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A combined experimental and computational study on the reaction dynamics of the 1-propynyl (CH_3CC , X^2A_1) – propylene (CH_3CHCH_2 , X^1A') system: formation of 1,3-dimethylvinylacetylene ($\text{CH}_3\text{CCCHCHCH}_3$, X^1A') under single collision conditions

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A combined experimental and computational study on the reaction dynamics of the 1-propynyl (CH_3CC , X^2A_1) – propylene (CH_3CHCH_2 , X^1A') system: formation of 1,3-dimethylvinylacetylene ($\text{CH}_3\text{CCCHCHCH}_3$, X^1A') under single collision conditions

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ABSTRACT

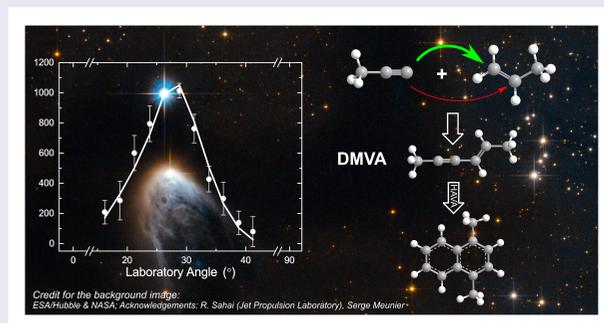
The reaction of the 1-propynyl radical (CH_3CC ; X^2A_1) with propylene (CH_3CHCH_2 ; X^1A') was studied in a crossed molecular beam machine at a collision energy of $37 \pm 1 \text{ kJ mol}^{-1}$. Experimental data combined with high-level electronic structure (CCSD(T)-F12/cc-pVTZ-F12// ω B97X-D/6-311G(d,p)) and RRKM calculations reveal the reaction mechanism. The overall barrierless and exoergic reaction involves indirect reaction dynamics and commences preferentially with addition of 1-propynyl with its radical centre to the carbon–carbon double bond at the terminal carbon atom of propylene. This work focuses on molecular mass growth process (hydrogen loss channels) although theory suggests methyl loss as a prevalent channel. In these processes, the C_6H_9 collision complexes either emit atomic hydrogen or undergo isomerisation followed by atomic hydrogen loss to preferentially yield the *cis/trans* isomers of 1,3-dimethylvinylacetylene (2-hexen-4-yne) as the primary product. Analysis of reaction dynamics of 1-propynyl and ethynyl radicals with propylene along with their fractional abundance in deep space suggests formation of methyl- and dimethyl derivatives of vinylacetylene in cold molecular clouds. Once formed they may engage in fundamental molecular mass growth processes via the barrierless Hydrogen Abstraction Vinylacetylene Addition mechanism that leads to the formation of methyl- and dimethylnaphthalenes thus providing a versatile route to methyl-substituted PAHs in interstellar medium.

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1. Introduction

Up to 20% of the interstellar carbon budget is considered to be locked up as polycyclic aromatic hydrocarbons (PAHs) [1] – molecules consisting of multiple fused aromatic rings – along with their protonated, ionised, (de)hydrogenated, alkylated, and nitrogen-substituted counterparts [2–7]. Their ubiquitous presence has been

inferred from the unidentified infrared emission (UIE) bands observed in the range of 3–14 μm [8] and through the diffuse interstellar bands [9,10], discrete absorption features superimposed on the interstellar extinction curve ranging from the blue part of the visible (400 nm) to the near-infrared (1.2 μm). PAHs are also suspected to play a significant role in the astrobiological evolution

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of the interstellar medium and are contemplated as key nucleation sites leading to carbonaceous nanoparticles also referred to as interstellar grains [11–14]. Although significant experimental and computational studies have been dedicated toward unravelling the elementary mechanisms synthesising PAHs in circumstellar envelopes [2,15–21], the origin of PAHs in deep space represents still a fundamental paradox of modern astrophysics with typical lifetimes of PAHs of 10^8 years, but time scales for their injection from carbon-rich circumstellar envelopes of 2×10^9 years [22–25]. This discrepancy could be resolved by inferring the existence of hitherto elusive low-temperature routes to a rapid growth of PAHs in molecular clouds to counterbalance their destruction [26]. One of these routes is the rapid, barrierless **H**ydrogen **A**bstraction **V**inylacetylene **A**ddition (HAVA) mechanism [2,27–32]. HAVA starts with a barrierless formation of a van-der-Waals complex, followed by isomerisation of this complex through an addition of the radical centre of the aromatic radical reactant to the terminal sp^2 -carbon atom of the vinylacetylene (CH_2CHCCH) molecule leading to a resonantly stabilised free radical (RSFR) intermediate. This RSFR undergoes hydrogen migration from the aromatic ring to the vinylacetylene followed by cyclisation, hydrogen migration, and atomic hydrogen loss along with aromatisation. Compared to competing mechanisms such as **H**ydrogen **A**bstraction – C_2H_2 (acetylene) **A**ddition (HACA) [17–20] and **P**henyl**A**ddition**D**ehydro **C**yclization (PAC) [2,21], HAVA has two notable features: (1) the lack of an entrance barrier and (2) a single bimolecular collision event leading de-facto to ring annulation; these characteristics make HAVA an ideal candidate for a low-temperature synthesis of aromatics in molecular clouds.

The formation of alkylated PAHs is even less understood. Alkylated aromatics such as methylphenanthrene ($C_{15}H_{12}$), methyltriphenylene ($C_{19}H_{14}$), methyl-, dimethyl-, and trimethylnaphthalene ($C_{11}H_{10}$, $C_{12}H_{12}$, $C_{13}H_{14}$) were detected in carbonaceous chondrites such as Murchison [33–37], Allende [6,37], Aguas Zarcas, Mukundpura, and Kolang [38,39]. Studies on their formation are contradictory. Speculative works link their origin to aqueous and thermal conditions experienced by the meteorites [40–42], while competing studies suggest that alkylated aromatics were formed prior to their incorporation into meteoritic parent-bodies [37,38,41,43]. Therefore, although meteorites present a record of the chemistry that occurred in the interstellar medium and in the solar nebula, the question ‘How alkylated PAHs were formed?’ remains open. An answer to this question is important because, at the present time, the $3.4 \mu m$ feature of the UIE [44–46] still cannot

be thoroughly accounted for. The C–H stretching in aliphatic group attached to PAHs are believed [47–51] to be responsible for that feature, but the lack of a reasonable mechanism of sustainable formation of alkylated PAHs in interstellar medium places fundamental constraints to this hypothesis [49].

The 1-propynyl radical (CH_3CC ; X^2A_1) has received considerable attention for its participation in molecular growth processes to hydrogen deficient hydrocarbons in cold molecular clouds such as toward TMC-1 [52–59]. Albeit 1-propynyl has not been detected in any extraterrestrial environment yet, its potential precursor methylacetylene (propyne; CH_3CCH) holds high fractional abundances of up to 1×10^{-8} in TMC-1 [60,61]. While thermal decomposition [62] of methylacetylene mostly produces the propargyl radical (CH_2CCH), UV photolysis [63–65] can lead to 1-propynyl radical (CH_3CC). This finding reveals that the 1-propynyl radical is likely present in cold molecular clouds. Being higher in energy by 168 kJ mol^{-1} compared to the propargyl radical [66], it is very reactive and can barrierlessly add to carbon–carbon double and triple bonds of hydrocarbons even at low temperatures [54–58]. This opens up barrier-free pathways to the formation of complex hydrocarbon molecules in cold, carbon-rich environments such as in the atmosphere of Titan [53] and toward molecular clouds like TMC-1 [52,59]. In this context, the 1-propynyl radical can be considered as an alkyl-substituted ethynyl radical (C_2H , $X^2\Sigma^+$). In this case, all 1-propynyl radical (CH_3CC) reactions studied under single collision conditions [54–58] (Figure 1) can be divided into two groups: (1) the methyl group of 1-propynyl acts as a spectator and (2) the methyl group is actively engaged in the reaction dynamics and hence reaction mechanism. The first group includes reactions with acetylene ($HCCH$; X^2A_1) [54], ethylene (H_2CCH_2 ; X^1A_{1g}) [57], methylacetylene (CH_3CCH ; X^1A_1) [56], 1,3-butadiene ($CH_2CHCHCH_2$; X^1A_g) [55], and benzene (C_6H_6 ; X^1A_{1g}) [58]. These bimolecular reactions lead predominantly to the formation of methyl-diacetylene (CH_3CCCCH) [54], 1-pentene-3-yne ($CH_2CHCCCCH_3$) [57], dimethyl-diacetylene ($CH_3CCCCCH_3$) [56], toluene ($C_6H_5CH_3$) [55], and 1-phenyl-propyne ($C_6H_5CCCH_3$) [58], respectively. The nascent molecules are methyl-substituted analogues of the product of the corresponding ethynyl reaction (Figure 1) [67–74]. On the other hand, the reaction of the 1-propynyl radical with allene (CH_2CCH_2 ; X^1A_1) [56] can be attributed to the second group. The potential energy surface for bimolecular reaction of 1-propynyl radical with allene includes channels that can lead to eleven distinct reaction products. Pathways to acyclic products are statistically more preferable although two

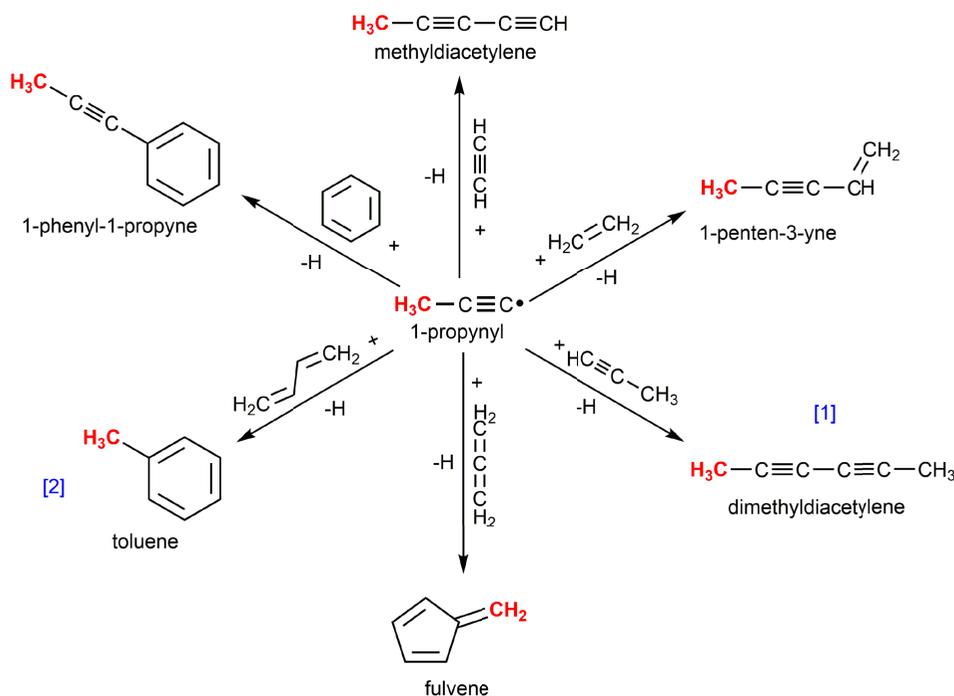


Figure 1. Elementary reactions of the 1-propynyl radical studied under single-collision conditions. [1] – 1-propynylallene is also formed at a ratio of dimethyldiacetylene versus 1 propynylallene of 9: 0.1. [2] – 1,3-heptadien-5-yne, 5-methylene-1,3-cyclohexadiene, 3-methylene-1-hexen-4-yne are also formed as minor products.

of the three initially formed C_6H_7 collision complexes have two low-energy vibrational modes that increase their life-time and promote rearrangement to the same intermediate. This dynamically narrows all possible pathways to one outcome where fulvene statistically dominates, which was observed experimentally [56]. The analogous reaction of ethynyl with allene only produces acyclic products, i.e. ethynylallene ($CHCCHCCH_2$) and 1,4-pentadiyne ($CHCCH_2CCH$) [75].

In this article, we present an experimental and theoretical investigation of the formation of 1,3-dimethylvinylacetylene (2-hexen-4-yne) under single collision conditions through the elementary gas phase reaction of the 1-propynyl radical (CH_3CC ; X^2A_1) with propylene (CH_3CHCH_2 ; X^1A') exploiting crossed molecular beams. We also discuss potential reaction pathways of 1,3-dimethylvinylacetylene (2-hexen-4-yne) to mono- and disubstituted isomers of methylvinylacetylene that adopt the HAVA mechanism leading to distinctly methyl-substituted naphthalene derivatives in the interstellar medium thus expanding our view of how alkylated PAHs may form in deep space.

2. Experimental and computational methods

2.1. Crossed molecular beams

The reaction of the 1-propynyl radical (CH_3CC ; X^2A_1) with propylene (CH_3CHCH_2 ; X^1A') was conducted

under single-collision conditions exploiting a crossed molecular beam machine [76,77]. The experimental setup is discussed in detail in references [54,55,58]; here we will only provide a brief description. A pulsed 1-propynyl radical beam was generated via photodissociation (193 nm; 20 mJ pulse⁻¹; 30 Hz) of 1-iodopropyne (CH_3CCI ; TCI, 99%+) seeded at a level of 0.5% in helium (99.9999%, Matheson) in the primary source chamber [54,55,58]. This beam was skimmed and velocity selected using a four-slot chopper wheel achieving a peak velocity $v_p = 1721 \pm 38$ m s⁻¹ and speed ratio $S = 11.5 \pm 1.8$. This supersonic radical beam crossed a pulsed molecular beam of propylene (Sigma-Aldrich, $\geq 99\%$; $v_p = 840 \pm 10$ m s⁻¹, $S = 11.0 \pm 0.2$) [78] perpendicularly in the scattering chamber at a mean collision energy of $E_C = 37 \pm 1$ kJ mol⁻¹. The secondary pulsed valve was triggered 86 μ s prior to the primary pulsed valve. The reactively scattered products were detected by a triply differentially pumped universal quadrupole mass spectrometric (QMS) detector under ultra-high vacuum (UHV; 10^{-12} Torr) conditions. The latter is operated in the time-of-flight (TOF) mode, i.e. recording the flight time of ions at a distinct mass-to-charge ratio (m/z), and is rotatable within the plane defined by both reactant beams. Neutral products were ionised by electron ionisation at 80 eV (2 mA), filtered according to the selected m/z , and then detected using Daly-type detector [79]. Angular resolved TOF spectra were recorded at discrete laboratory angles,

which were integrated and normalised with respect to the TOF at the centre-of-mass (CM) angle Θ_{CM} to extract the laboratory angular distribution. Up to 7×10^6 TOF spectra were taken in 2.5° steps between $16.25^\circ \leq \Theta \leq 41.25^\circ$ with the 1-propynyl beam defined at $\Theta = 0^\circ$. To gain information on the reaction dynamics, the laboratory angular distribution and TOF spectra were fit utilising a forward convolution routine; this created user-defined CM translational energy ($P(E_T)$) and angular ($T(\theta)$) flux distributions, which were refined iteratively until a satisfactory fit of the laboratory data was achieved [80,81]. These functions were exploited to develop a flux contour map $I(\mathbf{u}, \theta) \approx P(\mathbf{u}) \times T(\theta)$ with the centre-of-mass velocity \mathbf{u} [82], which reveals an overall image of the outcome of the reaction.

2.2. Electronic structure calculations

The hybrid density functional theory (DFT) ω B97X-D [83] method in conjunction with the 6-311G(d,p) basis set were utilised for geometry optimisation of various reactants, products, intermediates, and transition states on the C_6H_9 potential energy surface (PES) accessed by the reaction of propynyl radical with propylene and the same ω B97X-D/6-311G(d,p) level of theory was used to compute vibrational frequencies for each stationary structure, with the goal to evaluate zero-point vibrational energy corrections (ZPE) and to obtain molecular parameters required for rate constant calculations. Next, single-point energies of all optimised structures were refined employing the explicitly correlated

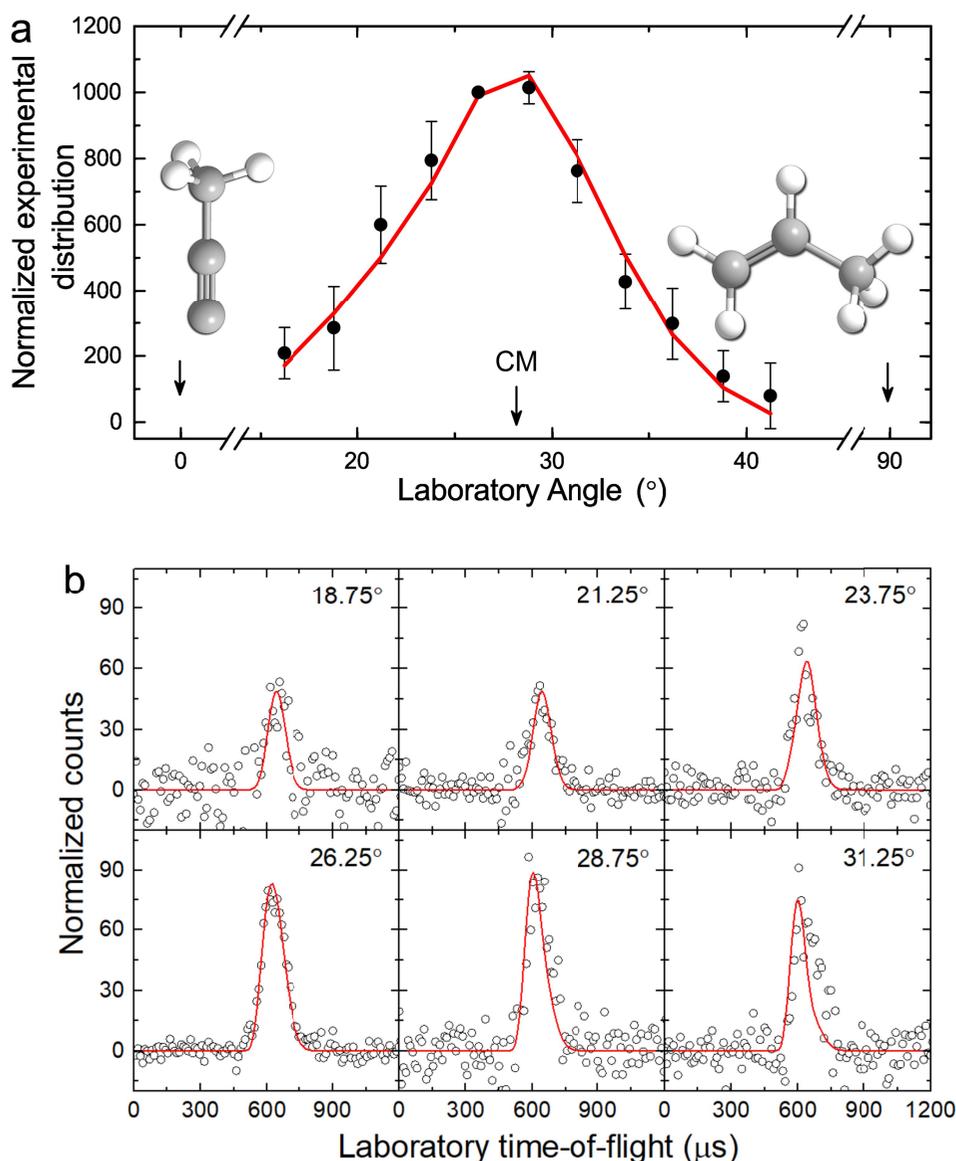


Figure 2. (a) Time-of-flight spectra and (b) laboratory angular distribution recorded at $m/z = 79$ (C_6H_7^+) for products formed in the reaction of the 1-propynyl radical ($\text{CH}_3\text{CC}; X^2A_1$) with propylene ($\text{C}_3\text{H}_6; X^1A'$). The circles represent the experimental data and the solid lines the best fit.

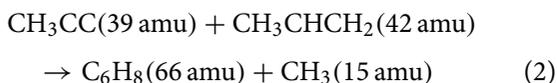
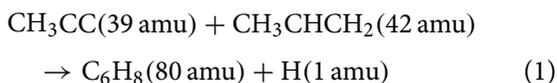
couple clusters method with single and double excitations and triple excitations treated perturbatively, CCSD(T)-F12 [84,85], with Dunning's correlation-consistent cc-pVTZ-f12 basis set [86]. The overall CCSD(T)-F12/cc-pVTZ-f12// ω B97X-D/6-311G(d,p) + ZPE(ω B97X-D/6-311G(d,p)) approach thus used to obtain relative energies of various species on the C_6H_9 PES is expected to be chemically accurate, within 4 kJ mol^{-1} or better [87]. The GAUSSIAN 09 [88] and MOLPRO 2010 [89] quantum chemistry packages were employed for the DFT and coupled clusters calculations, respectively.

The Rice–Ramsperger–Kassel–Marcus (RRKM) theory method [90–92] was applied to assess energy-dependent rate constants for all unimolecular reaction steps occurring on the C_6H_9 PES after the entrance bimolecular reaction steps. These computations utilised the relative energies and molecular parameters generated by the electronic structure calculations. The internal energy for each C_6H_9 species was taken as the sum of the collision and chemical activation energy, with the latter being defined as a negative of the relative energy of the particular structure on the PES with respect to the separated $C_3H_3 + C_3H_6$ reactants. The energy-dependent rate constant calculations were carried out using our in-house code at the zero-pressure limit [56], mimicking the crossed molecular beams and the outer space conditions. Finally, the RRKM-computed rate constants were used to evaluate the product branching ratios within steady-state approximation [56,93].

3. Results

3.1. Laboratory frame

Reactive scattering signal for the reaction of the 1-propynyl radical (CH_3CC ; 39 amu) with propylene (CH_3CHCH_2 ; 42 amu) was monitored at mass-to-charge ratios $m/z = 80$ ($C_6H_8^+$), 79 ($C_6H_7^+$), and 78 ($C_6H_6^+$). The TOF spectra obtained at all three m/z overlap after scaling suggesting that signal from $m/z = 80$, 79, and 78 originated from the same reaction channel forming the heavy product (C_6H_8 , 80 amu) and atomic hydrogen (H, 1 amu) (reaction 1). Signal at $m/z = 79$ and 78, therefore, arise from dissociative electron ionisation of the C_6H_8 product in the electron ioniser. The background interference at $m/z = 66$ and 65 prevented detection of a possible methyl loss (reaction 2).



The best signal-to-noise ratio was detected at $m/z = 79$; hence $m/z = 79$ was used to collect TOF spectra at discrete angular intervals 2.5° from 16.25° to $41.25^\circ \ominus$ (Figure 2(a)). The resulting TOFs were then normalised with respect to the CM angle to obtain laboratory angular distribution (Figure 2b). Notable features of the laboratory angular distribution include its width of at least 25° and symmetry around the CM angle ($28.5 \pm 0.3^\circ$); these findings propose that the C_6H_8 products were formed via

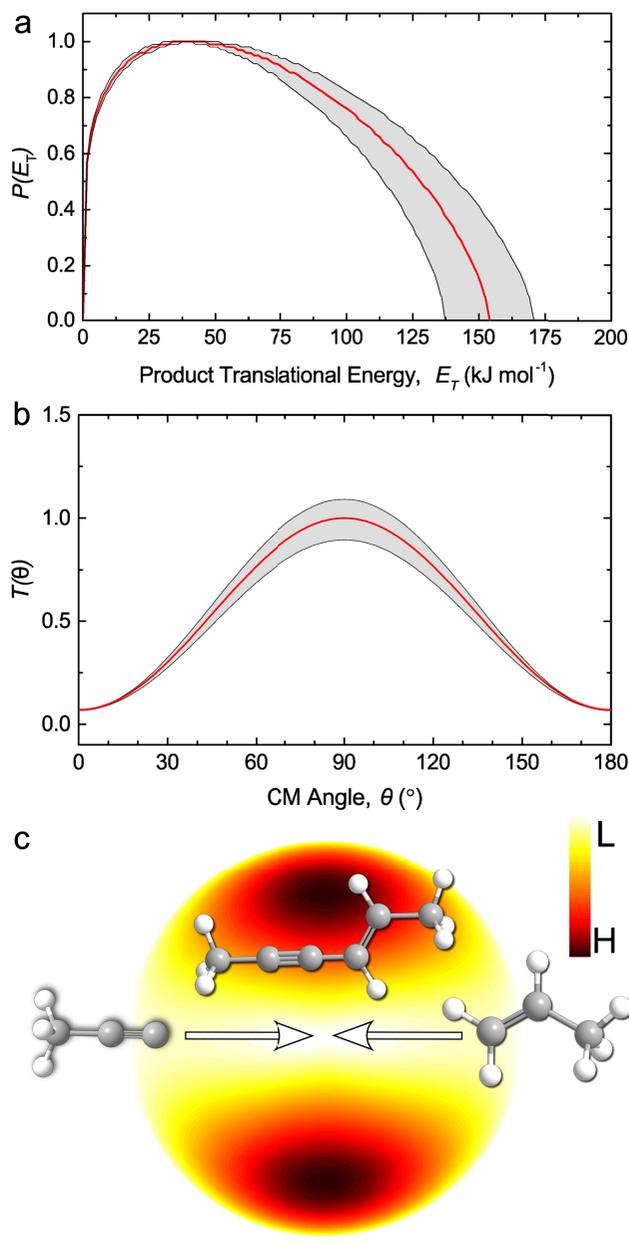


Figure 3. Centre-of-mass translational energy (a), angular flux distribution (b), and corresponding flux contour map (c) for the formation of C_6H_8 plus atomic hydrogen via the reaction of the 1-propynyl radical ($CH_3CC; X^2A_1$) with propylene ($C_3H_6; X^1A'$). Grey-filled areas represent regions of acceptable fits.

indirect scattering dynamics through complex formation involving one or more C_6H_9 intermediates [76,82,94].

3.2. Centre-of-mass frame

The laboratory data could be fit with a single channel (reaction 1) with a reaction cross section proportional to $E_C^{-1/3}$ for entrance-barrierless reactions (Figure 2(a)) dominated by long-range dipole – dipole interactions [95]. The best-fit CM functions are depicted in Figure 3; the grey-filled areas define the limits of the acceptable fits. The high-energy cut-off of the translational energy flux distribution $P(E_T)$ can be determined for those molecules born without internal excitation through energy conservation via $E_{max} = E_C - \Delta_r G$, where E_C and $\Delta_r G$ represent the collision energy and the reaction energy, respectively. The derived $P(E_T)$ reveals an E_{max} of $154 \pm 17 \text{ kJ mol}^{-1}$. Subtracting the collision energy of $37 \pm 1 \text{ kJ mol}^{-1}$, we derived a reaction energy of $117 \pm 18 \text{ kJ mol}^{-1}$ for the hydrogen loss product. Further, the distribution maximum of the $P(E_T)$ at $29\text{--}52 \text{ kJ mol}^{-1}$ indicates a tight exit translation state in the exit channel and hence a significant electron reorganisation from the decomposing C_6H_9 complex(es) to the final products. The average translation energy of $66 \pm 7 \text{ kJ mol}^{-1}$ suggests that $43 \pm 9\%$ of the total energy is channelled into product translation. Additional information on the reaction dynamics can be obtained by inspecting CM angular distribution $T(\theta)$ (Figure 3(b)). The $T(\theta)$ displays forward–backward symmetry and shows non-zero intensity from 0 to 180° . These findings propose indirect scattering dynamics through C_6H_9 complex(es) and

lifetime of C_6H_9 intermediates longer than the(ir) rotational period(s) [95]. Finally, the maximum of the $T(\theta)$ at 90° highlights geometrical constraints of the decomposing complex (‘sideways scattering’) revealing that the hydrogen atom is eliminated nearly perpendicularly to the plane of decomposing complex and almost parallel to the total angular momentum vector [95,96]. These findings are also supported by the flux contour map (Figure 3(c)), which shows an overall image of the reaction and the scattering process.

4. Discussion

We are combining now our experimental data with electronic structure and statistical calculations to reveal the underlying reaction mechanism(s). The full potential energy surface (PES) (Figure S1–S3), which includes 18 products isomers (**p1–p18**), 22 intermediates (**i1–i22**), and 65 transition states, along with results of RRKM calculations (Table S1 and S2) are compiled in the Supporting Information. Reaction energies were calculated with an accuracy of 4 kJ mol^{-1} . According to RRKM results, methyl loss channel should dominate in this reaction, however, its experimental detection was hidden by background interference. Notwithstanding, the main objective of this publication is to explore a molecular mass grow process, i.e. the potential formation of **p1–p6** along with atomic hydrogen elimination (Figure 4) that together account up to 17% of the total product yield. The energies of formation of 2-methylpent-1-en-3-yne (**p1**, -117 kJ mol^{-1}), *cis*-2-hexen-4-yne (**p2**, -117 kJ mol^{-1}), and *trans*-2-hexen-4-yne (**p3**, -116 kJ mol^{-1}) are in a good agreement with an experimentally derived

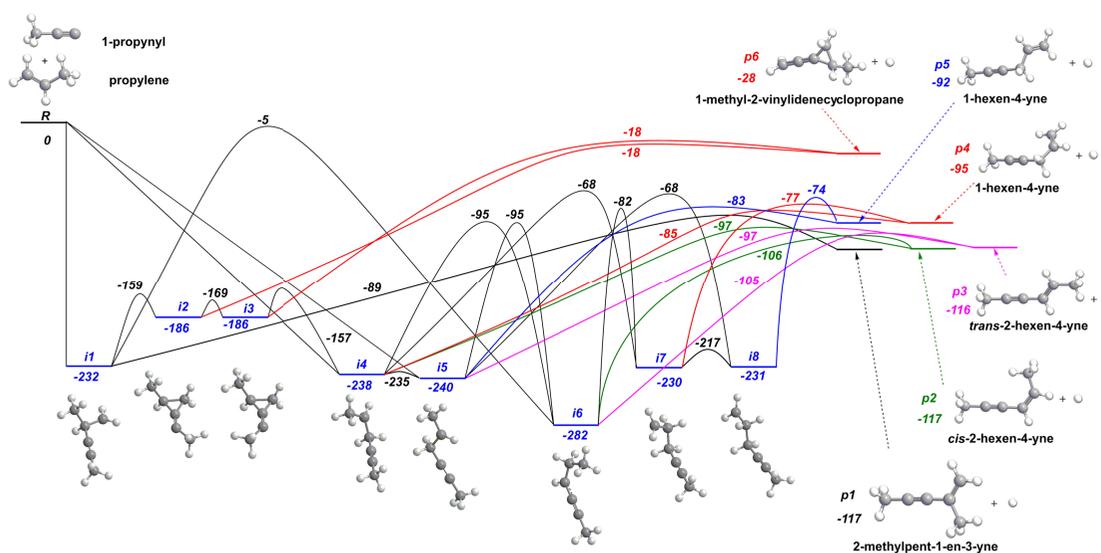


Figure 4. Potential energy surface for the bimolecular reaction of the 1-propynyl (CH_3CC ; X^2A_1) radical with propylene (CH_3CHCH_2 , X^1A') leading to C_6H_8 plus H products calculated at the CCSD(T)-F12/cc-pVTZF12// ω B97X-D/6-311G(d,p) level of theory. Relative energies of various species are shown in kJ mol^{-1} .

reaction energy of $-117 \pm 18 \text{ kJ mol}^{-1}$. We also cannot exclude the formation of the high-energy isomer 1-methyl-2-vinylidenecyclopropane (**p6**; -28 kJ mol^{-1}) and two conformers of 1-hexen-4-yne (**p4**, -95 kJ mol^{-1} ; **p5**, -92 kJ mol^{-1}), since they might be masked in the low energy section of the CM translational energy distribution (Figure 3(a)).

The calculations reveal that the reaction has three barrierless entrance channels via addition of the 1-propynyl radical to the double bond of propylene ($\gamma\text{CH}_3\text{-}\beta\text{CH}=\alpha\text{CH}_2$) at the α or β positions leading either to **i4/i5** or to intermediate **i1**, respectively. Intermediate **i1** can undergo migration of the 1-propynyl moiety to the α position via three-carbon ring structures (**i2** and **i3**) to **i4** with a barrier of 73 kJ mol^{-1} . Alternatively, intermediate **i1** undergoes a γCH_3 -shift to the αC atom forming **i6** passing a much higher transition state located only 5 kJ mol^{-1} below the energy of the separated reactants. Isomers **i4/i5** can easily be interconverted through the low energy barrier of only 3 kJ mol^{-1} or form **i7/i8**, respectively via hydrogen atom shift. Intermediate **i6** also can be formed by hydrogen migration from the central CH_2 group of **i4/i5**. In the next step, **i6** can undergo hydrogen migration from the terminal methyl group yielding **i7**, which can then isomerise to **i8** via a barrier of 13 kJ mol^{-1} .

How can the products be formed? **p1** can be accessed via hydrogen elimination from **i1** with an exit barrier 143 kJ mol^{-1} , while **p6** is synthesisable from **i2** and **i3**; the unimolecular decompositions of these intermediates have rather loose exit transition states located only 10 kJ mol^{-1} above the separated products. Note that the formation of **p1** and **p6** could only be the result of the addition of 1-propynyl to the less sterically accessible β carbon atom of propylene. Pathways leading to formation of **p2-p4** are more diverse and commence with the addition of 1-propynyl to the α position in propylene molecule. Notable, pathways leading to *cis/trans* 2-hexen-4-yne (**p2** and **p3**) may involve hydrogen loss from **i6** – a resonantly stabilised secondary carbon-centered radical which represents the global minimum of this part of the C_6H_9 PES. The computed geometries of these exit transition states leading to **p2** and **p3** reveal that the hydrogen atom is emitted at angles from 82 to 84° with respect to the rotation plane of the decomposing complexes (Figure 5). This finding is consistent with the experimentally observed sideways scattering depicted in $T(\theta)$ distribution. Therefore, the proposed pathways leading to **p2** and **p3** can be accounted for the experimental results.

Which products will dominate? The addition of the electrophilic 1-propynyl radical to the terminal carbon of propylene is favoured due to the higher cone of acceptance (less steric hindrance by the methyl group) and

an enhanced negative charge at α (-0.42) carbon atom as compared to the β (0) position [97]. Combining this addition mechanism with the location of the transition states to isomerisation, **p2/p3** should be the dominant products via reaction sequences (3) and (4). This analysis is supported by our RRKM calculations at collision energy of 37 kJ mol^{-1} with predicted fractions of 2-hexen-4-yne of 67% followed by 1-hexen-4-yne with 30% (Table S1). **p1 + H** only accounts for up to 3%, with calculated statistical branching ratios of high energy isomer **p6** yielding 0.0%. Note that 2-hexen-4-yne was also characterised as a main adduct of the hydrogen atom loss channel of the 1-propynyl plus propylene reaction in a slow flow reactor at 300 K via photoionization efficiency (PIE) curves [53]. The aforementioned findings are in

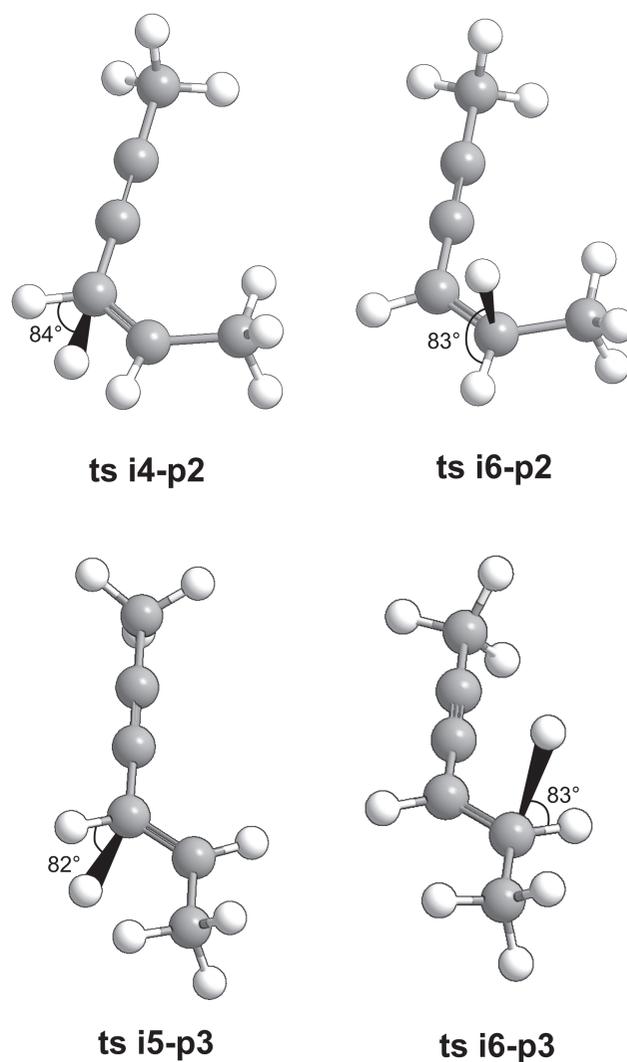


Figure 5. Computed geometries of the exit transition states from **i4**, **i5**, and **i6** leading to formation of *cis* (**p2**) and *trans* (**p3**) isomers of 2-hexen-4-yne. The angle for each departing hydrogen atom is given with respect to the rotation plane of the decomposing complex.

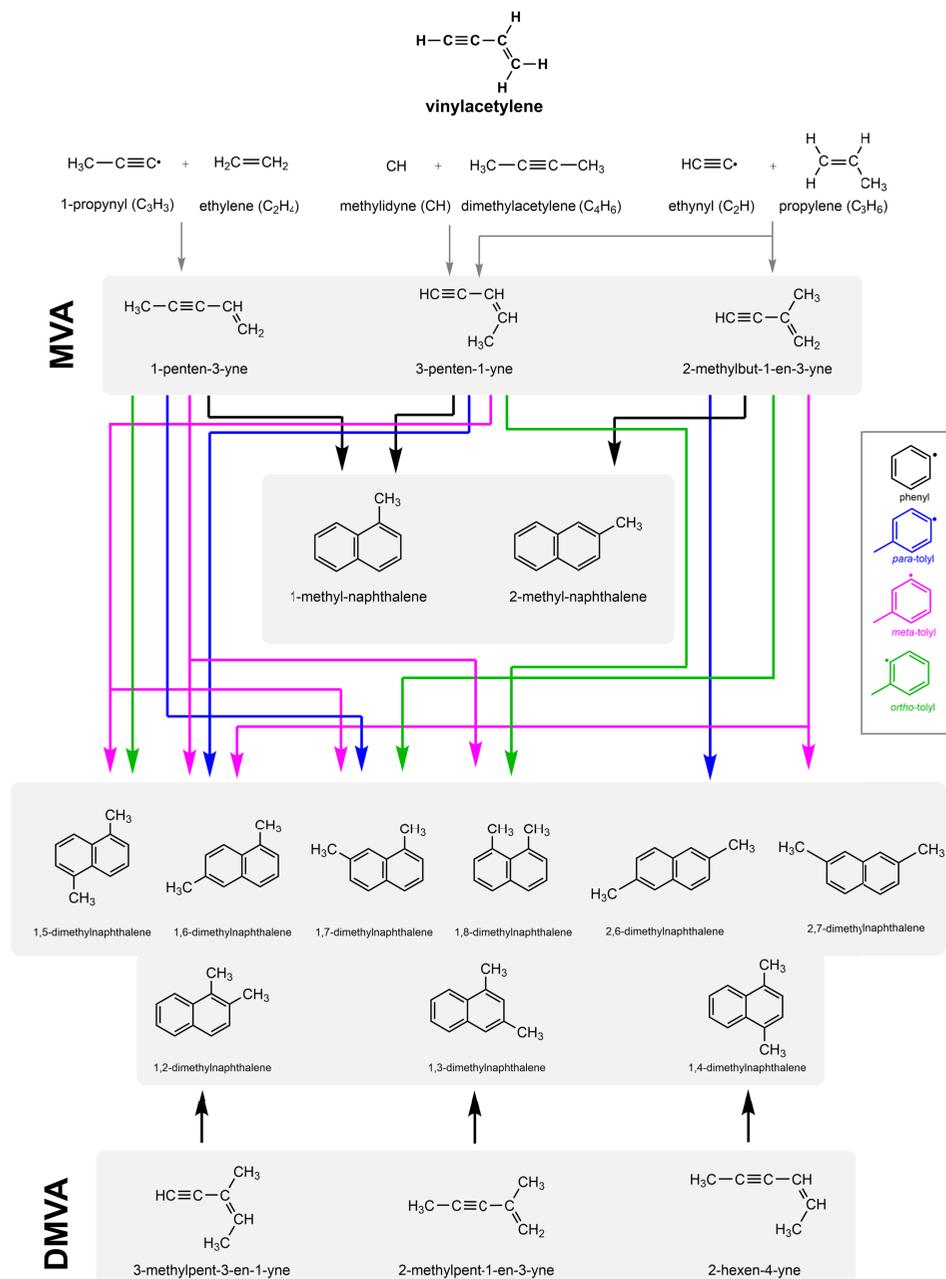
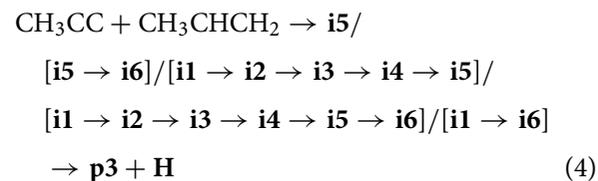
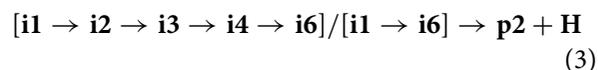
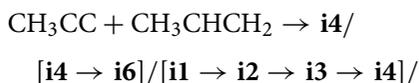


Figure 6. Reaction pathways leading to formation of methyl-substituted naphthalenes.

line with the results of the reaction of the D1-ethynyl radical (C_2D ; $X^2\Sigma^+$) with propylene (CH_3CHCH_2 ; X^1A') under single collision conditions [78]. In the ethynyl system, *cis/trans*-3-penten-1-yne ((HCC)CH = CH(CH₃), 3-methylvinylacetylene) – the mono-methyl substituted homologous counterpart – represents the dominating product. This reveals that the methyl group of the 1-propynyl radical acts solely as a spectator in the reaction with propylene.



5. Conclusion

We conducted the crossed molecular beam reaction of the 1-propynyl radical (CH_3CC ; X^2A_1) with propylene

(CH₃CHCH₂; X¹A') at a collision energy of 37 ± 1 kJ mol⁻¹ and merged the experimental data with electronic structure and RRKM calculations. The overall barrierless and exoergic reaction involves indirect reaction dynamics and commences preferentially with the addition of the 1-propynyl radical with its radical centre to the carbon-carbon double bond at the terminal (^αCH₂) carbon atom of propylene. RRKM results suggest that methyl loss channel should dominate in this reaction with branching ratio exceeding 80%, but its experimental detection was prevented by background interference. In this work we have focused on H-loss channels to explore a molecular mass growth processes accounted up to 17% of the total product yield. In these processes the C₆H₉ collision complexes either emit atomic hydrogen or undergo isomerisation via 1,2-H shift from ^αCH₂ group to ^βC-position followed by atomic hydrogen loss to preferentially yield the *cis/trans* isomers of 1,3-dimethylvinylacetylene (2-hexen-4-yne) as the primary product under single collision conditions. The methyl group of the 1-propynyl radical reactant remains a spectator throughout the reaction. Considering that the reaction has no entrance barrier, is exoergic, and all transition states involved are located below the energy of the separated reactants, the formation of 1,3-dimethylvinylacetylene (CH₃CCCHCHCH₃) via the reaction of the 1-propynyl radical with propylene represents a powerful molecular growth process to form a dimethylsubstituted vinylacetylene product – 2-hexen-4-yne – via a single collision event.

In deep space, propylene was detected toward TMC-1 with fractional abundances of 2 × 10⁻⁹ [98], while 1-propynyl is highly likely to be present in TMC-1 since its precursor methylacetylene holds a high fraction in TMC-1 up to 1 × 10⁻⁸ [60,61]. Therefore, we may predict that 1,3-dimethylvinylacetylene can be formed easily in TMC-1. Analogous barrierless reactions of the ethynyl radical with fractional abundances of 5 × 10⁻⁹ in OMC-1 [99] with propylene [78], and of 1-propynyl with ethylene (CRL 618 [100]) [54] may operate in cold molecular clouds. Once methyl- and dimethyl derivatives of vinylacetylene have been formed, these hydrogen deficient reactants may engage in fundamental molecular mass growth processes upon reactions with phenyl radicals (C₆H₅) [29] and tolyl radicals (CH₃C₆H₅) [31] via the barrierless HAVA mechanism (Figure 6). These processes can then yield to the formation of methyl and dimethyl naphthalenes thus providing a versatile route to methyl substituted aromatics and leading to a better understanding of the question 'How alkylated PAHs form in interstellar medium?'

Disclosure statement

No potential conflict of interest was reported by the author(s).

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