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

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Low-Temperature Formation of Polycyclic Aromatic Hydrocarbons in Titan's Atmosphere

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Supplementary Figure 1. Photoionization mass spectra recorded at a photoionization energy of 12.0 eV for the (a) 1-naphthyl ($C_{10}H_7^{\bullet}$) - vinylacetylene (C_4H_4) and (b) 2-naphthyl ($C_{10}H_7^{\bullet}$) - vinylacetylene (C_4H_4) systems. Note that at high temperatures, vinylacetylene can decompose to acetylene at fractions of about 2%^{1,2}. The photoionization energy of acetylene is 11.4 eV³. Mass spectra at photoionization energies of 12.0 eV were recorded to identify acetylene. Acetylene can react with naphthyl radicals to yield acenaphthylene ($C_{12}H_8$) (m/z = 152) as demostrated by Parker et al.⁴



Supplementary Figure 2. Supplementary photoionization efficiency curves (PIEs, black lines) recorded in the 1-naphthyl - vinylacetylene reaction. The black lines represent the experimental data along with the experimental errors denoted in gray areas; the reference PIE curves are color coded in blue, green, and red lines. In case of multiple contributions to one PIE curve, the red line resembles the overall fit. The species at m/z = 127 is identified as the 1-naphthyl radical (C₁₀H₇) generated from the pyrolysis of the precursor 1-bromonaphthalene. Ions at m/z = 126 and 128 are associated to the atomic hydrogen loss and addition to and from the 1-naphthyl radical, respectively. Signal at m/z = 128 is identified as naphthalene, and m/z = 129 as ¹³C-naphthalene. The ions at m/z = 152 are attributed to acenaphthylene (C₁₂H₈) and ethynylnaphthalene isomers (C₁₂H₈). Signals at m/z = 206 and 208 are attributed to the precursor 1-bromonaphthalene (C₁₀H₇⁷⁹Br and C₁₀H₇⁸¹Br).



Supplementary Figure 3. Supplementary photoionization efficiency curves (PIEs, black lines) recorded in the 2-naphthyl - vinylacetylene reaction. The black lines represent the experimental data along with the experimental errors denoted in gray areas; the reference PIE curves are color coded in blue, green, and red lines. In case of multiple contributions to one PIE curve, the red line resembles the overall fit. The species at m/z = 127 is identified as the 2-naphthyl radical (C₁₀H₇) generated from the pyrolysis of the precursor 2-bromonaphthalene. Ions at m/z = 126 and 128 are associated to the atomic hydrogen loss and addition to and from the 2-naphthyl radical, respectively. Signal at m/z = 128 is identified as naphthalene, and m/z = 129 as ¹³C-naphthalene. The ions at m/z = 152 are attributed to acenaphthylene (C₁₂H₈) and ethynylnaphthalene isomers (C₁₂H₈). Signals at m/z = 206 and 208 are attributed to the precursor 1-bromonaphthalene (C₁₀H₇⁷⁹Br and C₁₀H₇⁸¹Br).



Supplementary Figure 4. PIE calibration curves for anthracene and phenanthrene collected in this work. The ionization energies of anthracene and phenanthrene are 7.40 ± 0.05 eV and 7.85 ± 0.05 eV, respectively, corresponding well with the reported adiabatic photoionization energies of 7.44^5 and 7.90 eV^6 .



Supplementary Figure 5. Complete potential energy surfaces of the reactions of 1-naphthyl and 2-naphthyl radicals with vinylacetylene. Besides the 14- π -electron aromatic molecules anthracene (**p1**) and phenanthrene (**p2**) discussed in the manuscript, the doublet intermediates [5] – [8]

formed upon initial addition of the naphthyl radicals to vinylacetylene can also undergo unimolecular decomposition via hydrogen atom loss yielding four thermodynamically less stable naphthyl-vinylacetylene isomers: 1-naphthyl-vinylacetylene-1 ($C_{10}H_7CCC_2H_3$; **p3**), 1-naphthyl-vinylacetylene-4 ($C_{10}H_7HCCHCCH$; **p4**), 2-naphthyl-vinylacetylene-1 ($C_{10}H_7CCC_2H_3$; **p5**), and 2-naphthyl-vinylacetylene-4 ($C_{10}H_7HCCHCCH$; **p4**), 2-naphthyl-vinylacetylene-1 ($C_{10}H_7CCC_2H_3$; **p5**), and 2-naphthyl-vinylacetylene-4 ($C_{10}H_7HCCHCCH$; **p6**) in overall weakly exoergic reactions from 29 to 49 kJ mol⁻¹.

	1-naphthyl + C ₄ H ₄ \rightarrow phenanthrene + H <i>p</i> , bar								
<i>T</i> , K	1.00E-15	1.00E-10	1.00E-08	1.00E-06	0.0001	0.01			
70	1.46E-15	1.14E-15	7.86E-18	1.20E-21	1.21E-25	5.10E-30			
80	9.29E-16	7.36E-16	5.72E-18	8.93E-22	9.01E-26	4.18E-30			
90	7.09E-16	5.72E-16	5.02E-18	8.02E-22	8.13E-26	4.13E-30			
100	6.18E-16	5.07E-16	5.06E-18	8.25E-22	8.40E-26	4.64E-30			
110	5.94E-16	4.94E-16	5.64E-18	9.42E-22	9.64E-26	5.76E-30			
120	6.14E-16	5.18E-16	6.82E-18	1.17E-21	1.20E-25	7.73E-30			
130	6.73E-16	5.76E-16	8.81E-18	1.54E-21	1.61E-25	1.10E-29			
140	7.71E-16	6.68E-16	1.20E-17	2.16E-21	2.28E-25	1.66E-29			
150	9.14E-16	8.03E-16	1.71E-17	3.17E-21	3.39E-25	2.61E-29			
160	1.11E-15	9.88E-16	2.51E-17	4.84E-21	5.28E-25	4.25E-29			
170	1.38E-15	1.24E-15	3.79E-17	7.66E-21	8.54E-25	7.16E-29			
180	1.73E-15	1.57E-15	5.83E-17	1.25E-20	1.43E-24	1.24E-28			
<i>T</i> , K	0.03	0.1	0.3	1	3				
70	1.49E-31	1.76E-33	2.44E-35	2.06E-37	2.58E-39				
80	1.31E-31	1.62E-33	2.29E-35	1.94E-37	2.43E-39				
90	1.40E-31	1.82E-33	2.62E-35	2.24E-37	2.81E-39				
100	1.70E-31	2.35E-33	3.47E-35	3.00E-37	3.78E-39				
110	2.30E-31	3.41E-33	5.18E-35	4.53E-37	5.73E-39				
120	3.37E-31	5.39E-33	8.49E-35	7.55E-37	9.59E-39				
130	5.25E-31	9.14E-33	1.51E-34	1.37E-36	1.74E-38				
140	8.61E-31	1.65E-32	2.85E-34	2.65E-36	3.41E-38				
150	1.47E-30	3.11E-32	5.70E-34	5.46E-36	7.11E-38				
160	2.61E-30	6.08E-32	1.19E-33	1.19E-35	1.56E-37				
170	4.74E-30	1.23E-31	2.59E-33	2.69E-35	3.59E-37				
180	8.81E-30	2.53E-31	5.77E-33	6.29E-35	8.59E-37				

Supplementary Table 1. Rate constants (cm³ s⁻¹) and branching fractions of various products in the reactions of 1- and 2-naphthyl radicals with C₄H₄ under Titan's atmospheric conditions (10^{-8} bar at 800 km altitude).

	2-naphthyl + C ₄ H ₄ \rightarrow anthracene/phenanthrene + H <i>p</i> , bar											
	1.00E-15		1.00E-10		1.00E-08		1.00E-06		0.0001		0.01	
<i>T</i> , K	Anthr.	Phenan.	Anthr.	Phenan.	Anthr.	Phenan.	Anthr.	Phenan.	Anthr.	Phenan.	Anthr.	Phenan.
70	7.38E-15	8.49E-16	6.24E-15	6.59E-16	1.13E-16	4.31E-18	1.85E-20	6.07E-22	1.86E-24	6.09E-26	1.15E-29	2.66E-30
80	4.19E-15	5.19E-16	3.59E-15	4.10E-16	7.50E-17	3.02E-18	1.28E-20	4.33E-22	1.29E-24	4.36E-26	8.93E-30	2.07E-30
90	2.88E-15	3.88E-16	2.49E-15	3.12E-16	6.05E-17	2.60E-18	1.08E-20	3.78E-22	1.09E-24	3.82E-26	8.53E-30	1.97E-30
100	2.27E-15	3.35E-16	1.99E-15	2.73E-16	5.59E-17	2.58E-18	1.05E-20	3.82E-22	1.07E-24	3.88E-26	9.42E-30	2.16E-30
110	1.98E-15	3.21E-16	1.74E-15	2.66E-16	5.71E-17	2.87E-18	1.14E-20	4.32E-22	1.16E-24	4.41E-26	1.16E-29	2.64E-30
120	1.85E-15	3.36E-16	1.65E-15	2.82E-16	6.29E-17	3.48E-18	1.34E-20	5.33E-22	1.38E-24	5.47E-26	1.57E-29	3.51E-30
130	1.84E-15	3.73E-16	1.65E-15	3.18E-16	7.33E-17	4.53E-18	1.70E-20	7.06E-22	1.77E-24	7.31E-26	2.27E-29	4.99E-30
140	1.92E-15	4.38E-16	1.73E-15	3.78E-16	8.92E-17	6.25E-18	2.27E-20	9.93E-22	2.39E-24	1.04E-25	3.50E-29	7.50E-30
150	2.07E-15	5.33E-16	1.88E-15	4.66E-16	1.12E-16	9.05E-18	3.19E-20	1.47E-21	3.41E-24	1.56E-25	5.69E-29	1.18E-29
160	2.30E-15	6.70E-16	2.11E-15	5.92E-16	1.45E-16	1.36E-17	4.68E-20	2.28E-21	5.07E-24	2.45E-25	9.65E-29	1.94E-29
170	2.60E-15	8.57E-16	2.41E-15	7.66E-16	1.91E-16	2.11E-17	7.09E-20	3.66E-21	7.85E-24	4.00E-25	1.70E-28	3.30E-29
180	3.02E-15	1.12E-15	2.81E-15	1.01E-15	2.54E-16	3.33E-17	1.11E-19	6.08E-21	1.26E-23	6.76E-25	3.10E-28	5.77E-29
	0.03 0.1		.1	0.3		1		3				
<i>T</i> , K	Anthr.	Phenan.	Anthr.	Phenan.	Anthr.	Phenan.	Anthr.	Phenan.	Anthr.	Phenan.		
70	2.54E-31	8.17E-32	2.76E-33	9.87E-34	3.75E-35	1.38E-35	3.15E-37	1.17E-37	3.93E-39	1.46E-39		
80	2.06E-31	6.81E-32	2.31E-33	8.59E-34	3.19E-35	1.22E-35	2.70E-37	1.04E-37	3.37E-39	1.30E-39		
90	2.05E-31	6.97E-32	2.39E-33	9.22E-34	3.36E-35	1.33E-35	2.85E-37	1.14E-37	3.57E-39	1.43E-39		
100	2.37E-31	8.25E-32	2.88E-33	1.15E-33	4.11E-35	1.70E-35	3.52E-37	1.47E-37	4.42E-39	1.85E-39		
110	3.06E-31	1.09E-31	3.89E-33	1.63E-33	5.68E-35	2.46E-35	4.91E-37	2.15E-37	6.18E-39	2.72E-39		
120	4.33E-31	1.58E-31	5.76E-33	2.52E-33	8.65E-35	3.94E-35	7.57E-37	3.48E-37	9.56E-39	4.41E-39		
130	6.57E-31	2.44E-31	9.22E-33	4.23E-33	1.43E-34	6.84E-35	1.27E-36	6.14E-37	1.61E-38	7.82E-39		
140	1.06E-30	4.00E-31	1.57E-32	7.55E-33	2.52E-34	1.27E-34	2.28E-36	1.17E-36	2.91E-38	1.49E-38		
150	1.80E-30	6.85E-31	2.83E-32	1.42E-32	4.72E-34	2.52E-34	4.35E-36	2.36E-36	5.60E-38	3.04E-38		
160	3.20E-30	1.22E-30	5.34E-32	2.79E-32	9.29E-34	5.24E-34	8.78E-36	5.03E-36	1.14E-37	6.55E-38		
170	5.90E-30	2.23E-30	1.05E-31	5.66E-32	1.91E-33	1.13E-33	1.85E-35	1.13E-35	2.43E-37	1.48E-37		
180	1.12E-29	4.18E-30	2.11E-31	1.18E-31	4.05E-33	2.53E-33	4.07E-35	2.61E-35	5.40E-37	3.48E-37		

Modeling Complications: To explore the effects of a stepwise, vinylacetylene-mediated formation of PAHs in Titan's atmosphere quantitatively, atmospheric modeling would be beneficial. Even a simplified one-dimensional model would require three sets of input parameters. These are i) the aryl radical reactants (phenyl (C_6H_5), naphthyl ($C_{10}H_7$), anthracenyl ($C_{14}H_9$), phenanthrenyl ($C_{14}H_9$)) formed via photodissociation of benzene (C_6H_6), naphthalene ($C_{10}H_8$), anthracene ($C_{14}H_{10}$), and phenanthrene (C₁₄H₁₀) from the solar radiation field, ii) the reaction products, and iii) temperature and pressure dependent rate constants along with their branching ratios. A literature research failed to provide any experimental low temperature rate, pressure-dependent constants for the reactions of vinylacetylene with the aryl radicals. The calculated temperature-and pressure-dependent rate constants over Titan's relevant temperature range of 70 K to 180 K covering pressures from 10⁻¹⁵ to 3 bar are presented in Supplementary Information. Their values indicate that indeed, the formation of phenanthrene and anthracene from 1- and 2-naphthyl radical should be feasible at very low pressures up to 10⁻⁸ bar. However, considering the sensitivity of the rate constants to the heights of the submerged barrier and the resulting range of rate constants covering two orders of magnitude for 1-/2-naphthyl plus vinylacetylene and even for the simplest phenyl – vinylacetylene system⁷, experimental validation of the calculated rate constants is highly desirable. Likewise, wavelengthdependent, absolute photodissociation cross sections of naphthalene, anthracene, and phenanthrene leading to the corresponding aryl radicals are not available and need to be measured or accurately evaluated theoretically. Finally, while the reaction products of the phenyl and 1-/2-naphthyl radical reactions with vinylacetylene are known⁸, those of the phenanthrenyl-vinylacetylene and anthracenyl-vinylacetylene systems are lacking. Based on the aforementioned reaction mechanisms, anthracene and phenanthrene have three and five chemically non-equivalent hydrogen atoms respectively, which when photodissociated to three and five chemically distinct anthracenyl and phenanthrenyl radicals can subsequently serve as aryl reactants with vinylacetylene leading to five $C_{18}H_{12}$ isomers carrying four six-membered rings (benz[a]anthracene, tetracene, chrysene, benzo[c] phenanthrene and triphenylene) (Supplementary Figure 6). PAH formation might also involve ion-molecule reactions in the upper atmosphere⁹. Therefore, both neutral-neutral and ionmolecule reactions might produce PAHs, but the effectiveness of these processes depends on the temperature and pressure, with neutral-neutral reactions dominating in lower atmospheric layers where ions are absent, but photons can still penetrate to cleave carbon-hydrogen bonds of organic molecules forming the desired aryl radicals. This likely results in depth-dependent PAH production routes. Finally, Titan's hydrocarbon and nitrogen chemistries are strongly coupled; these processes might even lead to nitrogen substituted PAHs such as (iso)quinolone; their successive chemical reaction and photochemical properties are only beginning to emerge¹⁰⁻¹⁶, but a systematic understanding is unknown as of now, but critical to establish predictive photochemical models. Therefore, at this stage we did not attempt to develop an atmospheric model of PAH formation in Titan's atmosphere due to the lack of critical input parameters detailed above.

PAH-type Molecules for Titan's Atmosphere

Within this work, it is critical to highlight that the origin of heavy ions in the ionosphere and their implications for prebiotic chemistry,¹⁷ the incorporation of nitrogen into a carbon network,^{17,18} and the subsequent transition from the initial building blocks of PAH-type molecules toward aerosols and haze formation on Titan remains a much debated topic. Due to the lack of observational probes of Titan's atmosphere at the most fundamental, molecular level encompassing moderately large molecules and aerosols, the planetary science community turned to laboratory based measurements to simulate haze and aerosol formation on Titan.¹⁹⁻²¹ A key component of these experiments has been the photodissociation of gas phase mixtures incorporating, for instance, methane (CH4) and nitrogen (N₂) and subsequent analysis of the complex molecules that originate in these experiments most notably with infrared and mass spectrometry. While CH₄/N₂ mixtures resulted in high molecular weight polymers incorporating PAHs and polyphenyl type systems, seeding these mixtures with trace aromatic compounds like benzene and naphthalene gave rise to PAH-based ring structures reminiscent of a free radical chemistry such as via phenyl and naphthyl radicals prevalent in combustion environments.²⁰ Hence, our studies support that free radical based chain reactions could synthesize PAH systems, which act as nuclei for particle growth in Titan's atmosphere.



Supplementary Figure 6. Formation of PAH carrying four six-member rings initiated by anthracene (a) and phenanthrene (b) photodissociation accompanied by atomic hydrogen loss. Starting from anthracene and phenanthrene, three anthracenyl and five phenanthrenyl radicals can be produced via photodissociation. Reacting with vinylacetylene, these aryl radicals can yield five $C_{18}H_{12}$ isomers carrying four six-membered rings, which are benz[*a*]anthracene, tetracene, chrysene, benzo[*c*]phenanthrene and triphenylene.

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