October 3, 2023

Dear Executive Editors

Dr. Nathalie Weickgenannt,

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Enclosed please find our Research Article entitled ‘One Collision – Two Substituents: Gas-Phase Preparation of Xylenes under Single-Collision Conditions’ for the journal of the German Chemical Society – *Angewandte Chemie International Edition*.

The fundamental reaction pathways to the simplest dialkylsubstituted aromatics – xylenes (C6H4(CH3)2) – in high temperature combustion flames and in low temperature extraterrestrial environments are still unknown, but critical to understand the hydrocarbon chemistry and molecular mass growth processes in these extreme environments. Exploiting crossed molecular beam experiments augmented by state-of-the-art electronic structure and statistical calculations, this study uncovers a previously elusive, facile gas-phase synthesis of xylenes through an isomer- and stereoselective reaction of 1-propynyl radical (methylethynyl, CH3CC) with 2-methyl-1,3-butadiene (isoprene, C5H8). The reaction dynamics are driven by a barrierless addition of 1-propynyl radical to the diene moiety of 2-methyl-1,3-butadiene followed by extensive isomerization (hydrogen shifts, cyclization) prior to unimolecular decomposition accompanied by aromatization to xylenes via atomic hydrogen loss. This overall exoergic reaction affords a preparation of xylenes not only in high-temperature environments such as in combustion flames and around circumstellar enveloped of carbon-rich Asymptotic Giant Branch (AGB) stars, but also in low-temperature cold molecular clouds (10 K) and in hydrocarbon-rich atmospheres of planets and their moons such as Triton and Titan. Our study established a hitherto unknown gas-phase route to xylenes and potentially more complex, disubstituted benzenes via a single collision event highlighting the significance of an alkyl-substituted ethynyl-mediated driven preparation of aromatic molecules in our Universe.

This work is not under consideration for publication and has not been published elsewhere.

Selected publications [1-5] exploring reaction mechanisms and dynamics, astrochemistry, chemistry of hydrocarbons and PAHs, disseminated previously in *Angewandte Chemie* are listed below thus supporting the potential interest of or works to the readership of *Angewandte Chemie*.

1. Wu, Bo, et al. "The Effect of the Polyaromatic Hydrocarbon in the Formation of Fullerenes." *Angewandte Chemie International Edition* 59.10 (2020): 3942-3947.
2. Wu, Meng-Xiang, et al. "Functionalization of pentacene: a facile and versatile approach to contorted polycyclic aromatic hydrocarbons." *Angewandte Chemie International Edition* (2023): e202309619.
3. Jacobson, Rachelle S., et al. "The molecular composition of soot." *Angewandte Chemie* 132.11 (2020): 4514-4520.
4. Potapov, Alexey, et al. "Uniform supersonic chemical reactors: 30 years of astrochemical history and future challenges." *Angewandte Chemie International Edition* 56.30 (2017): 8618-8640.
5. Couch, David E., et al. "Experimental Observation of Hydrocarbon Growth by Resonance‐Stabilized Radical–Radical Chain Reaction." *Angewandte Chemie* 133.52 (2021): 27436-27441.

We would like to recommend the following reviewers:

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Please note that the following scientists have strong conflicts of interest that hinder a fair referee report:

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