

Low-temperature formation of polycyclic aromatic hydrocarbons in Titan's atmosphere

Long Zhao¹, Ralf I. Kaiser^{1*}, Bo Xu², Utuq Ablidik², Musahid Ahmed^{2*}, Mikhail M. Evseev³, Eugene K. Bashkirov³, Valeriy N. Azyazov³ and Alexander M. Mebel^{3,4*}

The detection of benzene in Titan's atmosphere led to the emergence of polycyclic aromatic hydrocarbons (PAHs) as potential nucleation agents triggering the growth of Titan's orange-brownish haze layers. However, the fundamental mechanisms leading to the formation of PAHs in Titan's low-temperature atmosphere have remained elusive. We provide persuasive evidence through laboratory experiments and computations that prototype PAHs like anthracene and phenanthrene (C₁₄H₁₀) are synthesized via barrierless reactions involving naphthyl radicals (C₁₀H₇•) with vinylacetylene (CH₂=CH-C≡CH) in low-temperature environments. These elementary reactions are rapid, have no entrance barriers, and synthesize anthracene and phenanthrene via van der Waals complexes and submerged barriers. This facile route to anthracene and phenanthrene—potential building blocks to complex PAHs and aerosols in Titan—signifies a critical shift in the perception that PAHs can only be formed under high-temperature conditions, providing a detailed understanding of the chemistry of Titan's atmosphere by untangling elementary reactions on the most fundamental level.

The Cassini–Huygens mission to Saturn's moon Titan—the only Solar System body besides Earth sustaining a dense, nitrogen-rich atmosphere and solid surface—has transformed our knowledge of the origin and evolution of the Solar System^{1,2}. Titan's most prominent optically visible features are the aerosol-based haze layers, which define its orange-brownish colour. These layers, composed of aerosol particles, are essential to Titan's climate, radiation balance and atmospheric chemistry. Polycyclic aromatic hydrocarbons (PAHs) have been the centre of attention as prospective candidates that initiate the formation and growth of complex organics in Titan's orange-brownish haze layers³. The existence of PAHs in Titan's atmosphere has been inferred from Cassini's Visual and Infrared Mapping Spectrometer (VIMS) attributing the 3.28 μm (3,049 cm⁻¹) absorption to stratospheric PAHs⁴ following an earlier PAH assignment in the upper atmosphere up to 1,300 km⁵. Likewise, Cassini's Plasma Spectrometer detected heavy positively (<350 Da) and negatively (<8,000 Da) charged particles, which have been proposed to carry PAHs⁶, possibly formed via reactions involving benzene (C₆H₆) and phenyl radical (C₆H₅•) in atmospheric regions between 350 and 1,200 km⁷. The most fundamental building block of all PAHs—the benzene molecule—was observed in Titan's atmosphere at levels of up to 10 ppm^{8–13}. These levels might signify benzene, and possibly heavier but hitherto undetected aromatics such as naphthalene (C₁₀H₈) and anthracene/phenanthrene (C₁₄H₁₀), as key building blocks participating in the growth processes to complex PAHs. However, there is a lack of understanding of the molecular mechanisms that initiate and drive the formation of PAHs in Titan's low-temperature atmosphere (70–180 K)¹⁴.

Popular routes to PAH formation on Titan have been derived from high-temperature combustion models and suggest sequential reactions of aromatic (phenyl; C₆H₅•)^{14–17} and resonantly stabilized radicals (propargyl; C₃H₃•)¹⁸. Together with acetylene (C₂H₂), these reactions constitute the backbone for a recurring sequence of hydrogen abstraction–acetylene addition (HACA) mechanism operating

at elevated temperatures of up to 1,000 K leading to facile synthesis of naphthalene (C₁₀H₈)^{19–22}. However, unsurmountable entrance barriers to addition up to 20 kJ mol⁻¹ cannot be passed under Titan's low-temperature conditions (70–200 K)²³, leading to a challenge to the traditional HACA concept^{24,25}. Parker et al.¹⁷ revealed that naphthalene (C₁₀H₈) can be synthesized via barrierless reactions at temperatures as low as 10 K, involving a bimolecular reaction between the phenyl radical (C₆H₅•) and vinylacetylene (C₄H₂), through the hydrogen abstraction–vinylacetylene addition (HAVA) pathway^{17,26–29}. Since the solar ultraviolet radiation penetrates deep into Titan's atmosphere³⁰, benzene (C₆H₆) photodissociates to the phenyl radical (C₆H₅•) plus atomic hydrogen (H•)³¹. Along with phenyl, the naphthyl radical (C₁₀H₇•) generated via photodissociation of naphthalene (C₁₀H₈) may initiate a barrierless, vinylacetylene-mediated low-temperature chemistry involving these aryl-type radicals and leading to naphthalene (C₁₀H₈) and anthracene/phenanthrene (C₁₄H₁₀) (Fig. 1). However, the validity of these mass growth processes beyond naphthalene has remained conjectural, since not a single laboratory experiment has been performed to corroborate to what extent complex PAHs such as anthracene (C₁₄H₁₀) and phenanthrene (C₁₄H₁₀) can be synthesized in these barrierless processes. Therefore, the proposed omnipresence of PAHs in Titan's haze layers⁵, but the lack of validated laboratory experiments demonstrating the synthesis of PAHs under Titan's low-temperature conditions and how they chemically link to Titan's haze layers represent a fundamental enigma to the planetary science and reaction dynamics communities. Sophisticated laboratory experiments simulating the formation of aerosols under the conditions of Titan's atmosphere using vacuum ultraviolet (VUV) light irradiation have consistently detected vinylacetylene^{32,33}. Also, crossed molecular beam experiments have demonstrated that vinylacetylene is formed in the photolysis of acetylene^{34,35} and in the reaction of the ethynyl radical (C₂H) with ethylene (C₂H₄), with these species being among the most abundant hydrocarbons in the atmosphere of Titan³⁶. Finally,

¹Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI, USA. ²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA. ³Samara University, Samara, Russia. ⁴Department of Chemistry and Biochemistry, Florida International University, Miami, FL, USA. *e-mail: ralfk@hawaii.edu; mahmed@lbl.gov; mebela@fiu.edu

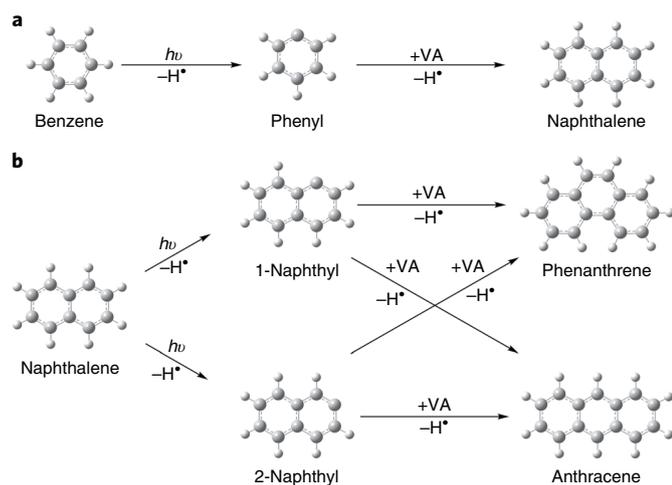


Fig. 1 | Schematic pathways involved in the synthesis of anthracene and phenanthrene. **a**, Naphthalene formation via the reaction of phenyl radical ($C_6H_5^*$) with vinylacetylene (VA; C_4H_4). **b**, Anthracene and phenanthrene formation via the reactions of 1- and 2-naphthyl radicals ($C_{10}H_7^*$) with VA. $h\nu$ represents Planck's constant and frequency.

photochemical models of Titan's atmosphere reveal that vinylacetylene prevails at mixing ratios exceeding 10^{-6} – 10^{-5} (refs 37–39).

Here, we report the results of the bimolecular gas phase reactions of the 1- and 2-naphthyl radical ($C_{10}H_7^*$; 127 amu; X^2A_1) with vinylacetylene ($CH_2=CH-C\equiv CH$; 52 amu; X^1A') (Fig. 1). By merging the experiments with electronic structure and statistical calculations, we present evidence of a barrierless formation of two prototype tricyclic PAHs—anthracene ($C_{14}H_{10}$; 178 amu; X^1A_1) and phenanthrene ($C_{14}H_{10}$; 178 amu; X^1A_1)—involving van der Waals complexes and submerged barriers to reaction in the entrance channels. These barrierless pathways defy conventional wisdom that PAH formation, such as to anthracene and phenanthrene, solely transpires in high-temperature environments such as in combustion flames. This facile route via bimolecular mass growth processes in low-temperature environments (such as Titan's atmosphere) involving vinylacetylene defines an essential shift in currently 'well-established' perceptions leading to PAHs, which have so far relied exclusively on a high-temperature, acetylene-based chemistry (HACA)^{19–22,24,40}. Here, the combination of laboratory experiments with electronic structure calculations enables unravelling of the chemistry of elementary reactions leading to PAHs at the microscopic level, via a hitherto overlooked vinylacetylene-mediated mass growth process to PAHs at ultralow temperatures, thus providing detailed chemical understanding of a macroscopic environment—Saturn's moon Titan.

Results

Experimental studies. A chemical reactor was used to explore the synthesis of anthracene ($C_{14}H_{10}$) and phenanthrene ($C_{14}H_{10}$) via the elementary reactions of 1- and 2-naphthyl radicals ($C_{10}H_7^*$) with vinylacetylene (Fig. 1). The products were entrained in a molecular beam, ionized via fragment-free, soft photoionization using synchrotron VUV light, and detected isomer-specifically with a reflectron time-of-flight mass spectrometer (Re-TOF-MS) (Methods). Representative mass spectra recorded at a photoionization energy of 9.50 eV for the reaction of 1- and 2-naphthyl radicals with vinylacetylene are displayed in Fig. 2a,b. Reference spectra were also collected by replacing vinylacetylene with non-reactive helium carrier gas (Fig. 2c,d). These data provide convincing evidence of the synthesis of molecules with the molecular formula $C_{14}H_{10}$ (178 amu) in the 1- and 2-naphthyl-vinylacetylene

systems, which are absent in the control experiments. Accounting for the molecular weights of the reactants ($C_{10}H_7^*$, 127 amu; C_4H_4 , 52 amu) and products ($C_{14}H_{10}$, 178 amu; hydrogen, 1 amu), the molecules with the formula $C_{14}H_{10}$ must be the reaction products of the bimolecular reaction of the 1- and 2-naphthyl radicals with vinylacetylene (Fig. 1). Signals associated with ion counts at a mass-to-charge (m/z) ratio of 152 can be linked to the reaction of the 1- and 2-naphthyl radicals (127 amu) with acetylene (C_2H_2 ; 26 amu) and the inherent formation of acenaphthylene ($C_{12}H_8$) and ethylnaphthalene isomers ($C_{12}H_8$) (Supplementary Figs. 1–3). Finally, ion counts at $m/z=209$ ($C_9^{13}CH_7^{81}Br^+$), 208 ($C_{10}H_7^{81}Br^+$), 207 ($C_9^{13}CH_7^{79}Br^+$), 206 ($C_{10}H_7^{79}Br^+$), 129 ($C_9^{13}CH_8^+$), 128 ($C_{10}H_8^+$), 127 ($C_{10}H_7^+$ and $C_9^{13}CH_6^+$) and 126 ($C_{10}H_6^+$) are also observable in the 1- and 2-naphthyl-helium systems. Hence, these masses do not originate from reactions between 1- and 2-naphthyl radicals and vinylacetylene. Signals between $m/z=209$ and 206 can be associated with the non-pyrolised 1- and 2-bromonaphthalene precursor. Signals at $m/z=128$ and 129 are attributed to naphthalene and ^{13}C -naphthalene formed via atomic hydrogen addition to the 1- and 2-naphthyl radicals. The ion counts at $m/z=127$ are linked to 1- and 2-naphthyl radicals ($C_{10}H_7^+$), while ions at $m/z=126$ are associated with naphthylene isomers ($C_{10}H_6^+$) (Supplementary Figs. 2 and 3). To summarize, analysis of the mass spectra reveals that the reaction of the 1- and 2-naphthyl radicals ($C_{10}H_7^*$) with vinylacetylene (C_4H_4) synthesizes hydrocarbon molecule(s) with the molecular formula $C_{14}H_{10}$.

With the detection of hydrocarbon molecule(s) of the molecular formula $C_{14}H_{10}$ via the reaction of the 1- and 2-naphthyl radicals with vinylacetylene, it is our objective to assign the structural isomer(s) formed in these elementary reactions (Fig. 1). This necessitates a detailed analysis of the corresponding photoionization efficiency (PIE) curves, which report the intensity of the ions at $m/z=178$ ($C_{14}H_{10}^+$) as a function of the photon energy from 7.20 to 9.50 eV (Fig. 3). These data are fit with newly recorded reference PIE curves for distinct $C_{14}H_{10}$ isomers (anthracene and phenanthrene) (Supplementary Fig. 4). The experimentally derived PIE curves at $m/z=178$ (black) can be reproduced effectively by a linear combination of two reference PIE curves of anthracene ($C_{14}H_{10}$, blue) and phenanthrene ($C_{14}H_{10}$, green) with the overall fit exhibited in red (Fig. 3a,c). The experimental PIE curves for $m/z=178$ illustrate both onsets of the ion signal at 7.40 ± 0.05 eV. This onset correlates nicely with the adiabatic ionization energy of anthracene of 7.44 eV⁴¹. The adiabatic ionization energy of phenanthrene was determined to be 7.90 eV⁴². Moreover, both PIE curves of $m/z=179$ could be reproduced with a linear combination of anthracene and phenanthrene (Fig. 3b,d). Consequently, signal at $m/z=179$ can be associated with ^{13}C -substituted anthracene and phenanthrene ($C_{13}^{13}CH_{10}$). The PIE curves of distinct $C_{14}H_{10}$ isomers are linked to individual molecules, underlining that the co-existence of other isomers in the molecular beam would change the shape of the PIE considerably and hence can be excluded. Therefore, we conclude that within our error limits, anthracene and phenanthrene denote the only contributions to signal at $m/z=178$ and 179. Accounting for the ionization cross-sections of phenanthrene and anthracene, branching ratios of 89:11 ($\pm 10\%$) and 80:20 ($\pm 10\%$) are derived for the 1-naphthyl and 2-naphthyl systems, respectively (that is, a dominant formation of the thermodynamically more stable phenanthrene isomer).

Electronic structure calculations and reaction mechanism. The present study reveals that two prototype PAHs composed of three benzene rings—phenanthrene and anthracene—can be synthesized via the elementary reactions of the 1- and 2-naphthyl radicals with vinylacetylene in the gas phase. We merged these findings with computational results to untangle the underlying reaction mechanism(s) (Fig. 4, labels [1]–[4], and Supplementary Fig. 5;

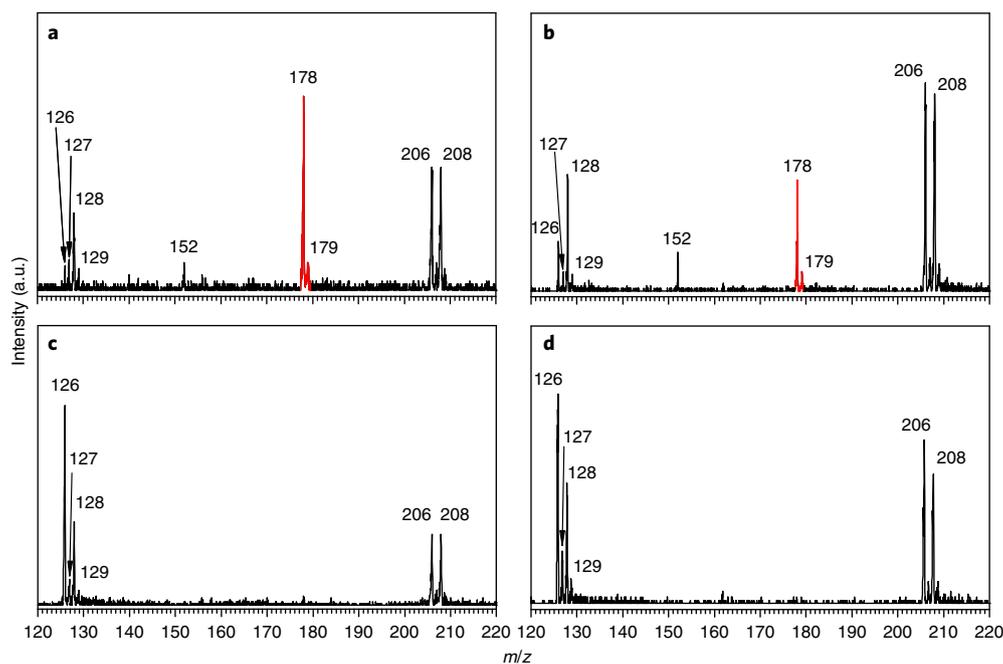


Fig. 2 | Comparison of the mass spectra recorded at a photoionization energy of 9.50 eV. a–d, 1-naphthyl-vinylacetylene (**a**), 2-naphthyl-vinylacetylene (**b**), 1-naphthyl-helium (**c**) and 2-naphthyl-helium (**d**) systems. The peaks of the $C_{14}H_{10}$ isomer(s) ($m/z = 178$) along with the ^{13}C substituted counterparts ($m/z = 179$) are highlighted in red.

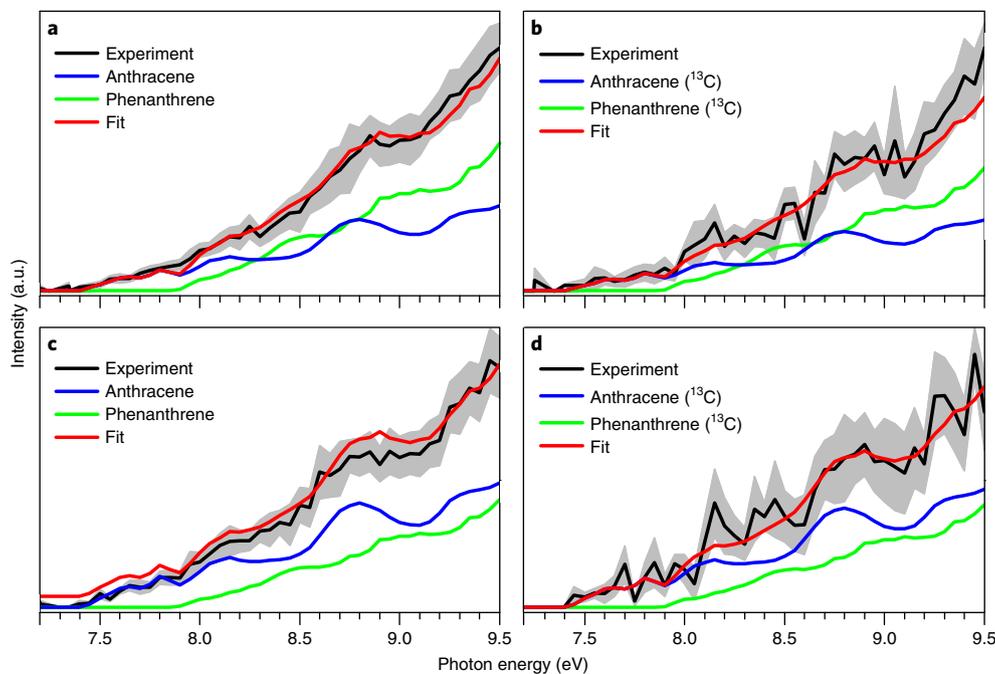


Fig. 3 | PIE curves for ion counts recorded at $m/z = 178$ and 179 . a–d, Curves for the 1-naphthyl-vinylacetylene (**a** and **b**) and 2-naphthyl-vinylacetylene systems (**c** and **d**) at $m/z = 178$ (**a** and **c**) and $m/z = 179$ (**b** and **d**). Black lines show experimentally derived PIE curves along with 1σ error limits (grey areas). Blue lines show anthracene reference PIE curves. Green lines show phenanthrene reference PIE curves. Red lines show the overall fit.

see Methods). For both systems—1-naphthyl-vinylacetylene and 2-naphthyl-vinylacetylene—our electronic structure calculations revealed two entrance channels to addition, and among them one de facto barrierless pathway. All reactions are initiated by addition of the radical centre of the naphthyl radical to the terminal C_1 or C_4 carbon atom of the vinylacetylene reactant carrying the acetylene

nic ($HCC-$) and vinyl moieties (H_2CCH-), respectively, via van der Waals complexes [1]–[4] weakly bound by 9–12 kJ mol^{-1} . For each complex, a closer approach of the radical centre leads to the formation of a covalent carbon–carbon bond and, hence, intermediates [5]–[8] via barriers of 7–13 kJ mol^{-1} . The addition of 1- and 2-naphthyl radicals to the C_4 carbon atom leads to resonantly stabilized

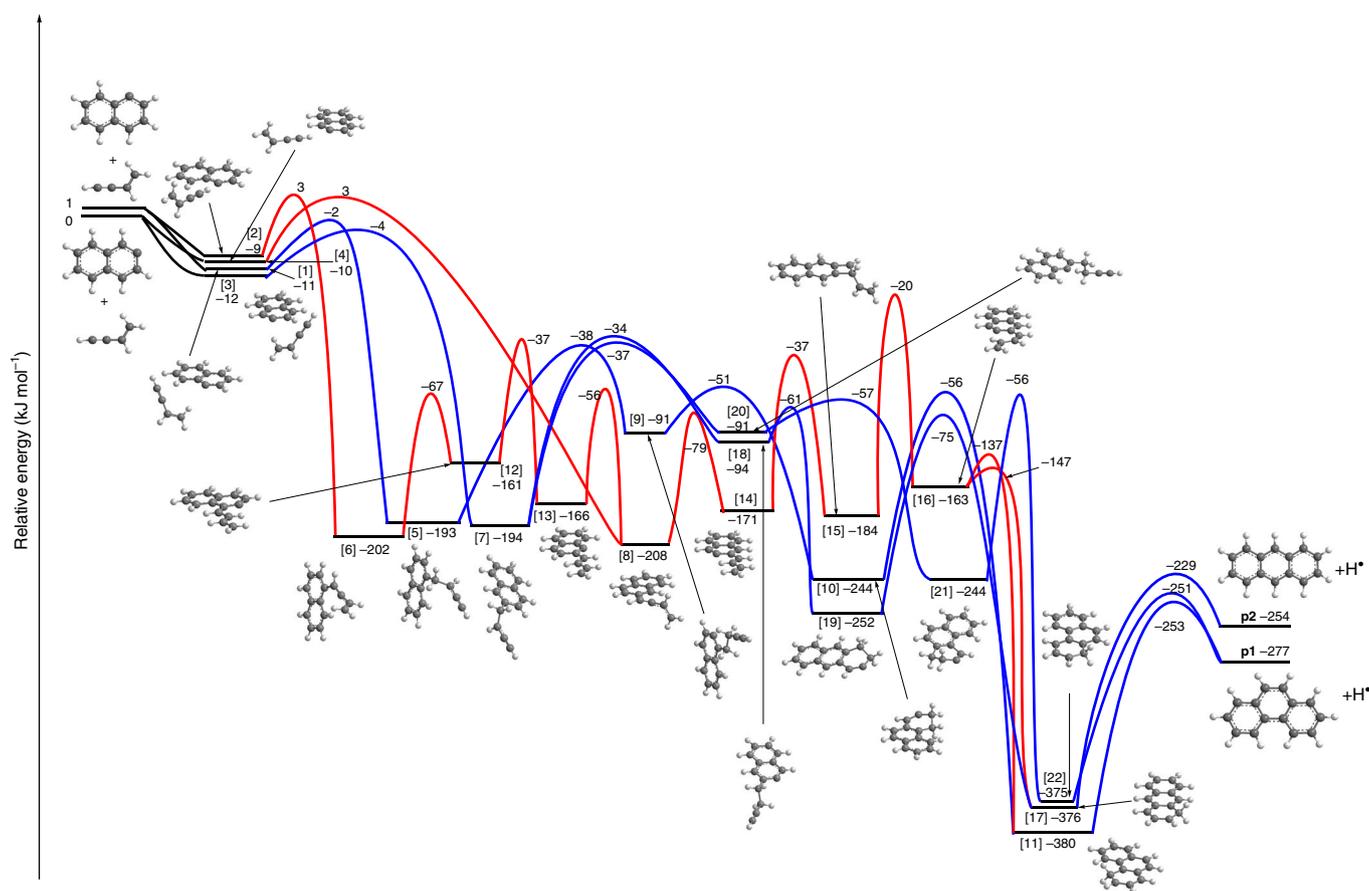


Fig. 4 | Potential energy surfaces of the reactions of 1-naphthyl and 2-naphthyl radicals with vinylacetylene leading to phenanthrene (p1) and anthracene (p2). The barrierless reaction pathways highlighted in blue dominate the anthracene and phenanthrene formation in cold environments, such as in Titan's atmosphere. The pathways denoted in red have entrance barriers and hence are only relevant at elevated temperatures as present (for instance, in combustion flames). They are closed at low temperatures due to the inherent barriers to reaction. Optimized Cartesian coordinates for all structures and a full version of this surface, including the pathways to substituted naphthalene isomers and hydrogen abstraction yielding naphthalene, are compiled in the Supplementary Information. Also, the initial covalently bound intermediates [5]–[8] can immediately lose a hydrogen atom from the attacking C₁ or C₄ atoms of vinylacetylene to form the naphthyl-vinylacetylene isomers 1-naphthyl-vinylacetylene-4 (1-((E)-but-1-en-3-ynyl)naphthalene, C₁₀H₇HCCHCCH; **p4**), 1-naphthyl-vinylacetylene-1 (1-(but-3-en-1-ynyl)naphthalene, C₁₀H₇CCC₂H₃; **p3**), 2-naphthyl-vinylacetylene-4 (2-((E)-but-1-en-3-ynyl)naphthalene, C₁₀H₇HCCHCCH; **p6**) and 2-naphthyl-vinylacetylene-1 (2-(but-3-en-1-ynyl)naphthalene, C₁₀H₇CCC₂H₃; **p5**), respectively. These products are thermodynamically less stable than anthracene and phenanthrene, and their formation is not competitive at the low temperatures characteristic of Titan, but they may prevail in combustion environments as the primary reaction products due to entropic favourability of the hydrogen atom loss.

free-radical intermediates [5] and [7], and the transition states to addition lie lower in energy than the separated reactants. Therefore, a barrier to addition exists, but since this barrier is located below the energy of the reactants, it is a submerged barrier. For the overall reaction of naphthyl plus vinylacetylene to the C₁₄H₁₁ intermediates [5] and [7], the reaction is de facto barrierless. This is in strong contrast with the addition of 1- and 2-naphthyl radicals to the C₁ carbon atom forming intermediates [6] and [8]. The transition states to addition reside above the energy of the separated reactants and hence a barrier to addition exists at the C₁ atom of vinylacetylene.

Within the 1-naphthyl-vinylacetylene system, intermediate [5] undergoes a [1,4] hydrogen shift from the *ortho* carbon of the ring to the β carbon of the side chain forming [9], followed by cyclization to gain the phenanthrene carbon backbone in [10], hydrogen shift to the carbene centre yielding [11], and ultimately atomic hydrogen loss from the CH₂ moiety followed by aromatization and formation of phenanthrene (**p1**) via a tight exit transition state in an overall exoergic reaction (−277 kJ mol^{−1}). All pertinent transition states leading to the formation of phenanthrene in the reaction sequence [1]→[5]→[9]→[10]→[11]→**p1**+H are below the energy of the separated reactants and hence accessible even at ultralow tem-

peratures. Radical intermediate [6], which can only be accessed at elevated temperatures due to the inherent addition barrier, can eventually react to form anthracene (**p2**) in an overall exoergic reaction (−254 kJ mol^{−1}) via seven isomerization steps from [6] to [12]→[13]→[8]→[14]→[15]→[16]→[17]. This sequence involves a [1,4] hydrogen shift from the ring to the side chain, migration of the former vinylacetylene moiety from the C₁ to the C₂ carbon atom of naphthalene, two more [1,4] hydrogen shifts (first from the side chain back to the radical site of the ring and then from the other ring to the side chain), *cis-trans* isomerization via a tricyclic intermediate, four-membered ring opening and six-membered ring closure to form the anthracene carbon backbone in [17], and finally a hydrogen loss from the CH₂ moiety, producing anthracene (**p2**) through a tight exit transition state in an overall exoergic reaction (−254 kJ mol^{−1}).

The 2-naphthyl-vinylacetylene system also connects both to the phenanthrene (**p1**) and anthracene (**p2**) isomers. Initiated by intermediates [7] and [8], the reaction sequence [7]→[18]→[19]→[17] proceeds via a [1,4] hydrogen shift, cyclization to the anthracene carbon skeleton, hydrogen migration from the CH₂ moiety to the carbene centre and hydrogen loss to anthracene (**p2**). In contrast, the rearrangement of [7] via [20]→[21]→[22] through [1,4]

hydrogen migration, cyclization and hydrogen atom migration to the carbene centre, followed by atomic hydrogen elimination, forms phenanthrene (**p1**). The two [1,4] hydrogen shifts in the phenanthrene and anthracene pathways take place from C₁ and C₃ carbons of the former 2-naphthyl moiety. Therefore, the 2-naphthyl-vinylacetylene system may essentially undergo ring closure to the C₁ or the C₃ carbon atoms of the naphthyl moiety, leading to phenanthrene (**p1**) and anthracene (**p2**), respectively. However, although in the 1-naphthyl-vinylacetylene system, the radical centre resides initially at the C₁ atom of the naphthyl radical and reaction with vinylacetylene should essentially lead only to phenanthrene (**p1**), our calculations identify—as verified experimentally—a potential shift of the radical centre from the C₁ to the C₂ carbon atom, which in turn also allows the formation of anthracene (**p2**). It should be noted that these ring-closure mechanisms also operate for substituted naphthalenes, as proposed by Zwier and colleagues⁴³, with reactions initiated by, for example, the addition of propargyl radicals to benzyl radicals followed by photoexcitation and reaction of the primary reaction products under Titan-like conditions.

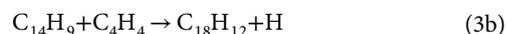
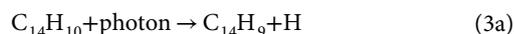
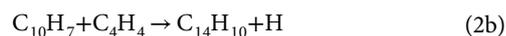
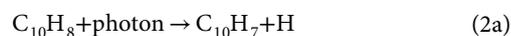
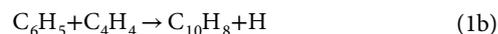
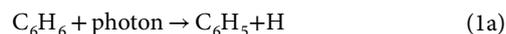
To summarize, our calculations reveal de facto two barrierless pathways for the formation of anthracene (**p1**) and phenanthrene (**p2**) in reactions of vinylacetylene with 1- and 2-naphthyl radicals involving van der Waals complexes and submerged barriers to addition. Due to the essential barrierless nature of these reactions, both pathways involving van der Waals complexes [1] and [3] can lead to the synthesis of anthracene (**p1**) and phenanthrene (**p2**) in low-temperature environments such as Titan's atmosphere, whereas two alternative routes initiated by van der Waals complexes [2] and [4] require elevated temperatures, such as those prevalent in combustion flames. At low temperature (collision energy) and within the limit of zero pressure, the reactions of 1- and 2-naphthyl radicals with vinylacetylene are initiated via barrierless additions of the radical centre to the terminal CH₂ moiety of the vinylacetylene reactant, leading to the resonantly stabilized free-radical intermediates [5] and [7]. At the vinyl group, these additions commence with the formation of long-range van der Waals complexes [1] and [3], respectively, which isomerize via submerged barriers to [5] and [7]. These intermediates eventually isomerize via successive hydrogen migrations, followed by ring closure, to ultimately form both anthracene (**p1**) and phenanthrene (**p2**) via tight exit transition states through hydrogen atom elimination. These tight exit transition states can be rationalized easily since the reversed reaction (that is, the addition of a hydrogen atom to a closed-shell 14π aromatic electron system) is associated with an entrance barrier similar to the reaction of atomic hydrogen with benzene (37 kJ mol⁻¹)⁴⁴ and naphthalene (24 kJ mol⁻¹)¹⁷.

Discussion

Titan's atmosphere. Having demonstrated the facile synthesis of anthracene (**p1**) and phenanthrene (**p2**) via molecular mass growth processes involving ring expansion through de facto barrierless reactions of aromatic radicals (naphthyl) with vinylacetylene, we transfer our findings from the laboratory and computer to the atmosphere of Saturn's moon Titan. The absence of any entrance barrier in a bimolecular reaction represents a crucial prerequisite for a chemical reaction to be feasible under the extreme low-temperature conditions in Titan's atmosphere (70–180 K). These low temperatures typically block reactions that have a significant entrance barrier, such as the pathways via intermediates [2] and [4] shown in the present study. Consequently, chemical reactions relevant to Titan's atmosphere must be exoergic, proceed without an entrance barrier, and must only involve transition states that are lower than the energy of the separated reactants. All these benchmarks are fulfilled in the bimolecular reactions of the 1- and 2-naphthyl radicals with vinylacetylene leading to anthracene (**p1**) and phenanthrene (**p2**) (Fig. 4, blue pathways). We would like to emphasize that the temperature

in our experiments is higher than in Titan's atmosphere. Likewise, the pressure conditions differ from 300 Torr in the entrance of our reactor to close to 100 Torr in the relevant atmospheric range in Titan; these ranges correspond to altitudes from 30 to 50 km in Titan's atmosphere¹⁰. Do these discrepancies have any influence on the implications of the formation of anthracene (**p1**) and phenanthrene (**p2**) on Titan? At higher temperatures, additional pathways can open up if the barrier to hydrogen abstraction forming naphthyl (C₁₀H₇[•]) and, for instance, 1-vinyl-ethyn-1-yl (H₂CCCCH) can be overcome. Likewise, pathways via intermediates [2] and [4] are accessible at elevated temperatures if the barriers to addition can be passed. Nevertheless, these additional channels do not change the reaction mechanism for the formation of anthracene and phenanthrene via intermediates [1] and [3], and we have to conclude that at the low-temperature conditions of Titan and high temperatures prevailing in our experiments, both anthracene (**p1**) and phenanthrene (**p2**) can be formed, albeit with different rate constants and at different branching ratios (Supplementary Table 1).

Our results predict critical trends in Titan's atmosphere, leading ultimately to mass growth processes of PAHs on the molecular level. First, starting with the phenyl radical (C₆H₅[•]), PAHs of the generic formulae C_(10+4n)H_(8+2n) with naphthalene (n=0), anthracene/phenanthrene (n=1) and, for example tetracene (n=2) are predicted to be readily formed in the atmosphere of Titan via stepwise molecular mass growth sequences via reactions of phenyl (C₆H₅[•]), naphthyl (C₁₀H₇[•]) and anthracenyl (C₁₄H₉[•]) with vinylacetylene (C₄H₄) (reactions 1–3). This mechanism contains two steps: the photolysis of the radical precursor (reactions 1a, 2a and 3a) and a molecular mass growth through a barrierless reaction with vinylacetylene (reactions 1b, 2b and 3b), leading effectively to PAH growth plus atomic hydrogen.



This growth sequence is assisted by two factors: the lack of reaction barriers discussed in this article for the reaction of naphthyl radicals with vinylacetylene and the escape of hydrogen atoms from the atmosphere of Titan as a consequence of its low gravity. Here, the production of PAHs is anticipated to be substantial throughout Titan's atmosphere considering the photolysis of low-molecular-mass PAH precursors such as benzene and naphthalene mainly by ultraviolet photons, where there is no or little shielding by the major constituents of Titan's atmosphere such as molecular nitrogen (N₂) and methane (CH₄). Consequently, once a PAH is formed in Titan's atmosphere via the aryl-vinylacetylene reaction, this PAH gains one six-membered ring compared with its aryl precursor. This molecular mass growth process can continue by photolysis of the newly formed PAH to its corresponding aryl reactants, which then react with another vinylacetylene molecule to give an even more complex PAH. This molecular mass growth may continue until the PAH agglomerates into the aerosol-based hazed layer or

precipitates onto Titan's surface. Lopez-Puertas et al.⁵ proposed that up to 19 PAHs—including phenanthrene and anthracene as molecular building blocks—represent a 'best fit' to the VIMS emission spectra in Titan's atmosphere. This finding correlates nicely with previous studies by Sagan et al.³, suggesting that phenanthrene and anthracene act as molecular carriers of tholins produced in Titan's atmosphere. Finally, Ali et al.⁴⁵ analysed data of Titan's upper atmosphere obtained by the Cassini Ion and Neutral Mass Spectrometer, concluding that nitrogen-substituted phenanthrene probably acts as a major contributor to Titan's haze precursors. Therefore, the 1-/2-naphthyl-vinylacetylene system represents a critical proof-of-concept study that elementary PAH growth processes may drive the low-temperature chemistry of complex aromatic molecules in Titan's atmosphere, providing an explanation for the potential presence of not only naphthalene, anthracene and phenanthrene as building blocks to even more complex PAHs in Titan's atmosphere. The transition from naphthalene¹⁷ to anthracene/phenanthrene and heavier PAHs via reactions 1–3 involving the barrierless HAVA mechanism therefore represents a critical, hitherto ignored reaction sequence for the build-up of complex PAHs via stepwise molecular mass growth processes at low temperatures in Titan's atmosphere.

Summary

To summarize, our experimental study identified anthracene and phenanthrene as key reaction products of the elementary reactions of 1-/2-naphthyl radicals with vinylacetylene. The reaction channels display no entrance barrier and are exoergic, and all transition states involved are located below the energy of the separated reactant molecules. Considering these features, the bimolecular reactions of the naphthyl radicals with vinylacetylene reveal a facile pathway for the synthesis of anthracene and phenanthrene in Titan's atmosphere in those regions, where the density profiles of photolytically generated naphthyl radicals and vinylacetylene intersect. These findings further propose that successive reactions of anthracene and phenanthrene molecules can synthesize even more complex PAHs via the HAVA mechanism. Here, anthracenyl or phenanthrenyl radicals ($C_{14}H_9^*$) generated via photodissociation of anthracene or phenanthrene ($C_{14}H_{10}$), respectively, could react with vinylacetylene to give five possible PAHs carrying four six-membered rings: benz[*a*]anthracene, tetracene, chrysene, benzo[*c*]phenanthrene and triphenylene. We provide data on the critical sinks of PAHs for the organic aerosol layers, as well as scientific groundwork for the previously tentative spectroscopic assignments of PAHs in Titan's atmosphere via Cassini's VIMS at 3.28 μm ($3,049\text{ cm}^{-1}$)⁴. These crucial data enable us to constrain the composition and density of minor neutral molecules in Titan's atmosphere and explain how they can be linked to the orange-brownish aerosol layers ultimately changing our paradigm that PAH can be solely formed in high-temperature environments via HACA^{19–22,24,40} or barrierless ion–molecule reactions^{17,26–29,46}. Therefore, we suggest that our combined experimental and computational study provides a template for a warranted investigation of the low-temperature organic chemistry of PAHs in Titan's atmosphere so that a comprehensive picture of the overall processes involved in the chemistry of Titan's atmosphere can emerge.

Methods

Experimental. The experiments were conducted at the Advanced Light Source at the Chemical Dynamics Beamline (9.0.2.), exploiting a high-temperature chemical reactor consisting of a resistively heated silicon carbide (SiC) tube of 20 mm length and 1 mm inner diameter^{21,40,47}. This reactor is incorporated in a molecular beam apparatus operated with a Wiley–McLaren Re-TOF-MS^{20–22,40,47–49}. This set-up investigates discrete chemical reactions to simulate PAH growth in situ through the reaction of radicals. 1-/2-naphthyl radicals ($C_{10}H_7^*$) were prepared at concentrations of less than 0.1% in situ via pyrolysis of the 1-/2-bromonaphthalene precursor ($C_{10}H_7\text{Br}$; TCI America; >95% for 1-bromonaphthalene and >98% for 2-bromonaphthalene) seeded in vinylacetylene/helium (5% C_4H_4 ; 95% helium; Applied Gas) carrier gas at a pressure of 300 Torr. The temperature of the SiC tube was monitored using a Type C thermocouple and maintained at $1,450 \pm 10\text{ K}$.

At this temperature, 1-/2-bromonaphthalene dissociates to atomic bromine plus the 1-/2-naphthyl radical in situ, which then reacts with vinylacetylene. The reaction products synthesized in the reactor were expanded supersonically and passed through a 2-mm-diameter skimmer located 10 mm downstream from the pyrolytic reactor. They then entered into the main chamber, which housed the Re-TOF-MS. The products within the supersonic beam were then photoionized in the extraction region of the spectrometer by exploiting quasi-continuous tunable synchrotron VUV light and detected with a microchannel plate. It is important to highlight that VUV single-photon ionization essentially represents a fragment-free ionization technique and is therefore characterized as a soft ionization method^{50,51} compared with electron impact ionization, leading to excessive fragmentation of the parent ion. The ions formed via photoionization were extracted and fed onto a microchannel plate detector through an ion lens. PIE curves, which report ion counts as a function of photon energy from 7.20 to 9.50 eV with a step interval of 0.05 eV at a well-defined m/z ratio, were produced by integrating the signal recorded at the specific m/z for the species of interest and normalized to the incident photon flux. The residence time in the reactor tube under our experimental conditions was up to hundreds of μs ⁵². Reference (blank) experiments were also conducted by expanding neat helium carrier gas with the 1-/2-bromonaphthalene precursor into the resistively heated SiC tube. No signals at $m/z = 178$ or 179 were observed in these control experiments.

Electronic structure and rate-constant calculations. The energies and molecular parameters of the local minima and transition states involved in the reaction were computed at the G3(MP2,CC)//B3LYP/6-311G(d,p) level of theory^{53–55} within a chemical accuracy of 3–6 kJ mol⁻¹ for relative energies, 0.01–0.02 Å for bond lengths and 1–2° for bond angles⁵⁶. The GAUSSIAN 09 (ref. 56) and MOLPRO 2010 programme packages⁵⁷ were used for the ab initio calculations. The MESS package⁵⁸ was exploited to solve the one-dimensional master equation and compute temperature-dependent rate constants in the zero- and high-pressure limits within the Rice–Rampsberger–Kassel–Marcus master equation method. The rigid-rotor, harmonic-oscillator model was used to compute densities of states and partition functions of local minima and numbers of states of transition states. Rice–Rampsberger–Kassel–Marcus master equation calculations at low temperatures in the 70–180 K range relevant to the atmosphere of Titan took into account radiative stabilization of various reaction intermediates through the emission of infrared photons.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Received: 9 May 2018; Accepted: 3 September 2018;

Published online: 08 October 2018

References

- Lorenz, R. & Mitton, J. *Titan Unveiled: Saturn's Mysterious Moon Explored* Ch. 2 (Princeton Univ. Press, Princeton, 2010).
- Brown, R., Lebreton, J. P. & Waite, J. H. *Titan from Cassini–Huygens* Ch. 7 (Springer Science+Business Media, New York, 2009).
- Sagan, C. et al. Polycyclic aromatic hydrocarbons in the atmospheres of Titan and Jupiter. *Astrophys. J.* **414**, 399–405 (1993).
- Delitsky, M. L. & McKay, C. P. The photochemical products of benzene in Titan's upper atmosphere. *Icarus* **207**, 477–484 (2010).
- Lopez-Puertas, M. et al. Large abundances of polycyclic aromatic hydrocarbons in Titan's upper atmosphere. *Astrophys. J.* **770**, 132–139 (2013).
- Jonker, M. T. O., Hawthorne, S. B. & Koelmans, A. A. Extremely slowly desorbing polycyclic aromatic hydrocarbons from soot and soot-like materials: evidence by supercritical fluid extraction. *Environ. Sci. Technol.* **39**, 7889–7895 (2005).
- Trainer, M. G., Sebree, J. A., Heidi Yoon, Y. & Tolbert, M. A. The influence of benzene as a trace reactant in Titan aerosol analogs. *Astrophys. J. Lett.* **766**, L4/1–L4/5 (2013).
- Coustenis, A. et al. Titan's atmosphere from ISO mid-infrared spectroscopy. *Icarus* **161**, 383–403 (2003).
- Capalbo, F. J. et al. New benzene absorption cross sections in the VUV, relevance for Titan's upper atmosphere. *Icarus* **265**, 95–109 (2016).
- Vinatier, S. et al. Analysis of Cassini/CIRS limb spectra of Titan acquired during the nominal mission: I. Hydrocarbons, nitriles and CO₂ vertical mixing ratio profiles. *Icarus* **205**, 559–570 (2010).
- Vinatier, S. et al. Study of Titan's fall southern stratospheric polar cloud composition with Cassini/CIRS: detection of benzene ice. *Icarus* **310**, 89–104 (2018).
- Coustenis, A. et al. The composition of Titan's stratosphere from Cassini/CIRS mid-infrared spectra. *Icarus* **189**, 35–62 (2007).
- Cui, J. et al. Analysis of Titan's neutral upper atmosphere from Cassini Ion Neutral Mass Spectrometer measurements. *Icarus* **200**, 581–615 (2009).

14. Wilson, E. H. & Atreya, S. K. Chemical sources of haze formation in Titan's atmosphere. *Planet. Space Sci.* **51**, 1017–1033 (2003).
15. Landera, A. & Mebel, A. M. Mechanisms of formation of nitrogen-containing polycyclic aromatic compounds in low-temperature environments of planetary atmospheres: a theoretical study. *Faraday Discuss.* **147**, 479–494 (2010).
16. Kaiser, R. I., Asvany, O. & Lee, Y. T. Crossed beam investigation of elementary reactions relevant to the formation of polycyclic aromatic hydrocarbon (PAH)-like molecules in extraterrestrial environments. *Planet. Space Sci.* **48**, 483–492 (2000).
17. Parker, D. S. et al. Low temperature formation of naphthalene and its role in the synthesis of PAHs (polycyclic aromatic hydrocarbons) in the interstellar medium. *Proc. Natl Acad. Sci. USA* **109**, 53–58 (2012).
18. Wilson, E. H., Atreya, S. K. & Coustenis, A. Mechanisms for the formation of benzene in the atmosphere of Titan. *J. Geophys. Res. Planets* **108**, 8/1–8/10 (2003).
19. Frenklach, M. & Feigelson, E. D. Formation of polycyclic aromatic hydrocarbons in circumstellar envelopes. *Astrophys. J.* **341**, 372–384 (1989).
20. Parker, D. S., Kaiser, R. I., Troy, T. P. & Ahmed, M. Hydrogen abstraction/acetylene addition revealed. *Angew. Chem. Int. Ed.* **53**, 7740–7744 (2014).
21. Parker, D. S. N. et al. Unexpected chemistry from the reaction of naphthyl and acetylene at combustion-like temperatures. *Angew. Chem. Int. Ed.* **54**, 5421–5424 (2015).
22. Yang, T. et al. Hydrogen-abstraction/acetylene-addition exposed. *Angew. Chem. Int. Ed.* **55**, 14983–14987 (2016).
23. Lorenz, R. D. & Lunine, J. I. Titan's surface reviewed: the nature of bright and dark terrain. *Planet. Space Sci.* **45**, 981–992 (1997).
24. Mebel, A. M., Landera, A. & Kaiser, R. I. Formation mechanisms of naphthalene and indene: from the interstellar medium to combustion flames. *J. Phys. Chem. A* **121**, 901–926 (2017).
25. Mebel, A. M., Georgievskii, Y., Jasper, A. W. & Klippenstein, S. J. Temperature- and pressure-dependent rate coefficients for the HACA pathways from benzene to naphthalene. *Proc. Combust. Inst.* **36**, 919–926 (2017).
26. Appel, J., Bockhorn, H. & Frenklach, M. Kinetic modeling of soot formation with detailed chemistry and physics: laminar premixed flames of C₂ hydrocarbons. *Combust. Flame* **121**, 122–136 (2000).
27. Slavinskaya, N. A. & Frank, P. A modelling study of aromatic soot precursors formation in laminar methane and ethene flames. *Combust. Flame* **156**, 1705–1722 (2009).
28. Shukla, B. & Koshi, M. Comparative study on the growth mechanisms of PAHs. *Combust. Flame* **158**, 369–375 (2011).
29. Aguilera-Iparraguirre, J. & Klopper, W. Density functional theory study of the formation of naphthalene and phenanthrene from reactions of phenyl with vinyl- and phenylacetylene. *J. Chem. Theory Comput.* **3**, 139–145 (2007).
30. Yoon, Y. H. et al. The role of benzene photolysis in Titan haze formation. *Icarus* **233**, 233–241 (2014).
31. Vuitton, V., Yelle, R. V. & Lavvas, P. Composition and chemistry of Titan's thermosphere and ionosphere. *Phil. Trans. R. Soc. A* **367**, 729–741 (2009).
32. Gautier, T. et al. Nitrile gas chemistry in Titan's atmosphere. *Icarus* **213**, 625–635 (2011).
33. Imanaka, H. & Smith, M. A. Formation of nitrogenated organic aerosols in the Titan upper atmosphere. *Proc. Natl Acad. Sci. USA* **107**, 12423–12428 (2010).
34. Jacovi, R., Laufer, D., Dimitrov, V. & Bar-Nun, A. Chemical composition of simulated Titan's midatmospheric aerosols. *J. Geophys. Res. Planets* **115**, E07006 (2010).
35. Kovács, T., Blitz, M. A. & Seakins, P. W. H-atom yields from the photolysis of acetylene and from the reaction of C₂H with H₂, C₂H₂, and C₂H₄. *J. Phys. Chem. A* **114**, 4735–4741 (2010).
36. Zhang, F., Kim, Y. S., Kaiser, R. I., Krishtal, S. P. & Mebel, A. M. Crossed molecular beams study on the formation of vinylacetylene in Titan's atmosphere. *J. Phys. Chem. A* **113**, 11167–11173 (2009).
37. Dimitrov, V. & Bar-Nun, A. Properties of the main high molecular weight hydrocarbons in Titan's atmosphere. *Prog. React. Kinet.* **22**, 67–81 (1997).
38. Dimitrov, V. & Bar-Nun, A. Kinetic pathways in the atmospheric chemistry of Titan—a generalized analysis. *Prog. React. Kinet. Mech.* **29**, 1–41 (2004).
39. Krasnopolsky, V. A. The photochemical model of Titan's atmosphere and ionosphere: a version without hydrodynamic escape. *Planet. Space Sci.* **58**, 1507–1515 (2010).
40. Yang, T. et al. HACA's heritage: a free-radical pathway to phenanthrene in circumstellar envelopes of asymptotic giant branch stars. *Angew. Chem. Int. Ed.* **56**, 4515–4519 (2017).
41. Hager, J. W. & Wallace, S. C. Two-laser photoionization supersonic jet mass spectrometry of aromatic molecules. *Anal. Chem.* **60**, 5–10 (1988).
42. Thantu, N. & Weber, P. M. Dependence of two-photon ionization photoelectron spectra on laser coherence bandwidth. *Chem. Phys. Lett.* **214**, 276–280 (1993).
43. Sebree, J. A. et al. Photochemistry of benzylallene: ring-closing reactions to form naphthalene. *J. Am. Chem. Soc.* **134**, 1153–1163 (2012).
44. Mebel, A. M., Lin, M. C., Yu, T. & Morokuma, K. Theoretical study of potential energy surface and thermal rate constants for the C₆H₅+H₂ and C₆H₆+H reactions. *J. Phys. Chem. A* **101**, 3189–3196 (1997).
45. Ali, A., Sittler, E. C., Chornay, D., Rowe, B. R. & Puzzarini, C. Organic chemistry in Titan's upper atmosphere and its astrobiological consequences: I. Views towards Cassini Plasma Spectrometer (CAPS) and Ion Neutral Mass Spectrometer (INMS) experiments in space. *Planet. Space Sci.* **109–110**, 46–63 (2015).
46. Lindstedt, P., Maurice, L. & Meyer, M. Thermodynamic and kinetic issues in the formation and oxidation of aromatic species. *Faraday Discuss.* **119**, 409–432 (2002).
47. Zhang, F. et al. A VUV photoionization study of the formation of the indene molecule and its isomers. *J. Phys. Chem. Lett.* **2**, 1731–1735 (2011).
48. Zhang, F., Kaiser, R. I., Golan, A., Ahmed, M. & Hansen, N. A VUV photoionization study of the combustion-relevant reaction of the phenyl radical (C₆H₅) with propylene (C₃H₆) in a high temperature chemical reactor. *J. Phys. Chem. A* **116**, 3541–3546 (2012).
49. Parker, D. S. N., Kaiser, R. I., Kostko, O. & Ahmed, M. Selective formation of indene through the reaction of benzyl radicals with acetylene. *ChemPhysChem* **16**, 2091–2093 (2015).
50. Qi, F. Combustion chemistry probed by synchrotron VUV photoionization mass spectrometry. *Proc. Combust. Inst.* **34**, 33–63 (2013).
51. Cool, T. A. et al. Photoionization mass spectrometer for studies of flame chemistry with a synchrotron light source. *Rev. Sci. Instrum.* **76**, 094102 (2005).
52. Guan, Q. et al. The properties of a micro-reactor for the study of the unimolecular decomposition of large molecules. *Int. Rev. Phys. Chem.* **33**, 447–487 (2014).
53. Curtiss, L. A., Raghavachari, K., Redfern, P. C., Rassolov, V. & Pople, J. A. Gaussian-3 (G3) theory for molecules containing first and second-row atoms. *J. Chem. Phys.* **109**, 7764–7776 (1998).
54. Baboul, A. G., Curtiss, L. A., Redfern, P. C. & Raghavachari, K. Gaussian-3 theory using density functional geometries and zero-point energies. *J. Chem. Phys.* **110**, 7650–7657 (1999).
55. Curtiss, L. A., Raghavachari, K., Redfern, P. C., Baboul, A. G. & Pople, J. A. Gaussian-3 theory using coupled cluster energies. *Chem. Phys. Lett.* **314**, 101–107 (1999).
56. Frisch, M. J. et al. *Gaussian 09 Revision A.02* (Gaussian, 2009).
57. Werner, H. J. et al. *MOLPRO Version 2010.1* (Univ. College Cardiff Consultants, 2010); <http://www.molpro.net>
58. Georgievskii, Y., Miller, J. A., Burke, M. P. & Klippenstein, S. J. Reformulation and solution of the master equation for multiple-well chemical reactions. *J. Phys. Chem. A* **117**, 12146–12154 (2013).

Acknowledgements

This work was supported by US Department of Energy, Basic Energy Sciences grants DE-FG02-03ER15411 (experimental studies) and DE-FG02-04ER15570 (computational studies) to the University of Hawaii and Florida International University, respectively. M.A., U.A., B.X. and the experiments at the chemical dynamics beamline at the ALS were supported by the Director, Office of Science, Office of Basic Energy Sciences, US Department of Energy under contract number DE-AC02-05CH11231, through the Gas Phase Chemical Physics Program, Chemical Sciences Division. Ab initio calculations of the C₁₄H₁₁ potential energy surface relevant to the reactions of 1- and 2-naphthyl radicals with vinylacetylene at Samara University were supported by the Ministry of Education and Science of the Russian Federation under grant number 14.Y26.31.0020. The authors thank V. Vuitton (Grenoble) and R. Yelle (Arizona) for stimulating discussions.

Author contributions

R.I.K. designed the experiment. L.Z., B.X. and U.A. carried out the experimental measurements. M.A. supervised the experiment. L.Z. performed the data analyses. M.M.E., E.K.B., V.N.A. and A.M.M. carried out the theoretical analyses. R.I.K., A.M.M. and M.A. discussed the data. R.I.K. wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at <https://doi.org/10.1038/s41550-018-0585-y>.

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Correspondence and requests for materials should be addressed to R.I.K. or M.A. or A.M.M.

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