An Aromatic Universe - Low Temperature Molecular Mass Growth Processes to Polycyclic Aromatic Hydrocarbons (PAHs)

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Polycyclic aromatic hydrocarbons (PAHs) represent key molecular building blocks leading to carbonaceous nanoparticles identified in combustion systems and extraterrestrial environments. However, the understanding of their formation and growth has remained elusive. Here, we present evidence based on laboratory data combined with electronic structure calculations on fundamental mass growth processes of PAHs in the gas phase via ring expansion and ring annulation. Key reaction pathways operate at ultralow temperatures such as at 10 K as present in cold molecular clods like TMC-1 synthesizing PAHs at least from two to five six membered rings such as naphthalene, anthracene, phenanthrene, triphenylene, [4]-helicene, and [5]-helicene. These elementary reactions are rapid, have no entrance barriers, and synthesize PAHs via van-der-Waals complexes and submerged barriers. This facile route to complex PAHs signifies a critical shift in the perception that PAHs can be only formed at high-temperature combustion and circumstellar conditions providing a detailed understanding of the low temperature chemistry through untangling elementary reactions on the most fundamental level. An outlook is also presented on the synthesis of PAHs in low temperature, hydrocarbon-dominated ices in deep space and in the outer Solar System upon interaction with (non)-ionizing radiation; these processes are driven by non-adiabatic reaction dynamics and low lying triplet states of acetylene leading to PAHs as complex as coronene. Overall, these mechanisms eventually lead to graphene-type PAHs and two dimensional nanostructures providing an exciting view about the transformation of carbon in our universe.

References

L. Zhao et al. Pyrene Synthesis in Circumstellar Envelopes and its Role in the Formation of 2D Nanostructures. Nature Astron. 2, 413-419 (2018).

L. Zhao et al. Low-Temperature Formation of Polycyclic Aromatic Hydrocarbons in Titan's Atmosphere. Nature Aston. 2, 973-979 (2018).

L. Zhao, R.I. Kaiser, B. Xu, U. Ablikim, W. Lu, M. Ahmed, M. Evseev, E. K. Bashkirov, V.N. Azyazov, M.V. Zagidullin, A.N. Morozov, A.H. Howlader, S.F. Wnuk, A.M. Mebel, D. Joshi, G. Veber, F. R. Fischer, Gas Phase Synthesis of [4]-Helicene. Nature Commun. 10, 1510 (2019).

L. Zhao et al. Molecular Mass Growth through Ring Expansion in Polycyclic Aromatic Hydrocarbons via Radical-Radical Reactions. Nature Commun. 10, 3689 (2019).

L. Zhao et al., A Unified Mechanism on the Formation of Acenes, Helicenes, and Phenacenes in the Gas Phase. Angewandte Chemie – International Edition 59, 4051-4056 (2020).

S. Doddipatla et al., Low-temperature Gas-phase Formation of Indene in the Interstellar Medium, Science Advances, 7, eabd4044 (2021).

R.I. Kaiser, N. Hansen, An Aromatic Universe – A Physical Chemistry Perspective, J. Chem. Phys. A, Invited Perspective 125, 3826-3840 (2021).

L. Zhao et al., Gas Phase Synthesis of Benzene via the Propargyl Radical Self Reaction. Science Advances 7, eabf0360 (2021).