November 30, 2023

Dear Editor,

Enclosed please find our **Full paper** entitled Elucidating the Chemical Dynamics of the Elementary Reactions of the 1‑Propynyl Radical (CH3CC; X2A1) with 2-Methylpropene ((CH3)2CCH2; X1A1) for the journal ***Physical Chemistry Chemical Physics (PCCP)***.

Exploiting the crossed molecular beam technique, we studied the reaction of the 1-propynyl radical (CH3CC; X2A1) with 2-methylpropene (isobutylene; (CH3)2CCH2; X1A1) at a collision energy of 38 ± 3 kJ mol–1. The experimental results along with *ab initio* and statistical calculations revealed that the reaction has no entrance barrier and proceeds via indirect reaction dynamics involving C7H11 intermediates with lifetimes longer than their rotation period(s). The reaction is initiated by the addition of the 1-propynyl radical with its radical center to the π-electron density at the C1 and/or C2 position in 2-methylpropene, which can isomerize to each other. Further, the C7H11 intermediate formed from the C1 addition either emits atomic hydrogen or undergoes isomerization via [1,2-H] shift from the CH3 or CH2 group prior to atomic hydrogen loss preferentially leading to 1,2,4-trimethylvinylacetylene (2-methylhex-2-en-4-yne) as the dominant product. The molecular structures of the collisional complexes promote hydrogen atom loss channels. RRKM results show that hydrogen elimination channels dominate in this reaction, with a branching ratio exceeding 70 %. Since the reaction of the 1-propynyl radical with 2-methylpropene has no entrance barrier, is exoergic, and all transition states involved are located below the energy of the separated reactants, bimolecular collisions are feasible to form trimethylsubstituted 1,3-enyne (p1) via a single collision event even at temperatures as low as 10 K prevailing in cold molecular clouds such as G+0.693. The formation of trimethylsubstituted vinylacetylene is the starting point of fundamental molecular mass growth processes leading to di- and trimethylsubstituted naphthalenes via the HAVA mechanism.

**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 the ***Physical Chemistry Chemical Physics (PCCP)*** *journal* are listed below thus supporting the potential interest of or works to the readership of ***PCCP***.

1. Li, H., & Suits, A. G. (2020). Universal crossed beam imaging studies of polyatomic reaction dynamics. *Physical Chemistry Chemical Physics*, *22*(20), 11126-11138.
2. Nuñez-Reyes, D., Loison, J. C., Hickson, K. M., & Dobrijevic, M. (2019). Rate constants for the N (2D) + C2H2 reaction over the 50–296 K temperature range. *Physical Chemistry Chemical Physics*, *21*(40), 22230-22237.
3. Steglich, M., Knopp, G., & Hemberger, P. (2019). How the methyl group position influences the ultrafast deactivation in aromatic radicals. *Physical Chemistry Chemical Physics*, *21*(2), 581-588.
4. Bouwman, J., Bodi, A., & Hemberger, P. (2018). Nitrogen matters: the difference between PANH and PAH formation. *Physical Chemistry Chemical Physics*, *20*(47), 29910-29917.
5. Fioroni, M., Savage, R. E., & DeYonker, N. J. (2019). On the formation of phosphorous polycyclic aromatics hydrocarbons (PAPHs) in astrophysical environments. *Physical Chemistry Chemical Physics*, *21*(15), 8015-8021.

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