ($\Delta_{\rm R}G = -195$ kJ mol⁻¹) formed only at the one percent level at the most. The indirect scattering dynamics of this reaction mirrors the reaction class of cyano radicals with unsaturated hydrocarbons studied earlier in our laboratory and involves a similar pattern:⁹¹⁻⁹³ barrierless addition of the cyano radical with its carbon atom to the sterically preferential carbon atom of the π -bond of the unsaturated hydrocarbon reactant yielding a doublet radical collision complex, atomic hydrogen loss to form a nitrile, or isomerization of the collision complex via hydrogen migration (and through ring closure as presented here) prior to atomic hydrogen loss and nitrile formation in overall exoergic reactions $(-90 \text{ kJ mol}^{-1} \text{ to } -110 \text{ kJ mol}^{-1})$.^{83,84}

3.1.2. Pyrolytic reactor. In the pyrolytic reactor, the pyridine molecule (C_5H_5N) was effectively formed at elevated temperatures of 1000 K *via* the barrierless and overall exoergic reaction of vinyl cyanide (C_2H_3CN) with the cyanovinyl radical (C_2H_2CN) (Fig. 7).⁸² Here, the reaction of vinyl cyanide with the cyanovinyl radical is initiated by the addition of the radical center to the α -carbon atom of vinyl cyanide. This process is barrier-less forming intermediate [1], which undergoes a hydrogen shift to [2] and in turn can ring-close to [3]. This intermediate either undergoes cyano group migration to the nitrogen atom to reach [4] or to the adjacent carbon atom to reach [5]. These each emit the cyano group to yield the aromatic pyridine molecule. The overall formation of pyridine is exoergic by 44 kJ mol⁻¹. This conclusion also gains support from statistical (RRKM)



Fig. 7 Section of the potential energy surface involved in the formation of pyridine (C_5H_5N) *via* the reaction of vinylcyanide (C_2H_3CN) with the cyanovinyl radical (C_2H_2CN). Reproduced from ref. 82 with permission from the *Phys. Chem. Chem. Phys.*, copyright 2015.

calculations suggesting an exclusive formation of pyridine at equivalent collision energies up to 42 kJ mol⁻¹. Therefore, this route would represent a more efficient pathway to pyridine formation compared to the cyano-1,3-butadiene system if both the vinyl cyanide and the cyanovinyl radical can be supplied in the interstellar medium. Vinyl cyanide has been observed in cold molecular clouds such as in TMC-1 as well as in the circumstellar envelope of IRC + 10216 at fractions of several 10^{-9} .^{94,95} These studies also infer that infrared (IR) pumping from the central star populates excited vibrational states of vinyl cyanide, which may decompose to cyanovinyl radicals plus hydrogen and/or vinyl plus cyano radicals.⁹⁶ Therefore, our investigations reveal that pyridine formation can take place either in low (molecular clouds) or high temperature (circumstellar envelopes) environments of the interstellar medium depending which precursor molecules/ radicals are readily available.

3.2. 1,4-Dihydro(iso)quinoline

The reaction of the *o*- and *m*-pyridyl radical (C_5H_4N ; 78 u) with 1,3-butadiene (C_4H_6 ; 54 u) was explored under single collision conditions in a crossed molecular beam machine at collision energies up to 50 kJ mol⁻¹ and also computationally (*o*, *m*, *p*).⁷⁷ Reactive scattering signal was observed at a mass-to-charge ratio (*m*/*z*) of 131 u ($C_9H_9N^+$) indicating that the reaction proceeds through hydrogen atom (1 u) ejection *via* a pyridyl radical *versus* a hydrogen atom substitution pathway (Fig. 8). The corresponding time-of-flight spectra for the reaction of *m*-pyridyl with 1,3-butadiene recorded at *m*/*z* = 131 u ($C_9H_9N^+$) along with the laboratory angular distribution are visualized in Fig. 8. The laboratory angular distribution is almost forward–backward symmetric around the center-of-mass angle of about 17° suggesting indirect scattering dynamics *via* the formation of a $C_9H_{10}N$



Fig. 8 Top left: Time-of-flight spectra for the reaction of *m*-pyridyl with 1,3-butadiene recorded at $m/z = 131 \text{ u} (C_9H_9N^+)$. Top right: Laboratory angular distribution recorded at $m/z = 131 \text{ u} (C_9H_9N^+)$. Bottom right: Center-of-mass translational energy ($P(E_T)$) and angular ($T(\theta)$) flux distributions exploited to fit the laboratory data exploiting a single channel with the product mass combination of C_9H_9N (131 u) plus H (1 u). Reproduced from ref. 77 with permission from the *Astrophys. J.*, copyright 2012.

complex. The center-of-mass translational energy $(P(E_T))$ and angular $(T(\theta))$ distributions provided additional information. First and foremost, the laboratory data could be fit with only one channel proposing that the reaction of pyridyl (78 u) with 1,3-butadiene (54 u) yields C₉H₉N (131 u) plus atomic hydrogen (1 u). The translational energy distributions depict maximum translational energy releases of 124 \pm 20 kJ mol⁻¹ and 122 \pm 42 kJ mol⁻¹, respectively, for the reactions with *o*- and *m*-pyridyl. A subtraction of the collision energy reveals the reaction exoergicities to be 75 \pm 20 kJ mol⁻¹ and 72 \pm 42 kJ mol⁻¹ in synthesizing C_9H_9N isomers plus atomic hydrogen. Further, the $P(E_T)$ s depict distinct distribution maxima at 25-35 kJ mol⁻¹ and 10-20 kJ mol⁻¹, respectively. This 'peaking away from zero translational energy' indicates a tight exit transition state to product formation. The center-of-mass angular distributions $(T(\theta))$ depict flux over the complete angular range thus revealing indirect scattering dynamics of the reactions via formation of C₉H₁₀N intermediates with life times longer than their rotational periods. Best fits were obtained with the $T(\theta)$ revealing a pronounced distribution maximum at 90°. This 'sideways' scattering reveals geometrical constraints of the fragmenting $C_9H_{10}N$ intermediate(s) with the hydrogen atom being ejected almost perpendicular to the molecular plane of the fragmenting complex(es).

The computational studies of the pyridyl radical reactions with 1,3-butadiene reveal common features,⁷⁷ which can be compared to the isoelectronic phenyl – 1,3-butadiene system.¹ In each case, the reaction of pyridyl with 1,3-butadiene is initiated by the barrierless formation of a van-der-Waals complex [0] (Fig. 9), which are bound by 5 to 8 kJ mol⁻¹ with respect to the separated reactants. These complexes isomerize by addition of the radical center to the H₂C-moiety of the 1,3-butadiene reactant through a submerged barrier located 1 to 4 kJ mol^{-1} below the energy of the reactants; therefore, a barrier to addition does exist in each system, but since it is located below the separated reactants, the reactions are de facto barrier-less. The resulting addition complexes [1] reside in deep potential energy wells of 166 to 187 kJ mol⁻¹, represent nitrogen-substituted resonance stabilized free radicals (NRSFRs), and eventually form bicyclic ring systems [2]. Compared to the phenyl-1,3-butadiene reaction, the incorporation of the nitrogen atom tends to destabilize the initial addition intermediates [1] by up to 27 kJ mol⁻¹. The latter were found to emit atomic hydrogen through rather tight exit transition states ranging 27 to 73 kJ mol⁻¹ above the final products, but below the separated reactants. This atomic hydrogen loss leads to aromatization and formation of 1,4-dihydroquinoline from o- and m-pyridyl and 1,4-dihydroisoquinoline from *p*-pyridyl with the hydrogen atom emitted almost perpendicularly with respect to the plane of the decomposing complexes. Therefore, these overall exoergic and barrier-less reactions provide an efficient route to synthesize 1,4-dihydro(iso)quinolines via bimolecular neutral-neutral reactions of 1,3-butadiene with pyridyl radicals in interstellar and circumstellar environments. Previously, aromatization reactions were proposed to involve significant energy barriers implying NPAHs could only be formed in high temperature environments such as in the inner regions of circumstellar envelopes of dying carbon stars like IRC + 10216 to supply the



Fig. 9 Sections of the potential energy surface involved in the formation of 1,4-dihydro(iso)quinoline (C_9H_9N) *via* the reaction of *o*-(top), *m*-(center), and *p*-(bottom) pyridyl radical (C_5H_4N) with 1,3-butadiene (C_4H_6). Reproduced from ref. 77 with permission from the *Astrophys. J.*, copyright 2015.

necessary kinetic translational energy to overcome the barriers. Although, circumstellar envelopes are highly relevant to organic radical mediated astrochemistry, the discovery of ultra-low temperature reaction channels of aromatization type reactions leading to PAHs and their nitrogen substituted counterparts reveal that cold interstellar environments could present ideal formation grounds of NPAHs as well, thus supplying a hitherto overlooked source to supply NPAHs in the interstellar medium.

3.3. (Iso)quinoline

The experimental studies were conducted in a pyrolytic reactor at a temperature of 788 K (2.2) *via* reaction of the *meta*-pyridyl



Fig. 10 Left: Mass spectrum recorded at a photoionization energy of 10.0 eV by probing the reaction products of the *meta*-pyridyl radical (C_5H_4N) with acetylene (C_2H_2). Right: Photoionization efficiency curves (PIE) and best fits identifying the quinoline and isoquinoline isomers (C_9H_7N). Reproduced from ref. 97 with permission from the *Astrophys. J.*, copyright 2015.

radical (C_5H_4N) with acetylene (C_2H_2) (Fig. 10).⁹⁷ Considering the molecular masses of the reactants of *meta*-pyridyl (C_5H_4N ; 78 u) and acetylene (C_2H_2 ; 26 u), these studies revealed that the C₇H₅N product (103 u) is synthesized through addition of acetylene (C₂H₂; 26 u) to meta-pyridyl (C₅H₄N; 78 u) forming a C₇H₆N intermediate (104 u), which then ejects atomic hydrogen (H; 1 u) to yield the C_7H_5N (103 u) product. The second product C_9H_7N (129 u) ranges 26 u higher in mass than C_7H_5N (103 u). This mass difference equals the molecular mass of one acetylene molecule (C₂H₂; 26 u). Therefore, these findings indicate that the $C_{9}H_{7}N$ product (129 u) is formed *via* reaction of essentially two acetylene molecules (C₂H₂; 26 u) with one meta-pyridyl radical $(C_5H_4N; 78 u)$ accompanied with an atomic hydrogen loss (1 u). Therefore, the interpretation of the raw data alone provides compelling evidence that in the reaction of meta-pyridyl radicals with acetylene, two products of the molecular formula C₇H₅N and C₉H₇N are formed. The photoionization efficiency (PIE) curves, which report the intensities of the ions at m/z 103 $(C_7H_5N^+)$ and m/z 129 $(C_9H_7N^+)$ as a function of photon energy, assist in the identification of the product isomer(s) via a comparison of the experimental PIEs with a (linear combination of) known reference curves of PIEs of the individual isomers. This approach reveals that the PIE curves at m/z 103 $(C_7H_5N^{\dagger})$ originates from the *meta*-ethynyl pyridine (C_7H_5N) isomer. The interpretation of the PIE curve at m/z 129 is more complex. The experimental data can be reproduced via reference PIEs of quinoline and isoquinoline; the PIE calibration curves of both isomers are indistinguishable.

With the identification of *meta*-ethynyl pyridine (C_7H_5N) and (iso)quinoline (C_9H_7N) together with the theoretical prediction of feasible reaction pathways to form quinoline and isoquinoline at elevated temperatures representative of inner regions of circumstellar envelopes of evolved carbon stars such as IRC + 10216, we merge our experimental and computational results in an attempt to propose the predominant reaction mechanism(s). First, the reaction of the *meta*-pyridyl radical (C_5H_4N) with acetylene (C_2H_2) leads to the formation of *meta*ethynyl pyridine (C_7H_5N) plus atomic hydrogen, in an overall exoergic reaction (-40 kJ mol⁻¹). The reaction follows *via* the

formation of a C₇H₆N complex and is initiated by the addition of the *meta*-pyridyl radical to the acetylenic carbon atom via a barrier of 14 kJ mol⁻¹. Second, we focus on the formation of (iso)quinoline (C_0H_7N) (Fig. 11). The experimental and computational investigations propose the domination of the Bittner-Howard reaction mechanism, in which the initial C7H6N collision complex [1] of the *meta*-pyridyl radical (C_5H_4N) – acetylene (C_2H_2) reaction isomerizes to [2-4]; the doublet radical intermediates [3] and [4] can react with a second acetylene molecule to form two doublet C₉H₈N intermediates [5] and [6]. Both latter were found to undergo ring closure to [7] and [8] followed by hydrogen atom loss and aromatization synthesizing isoquinoline and quinoline, respectively. Both reactions are in overall strongly exoergic by -432 and -437 kJ mol⁻¹, respectively. Note that from the mechanistical viewpoint, this reaction mechanism equals the formation of naphthalene $(C_{10}H_8)$ via the reaction of the phenyl radical (C_6H_5) with two acetylene molecules (C_2H_2) as probed experimentally in a pyrolytic reactor.⁴⁷ Considering the entrance barrier to the initial addition of acetylene to the meta-pyridyl radical, this pathway is blocked in cold molecular clouds, but can be opened up at elevated temperatures as representative of inner regions of circumstellar envelopes of evolved carbon stars such as IRC + 10216.

4. Summary & outlook

The work presented in this review highlights key stages in the gas phase radical mediated mass growth process leading from acyclic molecules *via* the key building block pyridine to bicyclic NPAHs. Each step in the mass growth process is observed experimentally and supported by electronic structure calculations. First, pyrolysis reactor experiments show that the simplest building block of NPAHs – pyridine – readily forms *via* the reaction between the cyanovinyl radical and vinyl cyanide. This reaction is significant in that it shows a route to incorporate nitrogen atoms from acyclic precursor molecules. Also, crossed molecular beam reactions reveal a barrier-less route to pyridine formation from the reaction of cyano radicals with 1,3-butadiene.



Fig. 11 Sections of the potential energy surface involved in the formation (iso)quinoline (C_9H_7N) *via* the reaction of two acetylene molecules following the Bittner–Howard mechanism. Reproduced from ref. 97 with permission from the *Astrophys. J.*, copyright 2015.

Therefore, our investigations revealed two entrance-barrier-less reaction pathways to synthesize pyridine either in cold interstellar or hotter circumstellar environments. Second, single collision investigations and electronic structure calculations show that the o-, m-, and p-pyridyl radicals react with 1,3-butadiene to form the NPAHs 1,4-dihydro(iso)quinoline. These reactions occur through a single reactive collision, have no entrance barrier, and are overall exoergic. Third, pyrolysis reactor experiments combined with electronic structure calculations reveal (iso)quinoline formation from the reaction of *m*-pyridyl radicals sequentially with two acetylene molecules. This follows the Bittner-Howard mechanism, occurring in high temperature environments such as CSEs. Consequently, these findings provide new insights into the formation mechanisms of aromatic molecules incorporating nitrogen atoms through gas phase radical mediated reactions both in high (CSEs) and low (ISM) temperature environments. NPAHs could be the key precursors to nucleobases, which are themselves the essential building blocks of fundamental to life molecules RNA and DNA. NPAHs and nucleobases have been found in significant proportions within meteorites and as such been proposed as a key link in the origin of life on Earth through their exogenous delivery.

It is important to stress that gas phase neutral-neutral reactions have long been known to be important in the molecular evolution of extraterrestrial environments.^{17,62,74,75,98-100} However, early studies that simplistically assumed significant entrance barriers in organic radical-mediated reactions centered on aromatization and the over emphasis on organic ionmolecule chemistry coupled with the lack of experimentally verified non-bulk mechanistical studies, lead to the predisposition to disregard gas phase radical reactions as key molecular growth routes to complex molecules such as PAHs and NPAHs. Recently, the use of single collision investigations coupled with

advanced electronic structure calculations discovered key barrierless reactions that lead to PAHs such as naphthalene through the reaction of phenyl radicals (C_6H_5) with acyclic unsaturated hydrocarbons that possess a vinylacetylene (C_4H_4) or 1,3-butadiene (C_4H_6) type backbone. The key finding here is that for a molecule with a double to triple (or double) bond conjugation forms a van der Waals complex on approach of an attacking aromatic radical (phenyl). This complex lowers the initial reaction barrier to below that of the reactants to form a de facto barrierless reaction route to addition leading to a resonance stabilized free radical intermediate. The inclusion of nitrogen (N) into the aromatic network makes no difference to the chemistry due to its isoelectronicity to methylidyne (CH) groups. This implies that the reaction routes leading to mass growth and PAH formation are open to nitrogen bearing systems as well. The work presented in this Review confirms this trend, and the NPAH-forming reactions listed above have analogous carbon-only-reactions. Differences exist in the overall energy of reaction being smaller and the number of product isomers being larger due to the incorporation of nitrogen.

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