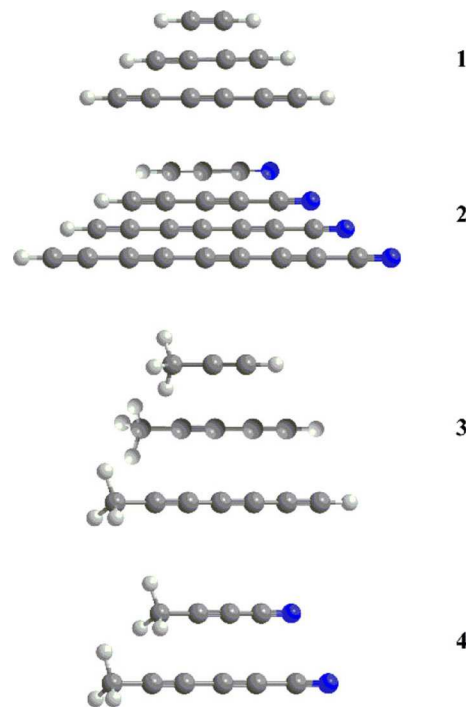


Gas Phase Formation of the Interstellar Molecule Methyltriacetylene

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Methyltriacetylene – the largest methylated polyacetylene detected in deep space – has been synthesized in the gas phase via the bimolecular reaction of the 1-propynyl radical with diacetylene under single-collision conditions. The barrier-less route to methyltriacetylene represents a prototype of a polyacetylene chain extension through a radical substitution mechanism and provides a novel low temperature route, in which the propynyl radical piggybacks a methyl group to be incorporated into methylated polyynes. This mechanism overcomes a key obstacle in previously postulated reactions of methyl radicals with unsaturated hydrocarbon, which fail the inclusion of methyl groups into hydrocarbons due to insurmountable entrance barriers thus providing a fundamental understanding on the electronic structure, chemical bonding, and formation of methyl-capped polyacetylenes. These species are key reactive intermediates leading to carbonaceous nanostructures in molecular clouds like TMC-1.

Since Swings' and Rosenfeld's pioneering detection of the very first molecule – the organic methylidyne radical $\text{CH}(X^2\Pi)$ – in the interstellar medium (ISM) more than 80 years ago,^[1] complex gas phase reaction networks integrating rapid ion-molecule^[2] and neutral-neutral reactions^[3] have played a central role in advancing our fundamental knowledge of the chemical evolution of the interstellar medium (ISM). Nonetheless, with close to 200 molecules detected in circumstellar and interstellar environments,^[4] these networks fail in rationalizing the reaction pathways leading to methylpolyynes ($\text{CH}_3(\text{C}\equiv\text{C})_n\text{H}$) ($n=1-3$)^[5] derivatives of ubiquitous polyynes ($\text{H}(\text{C}\equiv\text{C})_n\text{H}$) ($n=1-3$)^[6] and cyanopolyynes ($\text{H}(\text{C}\equiv\text{C})_n\text{CN}$) ($n=1-4$).^[7-10] These molecules were detected in cold molecular clouds like the Taurus Molecular Cloud (TMC)^[11-12] and the Orion Molecular Cloud (OMC) (Scheme 1) with models predicting fractional abundances



Scheme 1. Families of closed shell polyynes detected in the interstellar medium: polyynes 1 ($D_{\infty h}$; $X^1\Sigma_g^+$), cyanopolyynes 2 ($C_{\infty v}$; $X^1\Sigma^+$), methylpolyynes 3 (C_{3v} ; X^1A_1), and methylcyanopolyynes 4 (C_{3v} ; X^1A_1) with point groups and electronic ground states indicated in parentheses. Polyynes and methylpolyynes with up to ten carbon atoms were also detected in acetylene-doped hydrocarbon flames.^[22-23]

several orders of magnitude lower compared to astronomical observations.^[13-17] The recent microwave detection of the so far largest symmetric top molecule in deep space – methyltriacetylene ($\text{CH}_3(\text{C}\equiv\text{C})_3\text{H}$)^[12] – exploiting the 100 m Green Bank Telescope toward TMC-1 with relative abundances of methylacetylene (CH_3CCH):methyltriacetylene (CH_3CCCCCH) of $23 \pm 10:6 \pm 3:1$ emphasizes the hitherto elusive synthetic routes of methyl-capped polyynes in extraterrestrial environments.^[11-12]

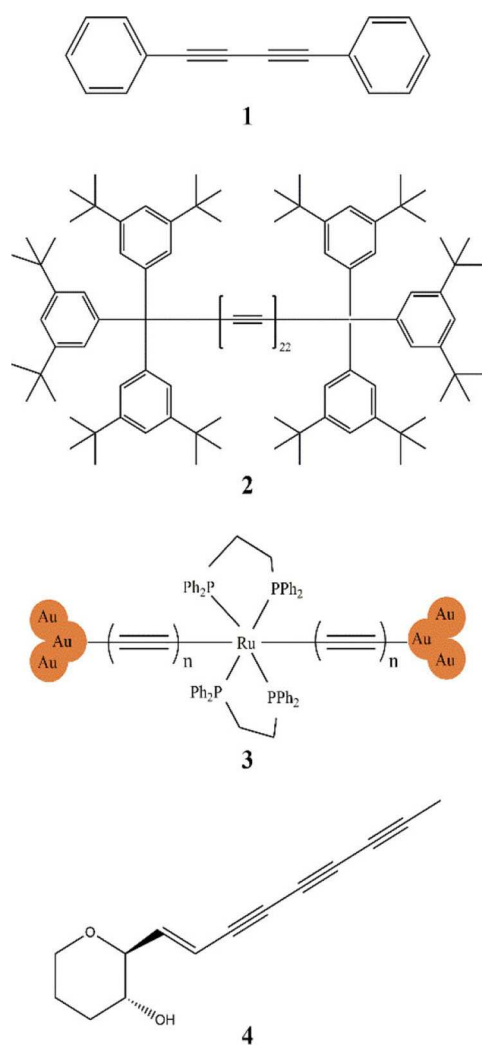
Here, we provide a unique glance into the chemistry of methyltriacetylene ($\text{CH}_3(\text{C}\equiv\text{C})_3\text{H}$; X^1A_1) and report on its first gas phase synthesis under single collision conditions via the bimolecular reaction of the 1-propynyl radical (CH_3CC ; X^2A_1) with diacetylene ($\text{H}(\text{C}\equiv\text{C})_2\text{H}$; $X^1\Sigma_g^+$) exploiting crossed molecular beams. An investigation of elementary reactions at the most fundamental, microscopic level conveys distinctive perceptions into the reaction mechanisms through which highly reactive,

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thermally labile and oxygen-sensitive molecules such as methyltriacetylene are formed. Since the nascent reaction products do not undergo succeeding reactions, but fly away undisturbed from the collision center, successive cross-linking of methyltriacetylene, which represent a common problem in preparing polyynes in the 'bulk',^[18] is eliminated. Hence, this method provides a versatile and clean gas phase synthesis of highly reactive polyynes, which cannot be always synthesized by traditional synthetic routes.^[19] This system is also stimulating for the physical organic and computational chemistry communities from the fundamental point of view of chemical bonding and material sciences as it represents a benchmark to understand the reactivity and electronic structure of polyynes versus cummulenic π systems with allene (H_2CCCH_2) – methylacetylene (CH_3CCH) being the prototype system.^[20–21]



Scheme 2. Since Glaser's pioneering synthesis of diphenylbutadiyne ($\text{C}_6\text{H}_5(\text{C}\equiv\text{C})_2\text{C}_6\text{H}_5$) **1** via oxidative dimerization of phenylacetylide (CuCC_6H_5),^[42] tris(3,5-di-*t*-butylphenyl)methyl end-capped polyynes with up to 44 carbon atoms have been synthesized **2**. The electrical and optical properties of end-capped, metal (ruthenium, gold) carrying polyynes^[24] **3** are tunable from isolators to conductors. Methyl-terminated polyynes have also been isolated in natural products like genus ichthyothereol **4**, which occurs in plants.

Polyynes end-capped with gold nanoclusters^[24] or ruthenium-based organometallic fragments^[25] also define molecular wires,^[26] in which the transition from insulators via semiconductors to metals can be selectively tuned by adjusting the length of the carbon chain (Scheme 2).^[25,27–29] In deep space, since hydrocarbon molecules carrying linear carbon chain backbones constitute nearly one third of all detected interstellar organic molecules,^[30] the elucidation of their formation routes will unravel the most fundamental processes that drive the hitherto poorly understood exotic organic chemistry in low temperature interstellar environments. Considering that hydrogen-deficient polyyne-type species may act as precursors to fullerenes (C_{60} , C_{70})^[31–32] and even to carbonaceous nanoparticles (carbon-based interstellar grains),^[22,33–41] our combined experimental and computational study helps defining the molecular complexity of organic molecules, which can be synthesized in our galaxy, thus ultimately predicting where else in the universe the molecular precursors to fullerenes and carbonaceous nanoparticles can be formed.

In the reaction of the 1-propynyl radical (CH_3CC ; X^2A_1 ; 39 amu) with diacetylene ($\text{H}(\text{C}\equiv\text{C})_2\text{H}$; $X^1\Sigma_g^+$; 50 amu), reactive scattering signal was observed at $m/z=88$ (C_7H_4^+) and 87 (C_7H_3^+) (Supplementary Information); the data at $m/z=88$ display the best signal-to-noise ratio. Note that after scaling, the time-of-flight (TOF) spectra at both mass-to-charge ratios were superimposable revealing that signal at $m/z=88$ originates from dissociative electron impact ionization of the C_7H_4 product in the electron impact ionizer of the detector. Therefore, the laboratory data alone disclose that only atomic hydrogen, but not molecular hydrogen, is lost. Figure 1 compiles the laboratory data (laboratory angular distribution, time-of-flight). The laboratory angular distribution of the C_7H_4 product(s) is

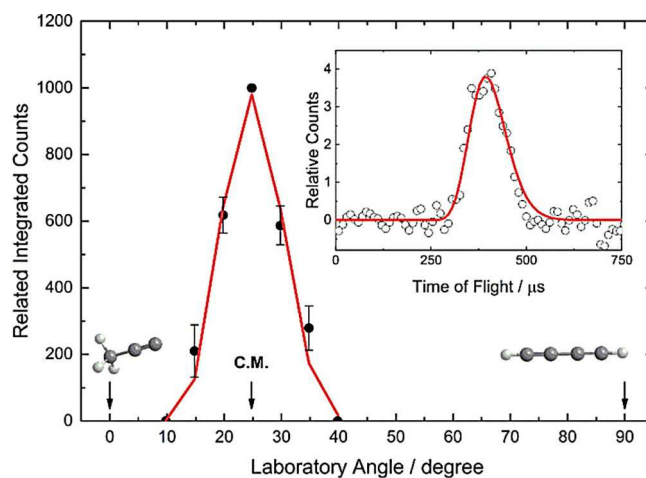


Figure 1. Laboratory angular distribution at $m/z=88$ of the C_7H_4 product from the reaction of the 1-propynyl radical (CH_3CC ; C_{3v} ; X^2A_1) with diacetylene ($\text{H}(\text{C}\equiv\text{C})_2\text{H}$; $\text{D}_{\infty h}$; $X^1\Sigma_g^+$); the direction of the radical beam is defined as 0° , that of the diacetylene beam as 90° . The solid line represents the angular distribution obtained from the best-fit center-of-mass angular and translational energy flux distributions, the black circles the experimental data. The time-of-flight spectrum recorded at the center-of-mass angle is shown as an inset (open circles, experimental data; solid line, best fit from the center-of-mass functions).

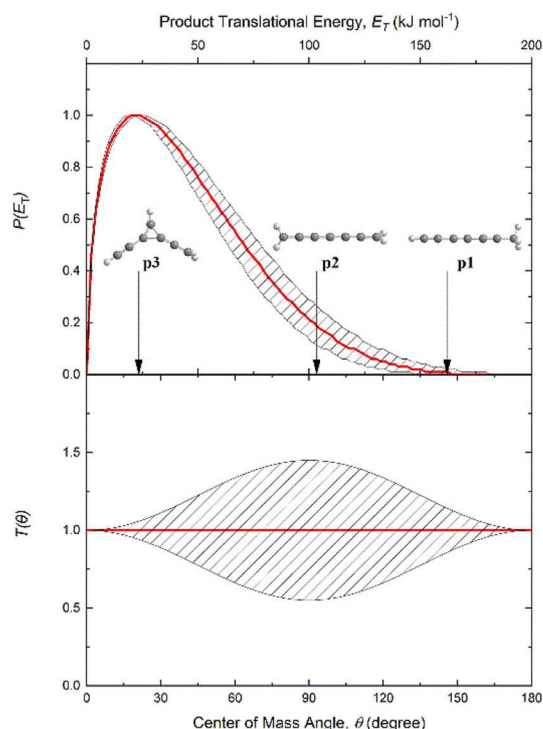


Figure 2. Best-fit center-of-mass angular ($T(\theta)$, lower) and translational energy ($P(E_T)$, upper) flux distributions of the reaction of the 1-propynyl radical with diacetylene to form the methyltriacetylene molecule plus atomic hydrogen. The red lines are the best fits; the shaded areas delimit the acceptable upper and lower error limits.

obtained by integrating the TOF spectra and peaks at the center of mass angle of $24.8^\circ \pm 0.5^\circ$. To conclude, the raw data alone reveal the existence of a molecule of the molecular formula C_7H_4 along with atomic hydrogen under single collision conditions.

However, the primary objective of our study is to elucidate the C_7H_4 isomer formed in the elementary reaction of the 1-propynyl radical with diacetylene. To accomplish this goal, the laboratory data were transformed from the laboratory frame to the center-of-mass (CM) reference frame to obtain the translational energy ($P(E_T)$) and angular ($T(\theta)$) flux distributions (Figure 2).^[43] The laboratory data could be replicated with a single reactive scattering channel exploiting the product mass combinations of 88 amu (C_7H_4) and 1 amu (H). The $P(E_T)$ ranges to a maximum translational energy release of 162 ± 17 kJ mol⁻¹. This data can be utilized to resolve the reaction energy and upon comparison with electronic structure calculations the structural isomer formed in this process. Here, it is important to recall that due to energy conservation, the maximum of the translational energy of the $P(E_T)$ equals the sum of the collision energy and the reaction energy for those product molecules without internal excitation. Consequently, subtracting of the collision energy of 37.4 ± 0.4 kJ mol⁻¹ reveals that the reaction to C_7H_4 plus atomic hydrogen is exoergic by 125 ± 17 kJ mol⁻¹. Moreover, the $P(E_T)$ shows a distribution maximum clearly away from zero translational energy at 22 kJ mol⁻¹. This finding correlates with a tight exit transition state and a repulsive energy release

combined with a significant electron rearrangement when the C_7H_5 intermediate undergoes unimolecular decomposition to the final products.^[44] Lastly, the $T(\theta)$ distribution shows a forward-backward symmetry with respect to 90° with flux distributed over the complete angular range of 0° to 180° . This finding recommends indirect scattering dynamics of the reaction via the formation of C_7H_5 reaction intermediate(s); this complex is rather long-lived holding a lifetime longer than its rotational period.^[45] The poor polarization of the center-of-mass angular distribution is the result of the inability of the light hydrogen atom to carry away a significant fraction of the total angular momentum. This is also mirrored in the flux contour map (Figure 2); this map signifies an overall image of the reaction and contains all the information of the reactive scattering process.

Having analyzed the center-of-mass functions in depth, we are now merging the experimental data with electronic structure calculations on the C_7H_5 potential energy surface (PES) (Figure 3; Supporting Information). Here, a comparison of the experimental reaction energy of 125 ± 17 kJ mol⁻¹ yielding a species with the molecular formula C_7H_5 along with atomic hydrogen with the computational data for product channels **p1** to **p4** reveals at least the formation of methyltriacetylene ($CH_3(C\equiv C)_3H$; C_{3v} ; X^1A_1 ; **p1**) plus atomic hydrogen (-124 ± 5 kJ mol⁻¹). The formation of the thermodynamically less stable heptahexene ($H_2CCCCCCH_2$; D_{2d} ; X^1A_1 ; **p2**), which is unfavorable by 58 kJ mol⁻¹ with respect to **p1**, may be masked in the low energy section of the $P(E_T)$. The synthesis of two cyclic products **p3** ($HCCCCCHCCCH_2$; $^1A'$; C_s) and **p4** ($HCCCCCHCC$; 1A_g ; D_{2h}) is highly endoergic and less competitive. Consequently, we can deduce that our experiments succeeded in the synthesis of free methyltriacetylene in the gas phase via a single collision event. The calculated standard enthalpy of formation of methyltriacetylene of 629 ± 5 kJ mol⁻¹ is in line with Rayne and Forest's data of 638 ± 10 kJ mol⁻¹,^[46] but lower by 14 and 45 kJ mol⁻¹ compared to Hansen et al.^[22] and Golovin et al.,^[47] respectively. A comparison of the molecular structures of the 1-propynyl radical and the diacetylene reactants with the methyltriacetylene product suggests that the hydrogen atom at the ethynyl moiety of diacetylene is de-facto replaced by the 1-propynyl group via a radical-triggered chain extension of the linear acetylenic moiety. Here, our computations reveal that the reaction is initiated by a barrier-less addition of the 1-propynyl radical with its radical center to the terminal C1/C4 or centered C2/C3 atoms of diacetylene leading to doublet radical intermediates **i1** and **i2**, respectively; both intermediates can be interconverted via two cyclic doublet intermediates **i3** and **i4** via low lying transition states. Intermediate **i1** was found to undergo unimolecular decomposition via hydrogen loss and formation of methyltriacetylene (**p1**) in an overall exoergic reaction (124 ± 5 kJ mol⁻¹) through a tight exit transition state located 20 kJ mol⁻¹ above the energy of the separated products. This hydrogen elimination is accompanied by a significant electron rearrangement changing the carbon-carbon double bond in intermediate **i1** (bond length: 132.1 pm) to a shorter carbon-carbon triple bond with a bond length of only 121.8 pm. Further, the computations predict that the hydrogen

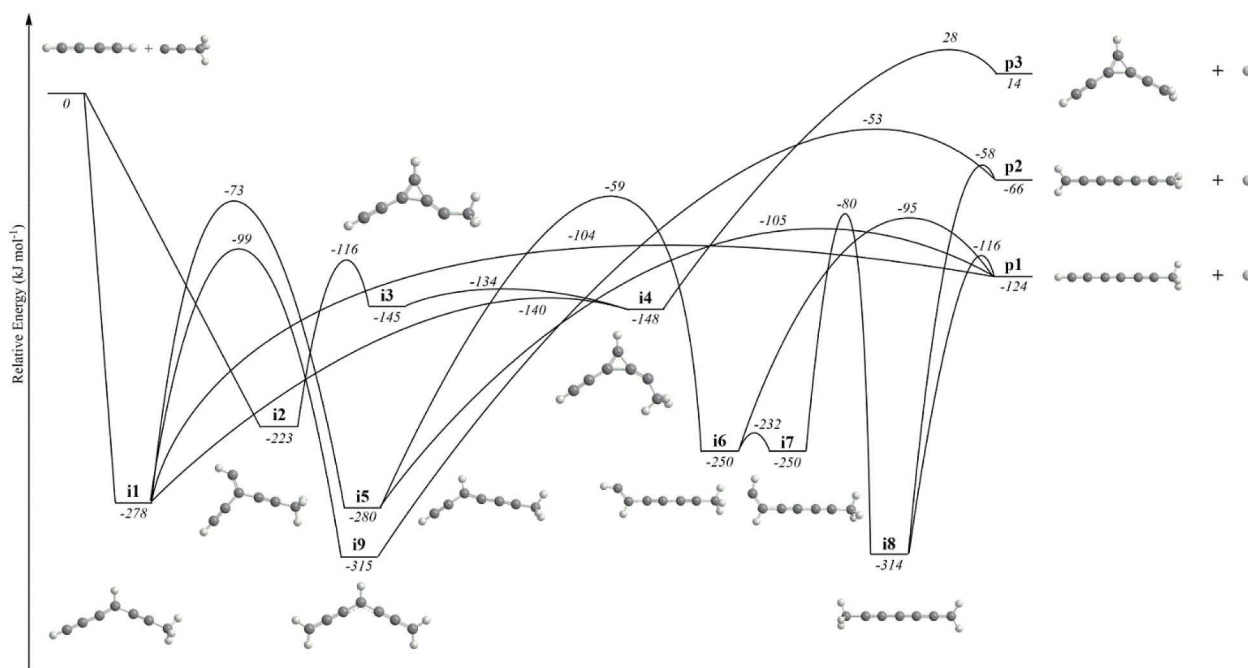


Figure 3. Schematic representation of the potential energy surface of the reaction of the 1-propynyl radical with diacetylene. Energies calculated at the CCSD (T)-F12/cc-pVTZ-f12//B3LYP/6-311G(d,p) + ZPE(B3LYP/6-311G(d,p) level are shown in kJ mol^{-1} and are relative to the energy of the separated reactants. The geometries of the transition states, reactants, intermediates, and products and their point groups and the symmetries of their electronic wave functions are compiled in the Supplementary Information.

atom is eliminated at an angle of 5.3° with respect to the principal rotational B axis of the quasilinear methyltriacetylene fragment (Figures 3 and 4). This tight exit transition state along

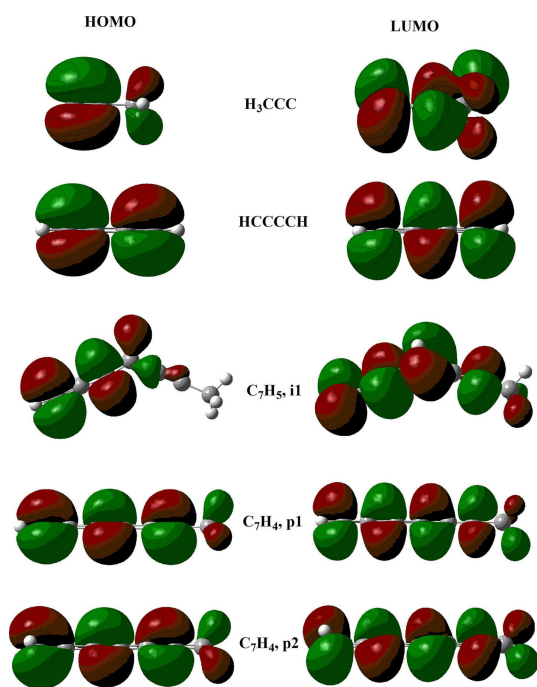


Figure 4. Frontier orbitals revealing the pathway of the 1-propynyl radical reaction with diacetylene to methyltriacetylene plus atomic hydrogen.

with the indirect (complex forming) scattering dynamics involving C_7H_5 intermediates were predicted based on the center-of-mass translational energy and angular distributions, respectively (Figure 2). Alternative reaction pathways to methyltriacetylene (**p1**) involve hydrogen shifts from **i1** via the sequence **i1**→**i5**→**i6**→**i7**→**i8** via barriers of up to 221 kJ mol^{-1} ; excluding **i7**, each of these intermediates can eject a hydrogen atom through transition states located between 8 and 19 kJ mol^{-1} above the separated products. Note that heptahexene ($\text{H}_2\text{CCCCCCH}_2$; **p2**) might be formed via unimolecular decomposition of **i9**, which can be accessed via a [1,7]-hydrogen shift from **i1**, or from **i8**. A comparison of the relatively high energies of the transition states inherent to these hydrogen shifts with the addition – elimination route through intermediate **i1** suggests that the latter route should dominate the reaction dynamics. Accompanying statistical (Rice-Ramsperger-Kassel-Marcus; Supporting Information) calculations suggest that **p1** methyltriacetylene ($\text{CH}_3\text{CCCCCCH}$) holds branching ratios of up to 99.9% under our experimental conditions with minor contributions from **p4** heptahexene ($\text{H}_2\text{CCCCCCH}_2$). Note that with respect to methyltriacetylene, 98% is formed via unimolecular decomposition of **i1**, while 2% can be accounted for through the fragmentation of **i5**, which is formed via hydrogen shift from **i1**. Therefore, we determine that the reaction of 1-propynyl with diacetylene to form methyltriacetylene represents a prototype of a polyene chain extension through a radical substitution (S_R) mechanism, albeit without entrance barrier to the reaction intermediate(s) **i1**.

In conclusion, our combined experimental and computational investigation of the elementary gas phase reaction of the 1-propynyl radical (CH_3CC ; X^2A_1) with diacetylene (HCCCCCH ; $X^1\Sigma_g^+$) shows a facile synthesis of methyltriacetylene ($\text{CH}_3\text{CCCCCCH}$; X^1A_1) under single collision conditions. Since this bimolecular reaction has no entrance barrier, is exoergic, and passes transition states below the total energy of the reactants, it represents a prototype pathway to form methyl-terminated polyacetylenes in dark (molecular) clouds like TMC-1 and OMC-1, where temperatures as low as 10 K reside. Along with typical number densities ranging from 10^4 to 10^6 cm^{-3} , molecular mass growth processes to more complex polyynes proceed solely via barrierless and exoergic bimolecular collisions due to the lack of a third body collision partner. Upon reactions with polyynes ($\text{H}(\text{C}\equiv\text{C})_n\text{H}$) and cyanopolyynes ($\text{H}(\text{C}\equiv\text{C})_n\text{CN}$), the 1-propynyl radical reactant essentially provides a novel route piggybacking a methyl group to be incorporated barrierlessly into hydrogen-deficient molecules in deep space. This mechanism overcomes a key obstacle in previously postulated reactions of methyl radicals with unsaturated hydrocarbons, which fail the incorporation of methyl groups into hydrogen-deficient interstellar molecules due to insurmountable entrance barriers ranging from typically 5 to 134 kJ mol^{-1} .^[48–51] Therefore, bimolecular reactions of 1-propynyl radical reactions with polyynes and their derivatives represent a previously overlooked class of neutral-neutral reactions leading to the synthesis of largely elusive methylpolyynes and methylcyanopolyynes at low temperatures in deep space with the methyl group acting as a spectator. The single collision environments both in our experiments and in molecular clouds provide unique settings for the nascent reaction products such as hitherto elusive alkylpolyynes to be synthesized via reactions of barrier-less alkylethynyl radicals (RCC*) with polyynes in the gas phase thus opening up unusual synthetic routes to alkylpolyynes, which cannot be synthesized by traditional organic chemistry routes in solution due to their sensitivity toward molecular oxygen and dimerization. It should be noted that there is considerable interest in the physical organic and theoretical chemistry communities in how long these substituted polyynes can be prepared in deep space as potential precursors to carbonaceous nanoparticles.^[22,31–41] The elucidation of the barrierless route to methyltriacetylene as presented here warrants future experimental studies under single collision conditions such as the reaction of 1-propynyl with triacetylene (HCCCCCCH) and cyanodiacetylene (HCCCCCN) probably leading to the synthesis of the hitherto elusive methyltetracetylene in deep space thus exploring systematically the elementary reactions leading to one of the least explored class of hydrogen-deficient organic molecules in extraterrestrial environments – polyynes – eventually gaining a comprehensive understanding of their electronic structure, stabilities, and chemical bonding.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: gas-phase chemistry · methyltriacetylene · reaction dynamics · reaction intermediates · single-collision conditions

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