

SUPPLEMENTAL INFORMATION

A Combined Experimental and Computational Study on the Reaction Dynamics of the 1-Propynyl (CH_3CC) – 1,3-butadiene ($\text{CH}_2\text{CHCHCH}_2$) System and the Formation of Toluene Under Single Collision Conditions

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Two Channel Fit

A two-channel fit (Figures S1-S3) of the laboratory data was also feasible based on the reaction energies of the most abundant products as predicted by RRKM (section 4.4) - an outcome that is biased by the computational arm of this study. This approach resulted in branching ratios of 62 ± 10 % (low exoergicity) and 38 ± 10 % (high exoergicity) for the 1,3-heptadien-5-yne (**p1**) and toluene (**p2**) product channels.

The $P(E_T)$ s have a maximum energy cutoff of 148 ± 20 kJ mol⁻¹ and 413 ± 36 kJ mol⁻¹ which, considering the experimental collision energy of 40 ± 1 kJ mol⁻¹, support the formation of **p1** and **p2** in overall exoergic reactions. The low energy product channel holds a distribution maximum at 17 ± 2 kJ mol⁻¹ with 30 ± 6 % of the available energy appearing as translational motion, while the high energy channel has its distribution maximum at 24 ± 2 kJ mol⁻¹ with 25 ± 3 % of the available energy deposited into the translational degrees of freedom. The relatively low fraction of energy used for translation of nascent C₇H₈ along with the away-from-zero translational energy peaking of the $P(E_T)$ for each channel suggests the reaction proceeds to products indirectly via activated C₇H₉ intermediate(s) that decompose via tight exit transition states. The **p1** isomer results from decomposition of **i1** and/or **i2** via exit barriers lying 14 and 20 kJ mol⁻¹ above the **p1** + **H** product channel, respectively, which agrees well with the low-energy channel's derived $P(E_T)$ holding a maximum near 17 kJ mol⁻¹. On the other hand, toluene (**p2**) can only be formed by hydrogen atom emission from **i16** over a barrier 20 kJ mol⁻¹ above the product channel and is consistent with the $P(E_T)$ of this channel whose maximum occurs near 24 kJ mol⁻¹.

The indirect aspect of the reaction mechanism is corroborated by the derived $T(\theta)$ functions where each is forward-backward symmetric and portrays nonzero intensity at all angles. The best-fitting $T(\theta)$ for the low-energy channel is flat (isotropic), while the high-energy channel has a maximum at 90° which suggests geometrical constraints on the exit transition state where the hydrogen atom is emitted perpendicular to the rotational plane of the decomposing intermediate and parallel to the total angular momentum vector. For the low energy channel, the computed exit geometries of the departing hydrogen atom via **i1** → **p1** + **H** and **i2** → **p1** + **H** are 69° and 0° (see Figure 7), i.e. elimination from **i1** is expected to occur almost perpendicularly to the plane of rotation, whereas elimination from **i2** occurs within the plane. This finding is in agreement with the derived $T(\theta)$ for the low-energy product channel (Figure 5) which has a best-fit distribution that is flat and could be varied slightly so that the maximum occurred at the poles (0° and 180°; in the plane) or at 90° (sideways). The computed exit geometry for the departing hydrogen atom in the **i6** → **p2** + **H** transition state is 72° with respect to the rotating plane of the decomposing complex (Figure 7) and is consistent with the sideways scattering depicted in the $T(\theta)$ of the highly exoergic channel.

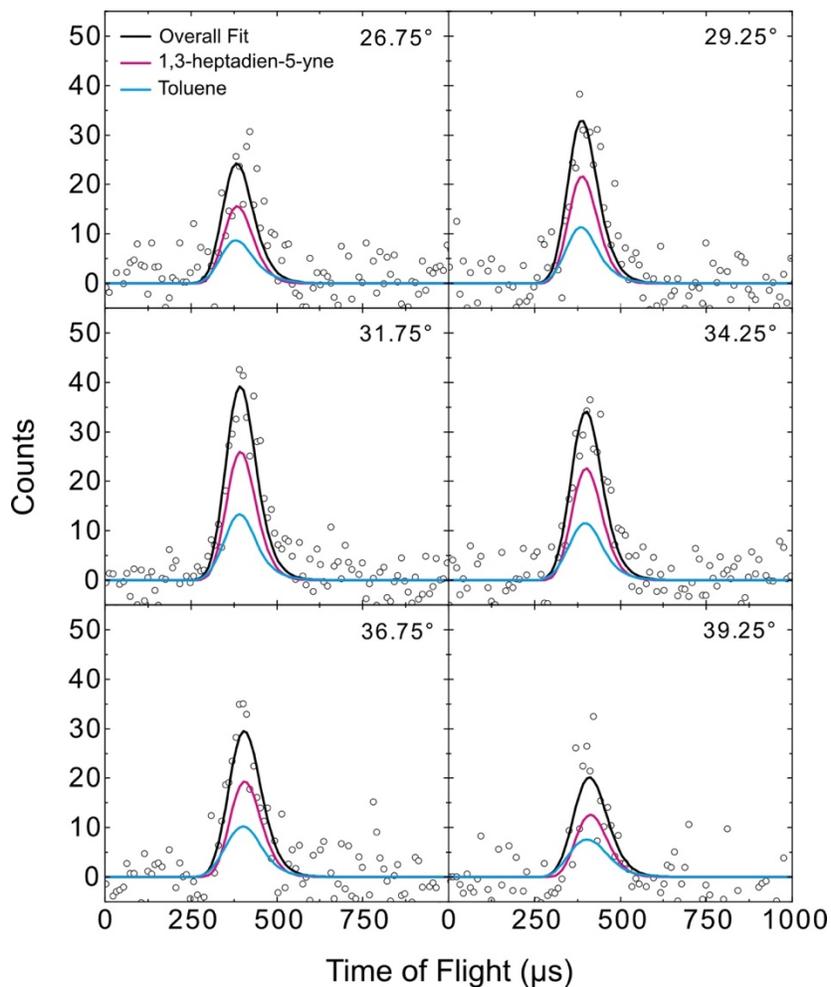


Figure S1. Time-of-flight data (TOF) recorded at m/z 91 ($C_7H_7^+$) for the reaction of 1-propynyl (CH_3CC ; X^2A_1) radicals with 1,3-butadiene ($CH_2CHCHCH_2$; X^1A_g). The circles represent the experimental data, red and blue lines represent the calculated distributions for the 1,3-heptadien-5-yne (**p1**) and toluene (**p2**) isomers, respectively, and the black line their sum.

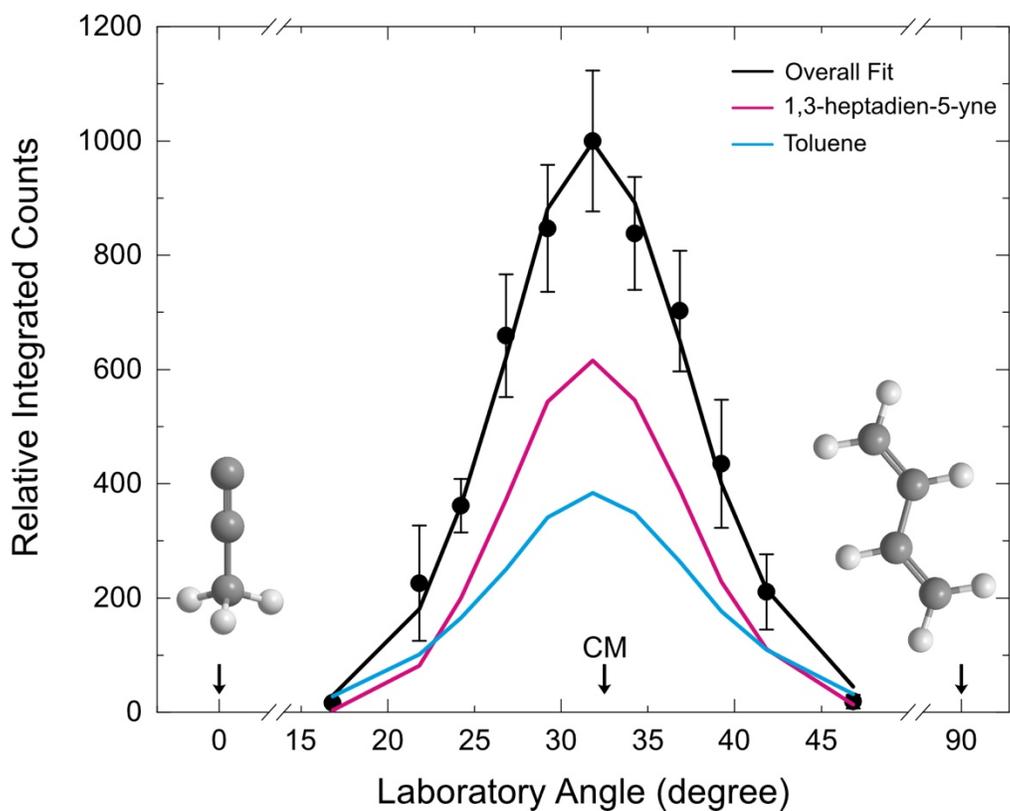


Figure S2. Laboratory angular distribution obtained at mass-to-charge ratio (m/z) 91 ($C_7H_7^+$) from the reaction of the 1-propynyl (CH_3CC ; X^2A_1) radical with 1,3-butadiene ($CH_2CHCHCH_2$; X^1A_g). The circles represent the experimental data, red and blue lines represent the calculated distributions for the 1,3-heptadien-5-yne (**p1**) and toluene (**p2**) isomers, respectively, and the black line their sum

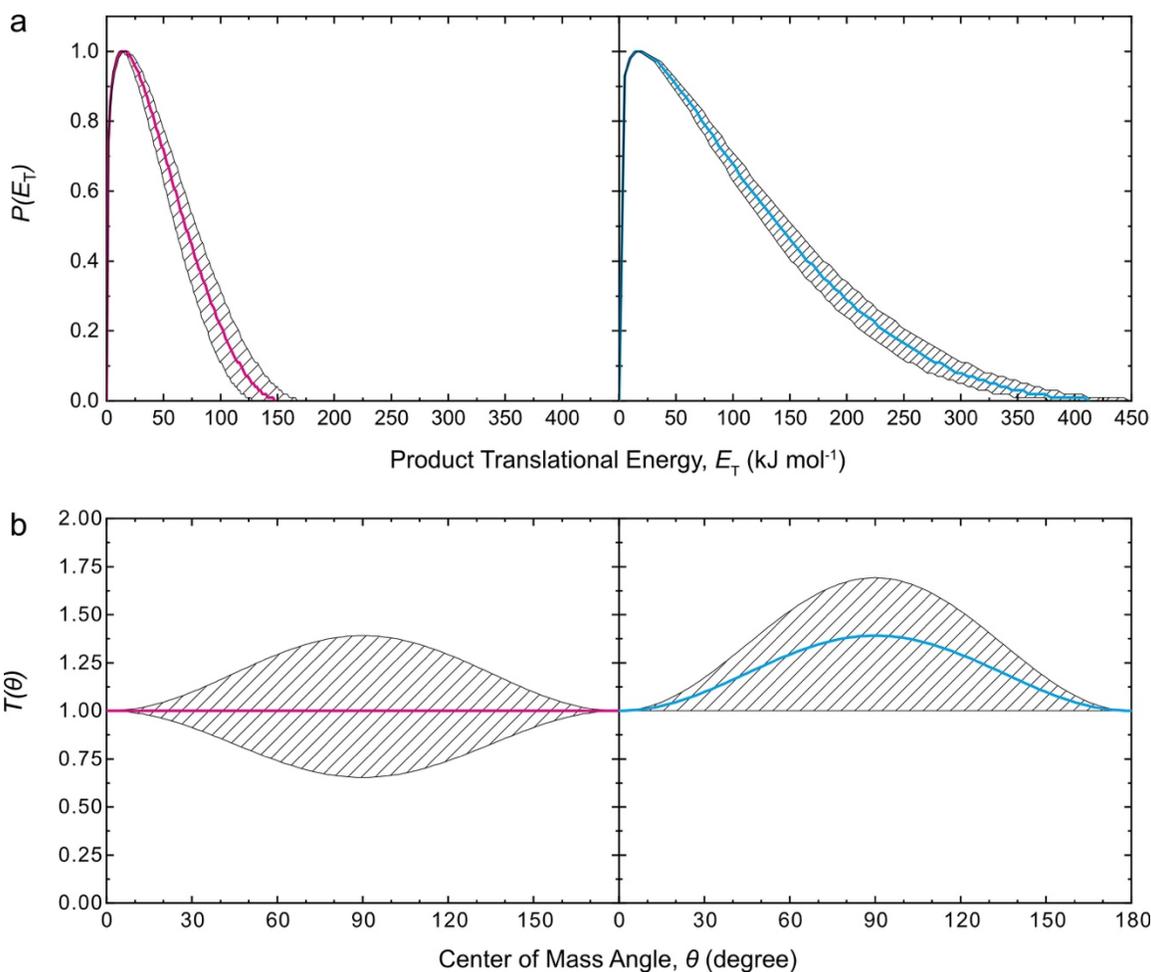


Figure S3. (a) Center-of-mass translational energy (a) and angular (b) flux distributions leading to the formation of the 1,3-heptadien-5-yne (red) and toluene (blue) molecules. Hatched areas indicate the acceptable upper and lower limits and solid lines the best-fit functions.