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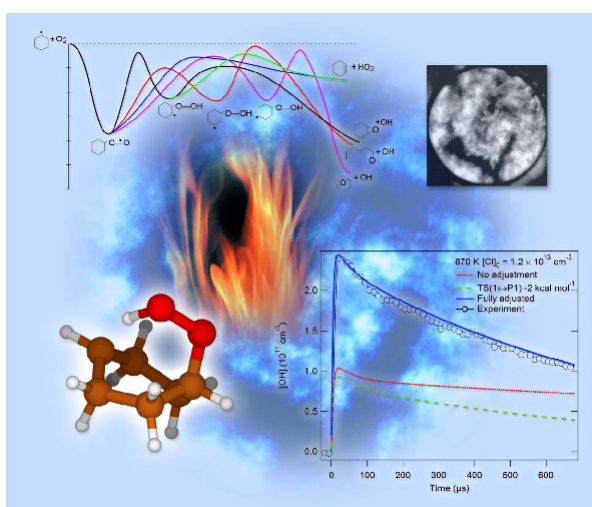


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Direct detection of polyynes formation from the reaction of ethynyl radical (C_2H) with propyne ($\text{CH}_3\text{-C}\equiv\text{CH}$) and allene ($\text{CH}_2=\text{C}=\text{CH}_2$)

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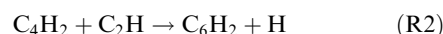
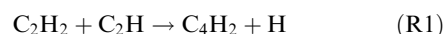
The reactions of the ethynyl radical (C_2H) with propyne and allene are studied at room temperature using an apparatus that combines the tunability of the vacuum ultraviolet radiation of the Advanced Light Source at Lawrence Berkeley National Laboratory with time-resolved mass spectrometry. The C_2H radical is prepared by 193-nm photolysis of CF_3CCH and the mass spectrum of the reacting mixture is monitored in time using synchrotron-photoionization with a dual-sector mass spectrometer. Analysis using photoionization efficiency curves allows the isomer-specific detection of individual polyynes of chemical formula C_5H_4 produced by both reactions. The product branching ratios are estimated for each isomer. The reaction of propyne with ethynyl gives 50–70% diacetylene ($\text{H-C}\equiv\text{C-C}\equiv\text{C-H}$) and 50–30% C_5H_4 , with a C_5H_4 -isomer distribution of 15–20% ethynylallene ($\text{CH}_2=\text{C}=\text{CH-C}\equiv\text{CH}$) and 85–80% methyldiacetylene ($\text{CH}_3\text{-C}\equiv\text{C-C}\equiv\text{CH}$). The reaction of allene with ethynyl gives 35–45% ethynylallene, 20–25% methyldiacetylene and 45–30% 1,4-pentadiyne ($\text{HC}\equiv\text{C-CH}_2\text{-C}\equiv\text{CH}$). Diacetylene is most likely not produced by this reaction; an upper limit of 30% on the branching fraction to diacetylene can be derived from the present experiment. The mechanisms of polyynes formation by these reactions as well as the implications for Titan's atmospheric chemistry are discussed.

1. Introduction

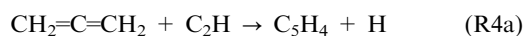
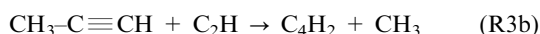
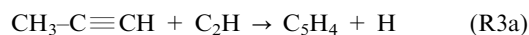
Polyynes¹ are molecules containing two or several adjacent acetylene units, diacetylene ($\text{H-C}\equiv\text{C-C}\equiv\text{C-H}$) being the simplest. These molecules and their derivatives are produced by plants and bacteria² and their organic synthesis in the laboratory has been extensively investigated.^{3–5} Moreover, small polyynes with the general formula $\text{H-(C}\equiv\text{C)}_n\text{-X}$ ($n = 2$ or 3 and $\text{X} = \text{H, CH}_3$) are detected in gas phase environments such as interstellar media,^{6–11} combustion flames,^{12,13} and planetary atmospheres, such as Saturn's moon Titan¹⁴ where they are considered as intermediates in the formation of aerosols through the production of polycyclic aromatic hydrocarbons.^{15–18} Polyynes have also been detected in meteorites.¹⁹ In the interstellar medium, they are candidates for carriers of the diffuse interstellar bands.²⁰ Polyynes with $n = 4$ have been observed in laboratory experiments designed to mimic the chemistry in Titan's atmosphere,²¹ and they are likely to be present in interstellar clouds and combustion flames. In addition, the photodissociation chemistry of these molecules by stellar light fluxes leads to the formation of large and very reactive radicals such as C_4H , C_6H and C_8H .^{10,16,22–24} However, our understanding of the role of polyynes in the chemistry of these gas phase media is limited by a lack of knowledge of the reaction mechanisms and the product distributions of those reactions that lead to polyne

formation. Therefore, experimental studies of the chemistry of polyynes are central to establishing accurate models of the atmosphere of Titan, interstellar clouds and combustion.

Wilson and Atreya¹⁵ proposed a chemical scheme leading to the formation of polyynes, such as C_6H_2 , starting with the basic reaction $\text{C}_2\text{H} + \text{C}_2\text{H}_2$ that forms diacetylene (C_4H_2):



In Titan's atmosphere the ethynyl radical (C_2H) is the main product of the photodissociation of acetylene by solar radiation and plays a central role in the chemical scheme leading to the formation of polycyclic aromatic hydrocarbons.^{25–28} In combustion, C_2H is also known to be an important radical.^{29,30} Previous theoretical and experimental studies^{31–35} have shown the importance of the $\text{C}_2\text{H} + \text{C}_3\text{H}_4$ reaction as a route for the formation of diacetylene, methyldiacetylene ($\text{CH}_3\text{-C}\equiv\text{C-C}\equiv\text{CH}$) and other 5-carbon-atom containing molecules in gas phase media. Propyne ($\text{CH}_3\text{-C}\equiv\text{CH}$) and allene ($\text{CH}_2=\text{C}=\text{CH}_2$), two isomers of C_3H_4 , have been detected and included in models of planetary atmospheres^{16,36} and combustion.³⁷ Reactions of C_3H_4 with the ethynyl radical (R3 and R4, respectively, for propyne and allene) can lead to the formation of C_4H_2 and/or C_5H_4 , and the products may depend on which isomer of C_3H_4 is considered:



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Table 1 C₅H₄ isomers and their ionization energies

	Isomer	Ionization energy/eV	Reference
1	Ethynylallene (CH ₂ =C=CH-C≡CH)	9.22	Hansen <i>et al.</i> ¹³
2	Methyldiacetylene (CH ₃ -C≡C-C≡CH)	9.5	Maier <i>et al.</i> ⁵⁷
3	1,4-Pentadiyne (HC≡C-CH ₂ -C≡CH)	10.28	Hansen <i>et al.</i> ¹³
4	1,2,3,4-Pentatetraene (CH ₂ =C=C=C=CH ₂)	8.67	Bieri <i>et al.</i> ⁵⁸

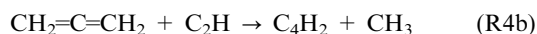
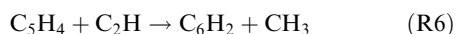
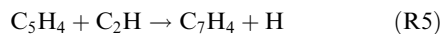


Table 1 presents the structure of 4 isomers of general formula C₅H₄.

The subsequent reaction of C₅H₄ with the C₂H radical can be a source of larger polyynes as well as a source of methyl radicals. Depending on the structure of the C₅H₄ isomers, the following reactions may occur:



Detection of the products of these reactions is of central importance for devising accurate models of polyyne formation in the gas phase.

The first product detection for the reactions R3a and R3b was performed by Cullis *et al.*³⁸ They detected C₅H₄ but were not able to distinguish among the different isomers. Kaiser and coworkers^{34,35} also performed a detailed study of the reaction mechanism of the C₂H radical with propyne. The reaction has two entrance channels based on the addition reaction and more than 11 exit channels. Ten isomers with the general formula C₅H₄ can be produced but only 6 are thermodynamically accessible. Combining a theoretical study with a crossed beam experiment, Kaiser and coworkers³⁴ were able to estimate a branching ratio for the production of methyldiacetylene (CD₃-C≡C-C≡CD), 80–90%, and ethynylallene (CD₂=C=CH-C≡CD), 10–20%, by detecting the H/D atom production from the reaction of C₂D with CD₃CCH. However, this technique does not allow the detection of a third isomer that is thermodynamically accessible, 1,4-pentadiyne (HC≡C-CH₂-C≡CH).

To our knowledge, there is no experimental detection of the C₂H + allene reaction products. Stahl *et al.*³⁵ provided a complete calculation of the C₅H₅ potential energy surface, predicting the main products for the reaction of the ethynyl radical with allene. There is no isomer branching ratio information for the C₂H + allene reaction, and a study of the deuterated compound, as performed for the C₂H + propyne reaction, would not give access to the isomer branching ratio due to the geometry of the molecule. A comparison of the isomer branching ratios for the reactions of C₂H with propyne and allene presents an opportunity to obtain precise information about the mechanisms of reactions of small carbon radicals with unsaturated hydrocarbons and to estimate the most favorable routes leading to the formation of polyynes in the gas phase.

In this paper, we present direct product detection and isomer identification for the gas phase reactions of the ethynyl radical with propyne and allene. This study is directly relevant to the *in situ* sampling of Titan's atmosphere obtained by the

Huygens probe.³⁹ The results obtained for the reaction of C₂H + propyne are compared to the previous experiments, and the new experimental results for the reaction C₂H + allene are compared to the previous theoretical calculations. The experiment is performed with a slow flow reactor at room temperature coupled to a photoionization mass spectrometer that uses tunable synchrotron radiation from the advanced light source (ALS) to detect individual product isomers according to their differing ionization energies. The implications of these results for an understanding of the mechanisms of carbon radical reactions with unsaturated hydrocarbons and their role in Titan's atmosphere are also discussed.

2. Experimental

A description of the experiment has been given previously⁴⁰ and only a brief overview will be presented here. The experimental apparatus used in this work is schematically illustrated in Fig. 1. It consists of a slow-flow reactor⁴¹ coupled to a multiplexed photoionization mass spectrometer. The gas reactor is a 60 cm long straight quartz tube with 10.5 mm id. The gas flow consists of small amounts of radical precursor ($1.3 \times 10^{15} \text{ cm}^{-3}$) and reactant molecules ($5.1 \times 10^{14} \text{ cm}^{-3}$) in a large excess of He buffer (total $1.3 \times 10^{17} \text{ cm}^{-3}$). The gas mixture moves down the flow tube at a velocity of $\sim 4 \text{ m s}^{-1}$ towards a vacuum pump throttled by a valve that regulates the tube pressure under active feedback control. All the gases are injected at room temperature.

A uniform initial concentration of the C₂H radical is produced coaxially in the flow by 193 nm photolysis of 3,3,3-trifluoropropyne (CF₃CCH) using an unfocused beam of an excimer laser with a 4 Hz repetition rate. Previous experiments⁴² have shown that the photodissociation of 3,3,3-trifluoropropyne is a factor of two more efficient in producing C₂H than photolysis of acetylene, which has an absorption cross section of $1.35 \times 10^{-19} \text{ cm}^2$.⁴³ Typical photolysis fluences inside the vacuum chamber are ~ 10 – 25

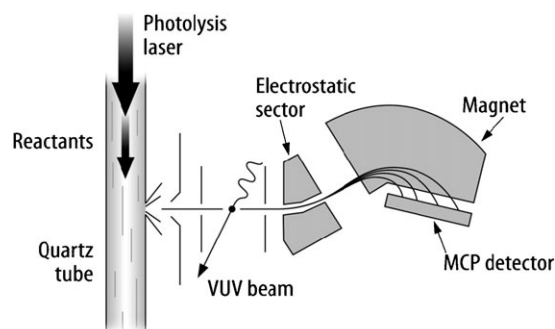


Fig. 1 Schematic of the experimental apparatus.

mJ cm⁻² in a 20 ns pulse. Chemical reactions proceed uniformly along the length of the reactor as the irradiated gas moves down the tube. The flow velocity is sufficient to sweep a fresh sample of gas into the tube before the next photodissociation laser pulse. Gas is extracted from the flow tube through a 650 µm diameter pinhole in the side of the tube into a chamber pumped by a 3200 L s⁻¹ turbomolecular pump. The effusive beam emerging from the pinhole is skimmed by a 1.5 mm diameter skimmer before entering a differentially-pumped ionization region. The temperature is monitored with a thermocouple placed just downstream of the pinhole in the quartz tube.

The gas beam is crossed in the ionization region by synchrotron undulator radiation that has been dispersed by a 3 m monochromator at the Chemical Dynamics Beamline of the Advanced Light Source at Lawrence Berkeley National Laboratory. A gas filter with Ar at 30 Torr is placed in the radiation beam path to suppress higher-order undulator harmonics. The quasi-continuous, tunable vacuum ultraviolet light from the synchrotron ionizes molecules from the reactor within the ionization region of a miniature double-focusing magnetic-sector mass spectrometer of the Mattauch-Herzog geometry.⁴⁴ Ions are accelerated, focused, and dispersed according to the square root of their mass in a 0.94 T magnetic field. At the exit plane of the magnet, all ions within a variable mass range of a factor of 6 (*e.g.*, $m/z = 14$ to $m/z = 84$) strike the active area of a time- and position-sensitive microchannel plate detector with a delay-line anode.⁴⁵ The position (corresponding to m/z) and time of arrival with respect to the photodissociation laser are recorded for each ion. The time resolution of the measurement is limited by the thermal spread in velocities in the effusive expansion through the pinhole. The ultimate temporal resolution is < 100 µs; in this paper we have binned the data at 250 µs intervals.⁴⁶ The experiment is repeated for 2000–5000 laser pulses and the data are averaged.

The photon energy of the synchrotron can be scanned during an acquisition yielding a complete series of time-resolved mass spectra at each photoionization energy that can be used to distinguish isomers. The photon energy and the energy resolution (40 meV for 600 µm exit slit width) are calibrated by measurement of known atomic resonances of Xe, absorption resonances of Ar (using the gas filter as an absorption cell), and narrow autoionization resonances in O₂.

Because the apparatus collects time- and photon energy-resolved mass spectra, a 3-D data block is available for each experiment consisting of ion intensity as a function of mass-to-charge ratio, reaction time, and photon energy. The photoionization efficiency (PIE) curves are constructed by integrating such data *versus* photon energy first over the desired mass-to-charge ratio, then over a time window that corresponds to the production of the species of interest in the photolytically-initiated reaction. Background contributions at the same m/z are removed by subtraction of a similarly-integrated signal taken before the photodissociation laser is triggered. Finally, these background-subtracted signals at each photon energy are normalized for the ALS photon fluxes and assembled into the PIE spectrum.

The purities of gases are as follows: He, 99.999%; 3,3,3-trifluoropropyne, 97%; propyne, 99%, allene, 97%. By look-

ing at the PIE scans of the propyne and allene samples it is possible to detect the impurities. Mass 54 is clearly detected in the propyne sample (mass 40). The measured photoionization thresholds, 9.02 and 10.2 eV, suggest that mass 54 is butadiene and 1-butyne, respectively.

3. Results

Time- and photon energy-resolved mass spectra have been measured for the reaction of the ethynyl radical with propyne and allene. Within our time resolution and at the reactant concentrations used, the risetime of the products cannot be measured. Mass spectra and photoionization efficiency curves are obtained by integrating the data over the entire measured reaction time (80 ms). For a given mass, the presence of several isomers with different ionization energies results in several thresholds in the photoionization efficiency curve corresponding to the ionization of each isomer. Using these data it is possible to identify all the species in the flow and especially the species formed by the 193 nm photodissociation. In the analysis only the exothermic pathways of the reaction of C₂H with propyne or allene are considered. The pathways leading to the formation of the two C₅H₄ isomers of ethynyl-cyclopropene, which are higher in energy,⁴⁷ are not considered. In their theoretical calculation, Stahl *et al.*³⁵ do not consider these pathways as significant due to the fact that the complicated rearrangement is improbable in the interstellar medium. Kaiser *et al.*³⁴ do not mention these two compounds in their high collision energy work. Therefore in the present work these two isomers are assumed either not to be produced or to be produced at a non-detectable level. Table 1 presents the 4 most probable isomers expected for the reaction of C₂H with propyne and allene and their ionization energies.

Most unsaturated hydrocarbons have a large photodissociation cross section at 193 nm. The resulting photofragments can react in the flow and therefore it is important to be aware of side reactions that can occur at the same time as the studied reactions. Fig. 2 presents the mass spectra taken at a photon energy of 10.4 eV in three different flow mixtures: propyne and 3,3,3-trifluoropropyne, allene and 3,3,3-trifluoropropyne and only 3,3,3-trifluoropropyne. All these experiments are performed with the same density of each molecule. For both the propyne and allene experiments the following sections briefly analyze the mass spectra in order to estimate the influence of these side reactions. A complete analysis of the photoionization efficiency curves allows a determination of the C₅H₄-isomer distribution for the two studied reactions. Diacetylene (H–C≡C–C≡C–H) is detected in all the experiments. However, the reaction of the ethynyl radical with C₃H₄ is not the only reaction able to produce diacetylene. The production of diacetylene in our experiment is discussed in Section 3.3.

3.1 C₅H₄ from reaction of the ethynyl radical with propyne

Propyne has a moderate photodissociation cross section at 193 nm (3×10^{-19} cm²).⁴⁸ At the laser fluences used, the fraction of dissociated propyne is less than 1%. The main photoproduct is known to be the propargyl radical (C₃H₃)⁴⁹ which reacts with itself to give C₆H₆ ($m/z = 78$); C₆H₆ is observed in our experiment with and without CF₃CCH in the

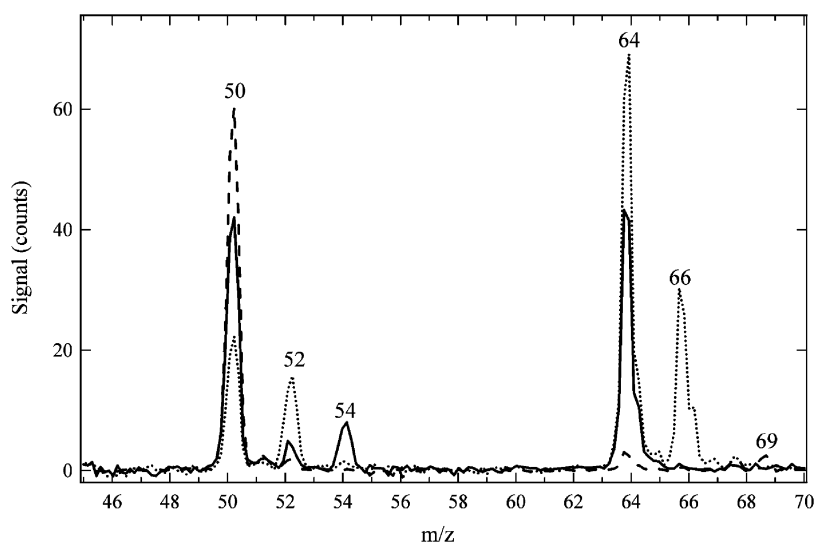


Fig. 2 Mass spectra obtained at 10.4 eV by injecting allene and trifluoropropyne (···), propyne and trifluoropropyne (—) and only trifluoropropyne (---) in the flow, for 2500 laser pulses.

flow. Reaction of the propargyl radical with ethynyl might be a source of C_5H_4 at mass 64. However at the low pressure of the experiment (4 Torr) it is expected that the radical–radical reaction product is not stabilized and would dissociate to give C_5H_3 at mass 63, which is not observed in our experiment. Fig. 2 presents part of the mass spectra obtained at a photon energy of 10.4 eV for photolysis of CF_3CCH in the presence of propyne at 193 nm (full line). As discussed in the experimental section, butadiene and 1-butyne ($m/z = 54$) are present as impurities in the propyne sample. Signal at $m/z = 52$ (C_4H_4) is detected and the measured ionization threshold suggests that 1-buten-3-yne (9.58 eV) and 1,2,3-butatriene (9.25 eV) are produced in the flow as products of the side reactions initiated by the photodissociation of butadiene⁵⁰ or 1-butyne⁵¹ at 193 nm, which have large photoabsorption cross sections, respectively, $3.6 \times 10^{-17} \text{ cm}^2$ and $1 \times 10^{-18} \text{ cm}^2$. The photoproducts of butadiene at this wavelength are mainly butynyl radical, propargyl radical, methyl radical and vinyl radical,⁵⁰ all of which can react with C_3H_4 . However, none of these side reactions is considered to be efficient to give a compound of mass 64 (C_5H_4) in our experiment. Acetylene is detected at $m/z = 26$. Acetylene can be the product of many reactions, such as $C_2H + H$ or any abstraction channel of C_2H with a hydrocarbon. Acetylene is also one of the photoproducts of propyne at 193 nm. Mass 69 is identified as CF_3 , which has an ionization energy of 9.05 eV. The trifluoromethyl radical is produced at the same time as the ethynyl radical and is likely to react with the studied molecules to produce fluorinated species. Within our ionization energy range these species are not detected. Based on the above analysis, all the following results and discussion are presented assuming that $C_2H +$ propyne is the only process leading to $m/z = 64$.

Fig. 3 presents the PIE curve for $m/z = 64$, from the reaction of C_2H with propyne. The photoion signal of mass 64 has been normalized using an estimate of the total photoionization cross section (see below). Using the values of Table 1 it is possible to identify the formation of methyl-

diacetylene ($CH_3-C\equiv C-C\equiv CH$) and ethynylallene ($CH_2=C=CH-C\equiv CH$). Concerning the two isomers 1,4-pentadiyne ($HC\equiv C-CH_2-C\equiv CH$) and 1,2,3,4-pentatetraene ($CH_2=C=C=C=CH_2$), no thresholds in the signal are observed at 10.28 eV or 8.67 eV. By comparing the PIE curve of Fig. 3 and the one of Fig. 4, where 1,4-pentadiyne is detected, we conclude that 1,4-pentadiyne ($HC\equiv C-CH_2-C\equiv CH$) production is negligible in the reaction of C_2H with propyne.

The branching fraction for the production of each isomer is determined by fitting the PIE curve with an estimate of the total C_5H_4 -isomer photoionization cross section σ^E (cm^2). The photoionization efficiency signals S^E at photon energies E (eV) are proportional to σ^E which is the summation of the molar fractions n_I times the photoionization cross section σ_I^E (cm^2) of the isomer I (eqns (E1) and (E2)).

$$S^E \propto \sigma^E = \sum_I \sigma_I^E n_I \quad (\text{E1})$$

$$\sum_I n_I = 1 \quad (\text{E2})$$

The photoionization cross sections for C_5H_4 isomers are experimentally unknown. However, estimated values for the cross sections for the different isomers of mass 64 can be inferred from semi-empirical models. It is necessary to approximate the cross sections for the three C_5H_4 isomers as a function of the photon energy. We choose three different photon energies located above the ionization threshold of each of the three relevant C_5H_4 isomers (9.4, 9.8 and 10.4 eV). At 10.4 eV the photoionization cross section can be estimated (eqn (E3)) using the semi-empirical model of Bobeldijk *et al.*,⁵² in which the photoionization cross section at an energy E of a molecule σ_M is estimated by adding the contributions to the photoionization cross section σ_{X-Y} of all the bonded atom pairs $X-Y$ of the molecules (*e.g.*, $C-H$, $C-C$, $C=C$ or $C\equiv C$ atom pairs of ethynylallene). The

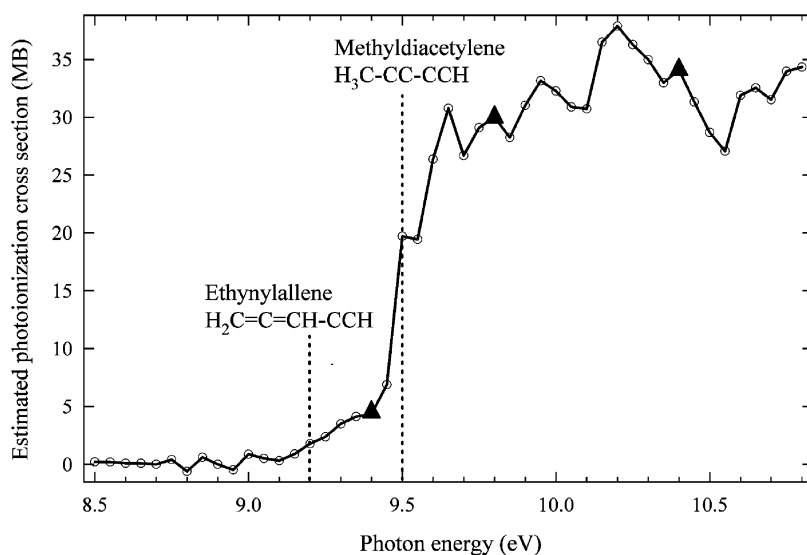


Fig. 3 (○) PIE curve of mass 64 obtained by reaction of the ethynyl radical with propyne; the signal is normalized to the total estimated photoionization cross section at 9.8 eV. The branching fraction for the production of each isomer is determined by fitting the PIE curve with an estimate of the total C_5H_4 -isomer photoionization cross section at 9.4, 9.8 and 10.4 eV (see text). (▲) Fit of the data using estimated photoionization cross sections of a mixture of 18% ethynylallene and 82% methylidyneacetylene.

contributions for different chemical bonds are derived from species with known photoionization cross sections.

$$\sigma_M(E) = \sum_{X-Y} \sigma_{X-Y}(E) \quad (E3)$$

Using eqn (E3) and the known absolute photoionization cross section of propyne, allene³⁷ and diacetylene¹² we can estimate the photoionization cross section for the three observed isomers at 10.4 eV (see Table 2). This semi-empirical model is not consistent close to a resonance. Therefore it is not used to estimate the cross section at 9.4 and 9.8 eV. The value at 9.4 eV

is the estimate of Hansen *et al.*¹³ who also performed a Franck–Condon simulation for the ionization efficiency of the C_5H_4 isomers. At 9.8 eV, assuming a slight rise of the cross section after the threshold, a value of 30 MB can be expected for both isomers 1 and 2 in Table 1. The branching ratios are determined using these values (Table 2) and by fitting σ^E values to the experimental PIE curve at 9.4, 9.8 and 10.4 eV. For the reaction of C_2H + propyne the best fit is found to be an isomer distribution of 18% ethynylallene and 82% methylidyneacetylene. In Fig. 3, the triangles represent the values of the estimated total cross section σ^E at 9.4, 9.8 and

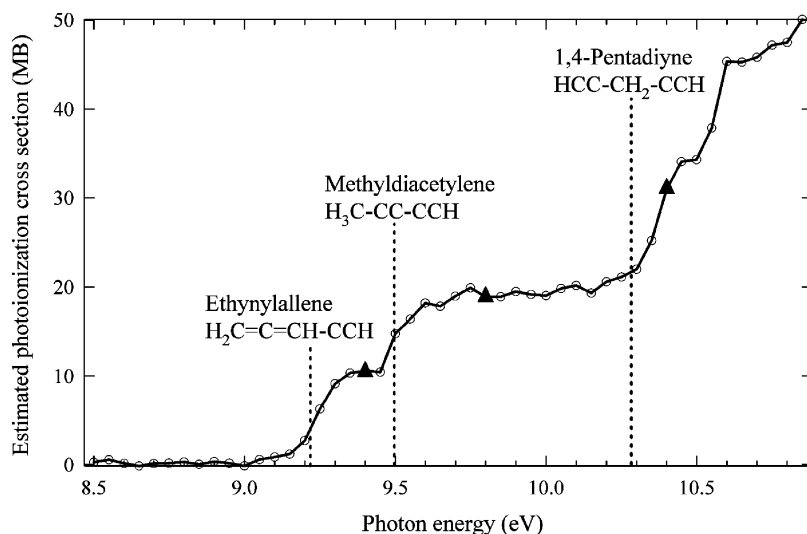


Fig. 4 (○) PIE curve of mass 64 obtained by reaction of the ethynyl radical with allene; the signal is normalized to the total estimated photoionization cross section at 9.8 eV. The branching fraction for the production of each isomer is determined by fitting the PIE curve with an estimate of the total C_5H_4 -isomer photoionization cross section at 9.4, 9.8 and 10.4 eV (see text). (▲) Fit of the data using estimated photoionization cross sections of a mixture of 40% ethynylallene, 20% methylidyneacetylene and 40% 1,4-pentadiyne.

Table 2 Estimated Photoionization cross sections in MB (1 MB = 1×10^{-18} cm²) for C₅H₄ isomers. The value at 9.4 eV is an estimate by Hansen *et al.*¹³

	Photon energy	9.4 eV ¹³	9.8 eV	10.4 eV
1	Ethynylallene (CH ₂ =C=CH-C≡CH)	25 MB	30 MB	30 MB
2	Methyldiacetylene (CH ₃ -C≡C-C≡CH)		30 MB	35 MB
3	1,4-Pentadiyne (HC≡C-CH ₂ -C≡CH)			30 MB

Table 3 C₅H₄ Isomer distribution produced by reactions of the ethynyl radical with C₃H₄

		C ₂ H + propyne		C ₂ H + allene
		This work	Kaiser <i>et al.</i> ³⁴	This work
1	Ethynylallene (CH ₂ =C=CH-C≡CH)	15–20%	10–30%	35–45%
2	Methyldiacetylene (CH ₃ -C≡C-C≡CH)	85–80%	90–70%	20–25%
3	1,4-Pentadiyne (HC≡C-CH ₂ -C≡CH)	0%	0%	45–30%

10.4 eV. The photoion signal at mass 64 is normalized to the value of σ^E at 9.8 eV. The values of the cross sections in Table 2 are expected to be reliable within 20% error bars.⁵² However, only the relative value of the photoionization cross section at each energy has an influence on the isomer distribution. Looking at the best fit between σ^E and the PIE curve we can estimate the lower and upper limits for the isomer branching ratios: 15–20% for ethynylallene, 85–80% for methyldiacetylene (see Table 3). These error bars also take into account the experimental uncertainty of the measurement.

3.2 C₅H₄ from reaction of the ethynyl radical with allene

Fig. 2 displays the mass spectra, obtained at a photon energy of 10.4 eV, in the presence of allene and CF₃CCH initiated by 193 nm photodissociation (dotted line). As in the case of propyne, allene is photodissociated at 193 nm producing mainly the propargyl radical, which self-reacts to give C₆H₆. However, the photodissociation of propyne and allene is expected to be of minor importance in the study of the title reactions.

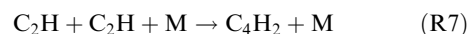
Molecules of mass 52 and 66 are produced by side reactions in the allene experiment. The measured ionization thresholds at $m/z = 52$ and $m/z = 66$ suggest that, respectively 1-buten-3-yne (9.58 eV) and 1,2,4-pentatriene (8.88 eV) are produced. These molecules are the product of reactions of allene or allene photofragments with impurities or photofragments of impurities. Based on the above analysis, all the following results and discussion are presented assuming that the reaction of C₂H with allene is the only process leading to $m/z = 64$. Moreover, the PIE curve of mass 40 does not show any observable threshold at 10.4 eV, which would correspond to the ionization of propyne. Allene is therefore the only significant isomer of mass 40 in the flow.

Fig. 4 presents the PIE curve of mass 64 for the reaction of C₂H with allene. Using the calculated or measured photoionization thresholds for the C₅H₄ isomers presented in Table 1 we are able to clearly detect ethynylallene, methyldiacetylene and 1,4-pentadiyne. Using the cross section values of Table 2 for the 3 isomers and eqns (E1) and (E2), the best fit is obtained for 40% ethynylallene, 20% methyldiacetylene and 40% 1,4-pentadiyne. The experimental data are normalized to

the value of σ^E at 9.8 eV. As discussed previously for the reaction with propyne, the branching ratios must be considered with error bars. These values are given as follows: 35–45% ethynylallene, 20–25% methyldiacetylene and 45–30% 1,4-pentadiyne.

3.3 Formation of diacetylene

Strong signals at $m/z = 50$ (C₄H₂) are observed in all experiments. Fig. 5 presents the PIE curve for $m/z = 50$ obtained after photodissociation of 3,3,3-trifluoropropyne in the flow. The same PIE curve at mass 50 is observed in all considered experiments. By comparing this PIE curve to recently published experimental data¹² we can identify the observed mass 50 as diacetylene (HC≡C-C≡CH). The main features of the PIE curve are identified using the work of Cool *et al.*¹² The CH₃ radical (mass 15) is detected only in the propyne experiment. In the flow, diacetylene can be produced by the self reaction of the C₂H radical (R7) and by reaction of C₂H radical with the C₃H₄ isomer (R3b, R4b) or with the CF₃CCH precursor (R8):



A large signal of diacetylene is observed in the case of only 3,3,3-trifluoropropyne in the flow subjected to 193 nm radiation. Within the 6.5–25 mJ cm⁻² laser fluence range, the total signal of C₄H₂ has a linear dependence on the power of the 193 nm laser. This behavior suggests that the self-reaction of the ethynyl radical is probably not the source of diacetylene in our experiment and that only R8, R3b and R4b must be considered as a source of diacetylene. The rate coefficient for R8 is unknown; therefore the branching ratio for the production of diacetylene through the reaction of the ethynyl radical with propyne or allene cannot be directly measured. However, assuming that reactions R3b and R4b are the only sources of diacetylene it is possible to calculate an upper limit for the diacetylene branching ratios by comparing the intensity of the signal at mass 50 and mass 64. Using the mass spectra presented in Fig. 2, the estimated photoionization cross sections for C₅H₄, and the measured¹² cross section for diacetylene at 10.4 eV, we calculate an upper limit for the

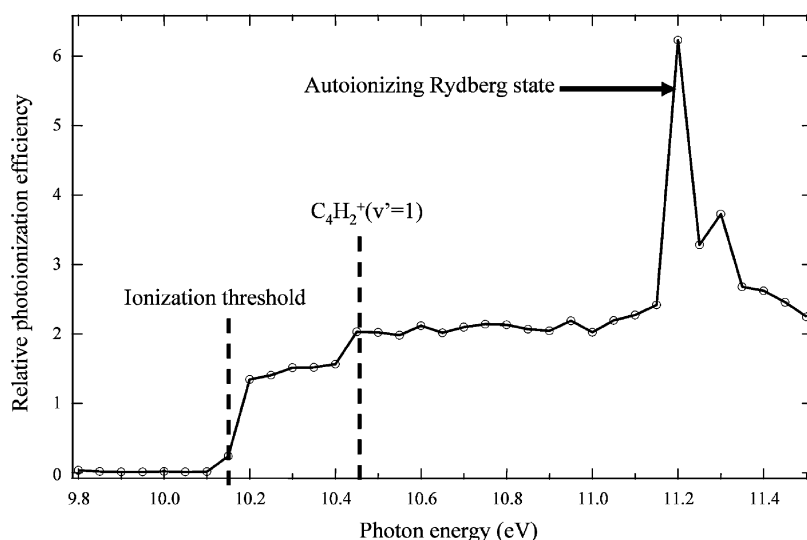


Fig. 5 PIE curve of diacetylene obtained by reaction of the ethynyl radical with CF_3CCH . The ionization threshold and the direct ionization to the $v' = 1$ vibrational level of the cation are indicated.¹² The feature at 11.2 eV may be due to an autoionizing Rydberg state.¹²

diacetylene branching ratio of 70% for the reactions of the ethynyl radical with propyne and 30% for the reactions of the ethynyl radical with allene.

If we assume that R8 is the only exit channel for the reaction of C_2H with CF_3CCH and that the signal is measured after reaction is complete, we can establish a general relation between the diacetylene branching ratios of reactions R3 and R4. First we can express the ratio of the diacetylene concentrations measured with and without C_3H_4 present (always maintaining a constant 3,3,3-trifluoropropyne concentration):

$$R_p = \frac{k_8[\text{CF}_3\text{CCH}] + k_{3b}[\text{CH}_3\text{CCH}]}{k_8[\text{CF}_3\text{CCH}] + k_3[\text{CH}_3\text{CCH}]}, \quad (\text{E4})$$

$$R_a = \frac{k_8[\text{CF}_3\text{CCH}] + k_{4b}[\text{CH}_2\text{CCH}_2]}{k_8[\text{CF}_3\text{CCH}] + k_4[\text{CH}_2\text{CCH}_2]}, \quad (\text{E5})$$

Here k_i is the rate constant for reaction R_i , whereas R_p and R_a are the fractions of C_2H converted to C_4H_2 in the reaction systems containing propyne or allene, respectively. R_p and R_a are determined from the mass spectra as the ratio between the signal of mass 50 obtained with propyne and 3,3,3-trifluoropropyne over the signal of mass 50 with only 3,3,3-trifluoropropyne, and R_a is the ratio between the signal of mass 50 obtained with allene and 3,3,3-trifluoropropyne over the signal of mass 50 with only 3,3,3-trifluoropropyne. Rearranging the second equation, we can derive an expression for k_8 :

$$k_8 = \frac{(k_{4b} - k_4 R_a) [\text{CH}_2\text{CCH}_2]}{(R_a - 1) [\text{CF}_3\text{CCH}]} = \frac{k_4 \left(\frac{k_{4b}}{k_4} - R_a \right) [\text{CH}_2\text{CCH}_2]}{(R_a - 1) [\text{CF}_3\text{CCH}]} \quad (\text{E6})$$

Substituting this into E4 and making use of the fact that the concentrations of allene and propyne are equal gives the relation:

$$\frac{k_{3b}}{k_3} = R_p + \frac{(R_p - 1) k_4 \left(\frac{k_{4b}}{k_4} - R_a \right)}{k_3 (R_a - 1)} \quad (\text{E7})$$

which can be rearranged to give:

$$\frac{k_{3b}}{k_3} = \frac{R_a}{1 - R_a} \frac{k_4}{k_3} (R_p - 1) + R_p + \frac{k_{4b}}{k_3} \frac{1 - R_p}{1 - R_a} \quad (\text{E8})$$

As reaction (R8) probably has other exit channels, eqn (E8) gives only a lower value of the branching ratio. The lowest value of the ratio k_{3b}/k_3 is obtained if $k_{4b} = 0$, assuming that reaction R4b does not occur. Using the mass spectra presented in Fig. 2 and the values of k_3 and k_4 measured by Carty *et al.*³¹ we calculate a lower limit for k_{3b}/k_3 , the diacetylene branching ratio for reaction R3, of 50%. Considering the lower and upper limits calculated above, the value of the diacetylene branching ratio for the reaction of the ethynyl radical with propyne is between 50% and 70%. For the reaction of C_2H with allene the diacetylene branching ratio is lower than 30% and is believed to be relatively small, since the methyl radical (CH_3) is not detected. Furthermore, in their theoretical work, Stahl *et al.*³⁵ do not show this channel as favorable.

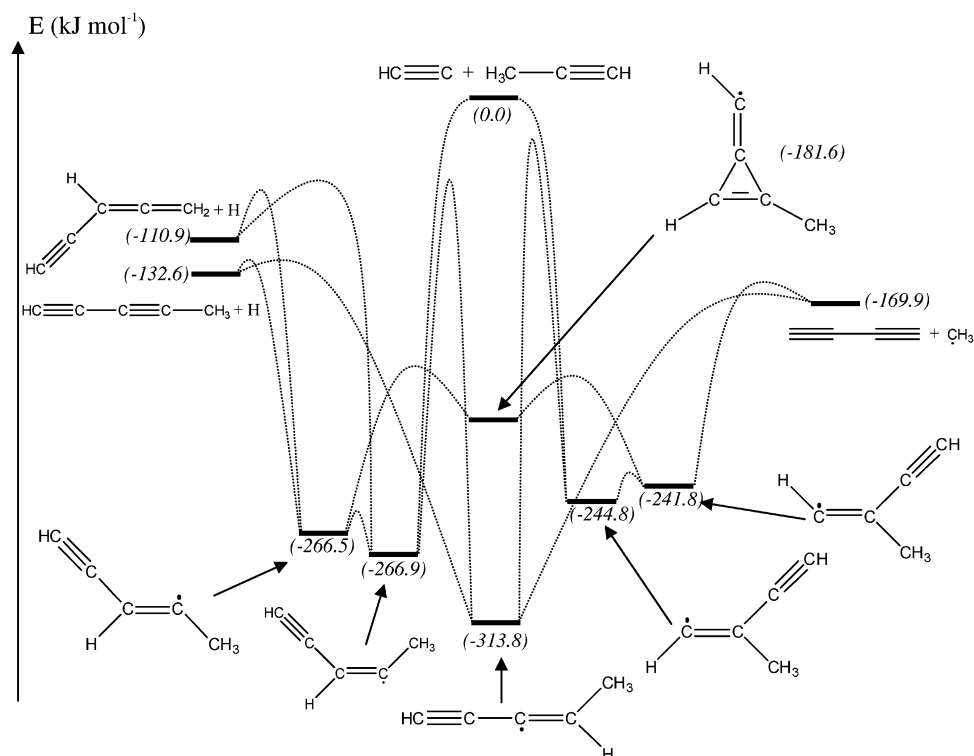
4. Discussion

4.1 The reaction mechanism

Table 3 is a summary of the relative abundances of the isomer distributions of mass 64 displayed together with values obtained from the crossed beam experiment for the two reactions.³⁴ The reaction of C_2H with propyne produces both diacetylene and C_5H_4 , with our isomer distribution of 15–20% for ethynylallene and 85–80% for methyl diacetylene. The estimated branching ratios for this reaction are in agreement with the results of Kaiser *et al.*³⁴ The present work experimentally demonstrates that 1,4-pentadiyne is not produced by this reaction. For the allene + ethynyl reaction, our work is the first measurement of the C_5H_4 isomer distribution. Contrary to the propyne reaction where methyl diacetylene is the main C_5H_4 -isomer, the reaction of allene gives mainly ethynylallene and 1,4-pentadiyne. Methyl diacetylene is a lesser

It is commonly accepted that reactions of carbon-containing radicals with unsaturated hydrocarbons proceed *via* the formation of an initial addition intermediate.^{28,53} This intermediate, which is formed without any activation energy, is expected to have a very short lifetime²⁹ and to decompose to give the substitution products. The absence of any pressure dependence in the total rate constant of most $\text{C}_2\text{H} + \text{hydrocarbon}$ reactions combined with the high value for the rate coefficients suggest that the dissociation of the intermediate to form reagents is not a major exit channel. Experimental works^{54,55} coupled with theoretical calculation³⁵ show that the entrance channel of the reaction of C_2H with acetylene is the attack on the π electrons by the radical to form an intermediate that decomposes to give the final products. The H-atom abstraction channel that forms acetylene and a radical is also thermodynamically allowed. Nevertheless, the fast rates and the zero-to-slightly-negative temperature dependences of the reactions of C_2H with unsaturated hydrocarbons are indicative of the addition-elimination mechanism's domination over the hydrogen abstraction. Concerning the reaction of C_2H with propyne, it has been theoretically³⁵ and experimentally³⁴ shown that the main pathway is the addition of the ethynyl radical to the carbon-carbon triple bond forming two isomers of C_5H_5 , which decompose to give mainly methyldiacetylene and some ethynylallene. Fig. 6 shows the most accurate potential energy surface for this reaction.^{34,35} The product isomer 1,4-pentadiyne is theoretically predicted but not considered by Stahl *et al.*³⁵ who argue that rearrangement leading

As presented in Fig. 7, the calculated mechanism³⁵ for the reaction of ethynyl radical with allene is the addition of ethynyl to a terminal carbon of allene. The decomposition of the thus formed adduct leads to the formation of ethynylallene and 1,4-pentadiyne. The attack of the radical on the central carbon producing methyldiacetylene is assumed to be less favorable.³⁵ The results presented in Table 3 show that ethynylallene, 1,4-pentadiyne and methyldiacetylene are produced in our experiment. These results are in agreement with the calculated pathways and suggest that the attack of the ethynyl radical on the central carbon is favorable. Diacetylene is predicted not to be formed by this reaction. It is most likely that the diacetylene observed in our experiment is due to the reaction of C_5H with its precursor.

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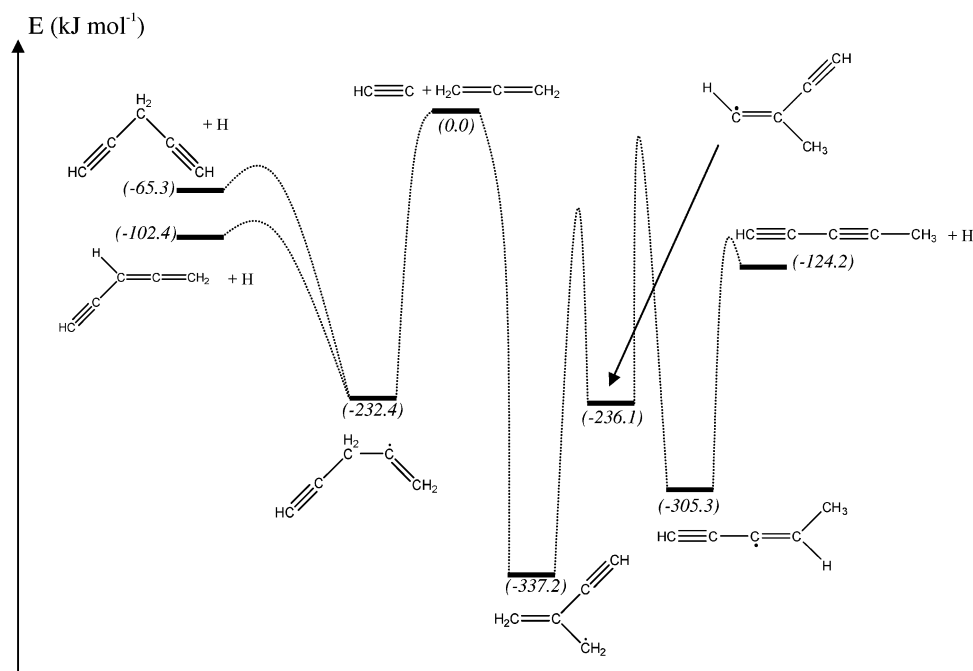


Fig. 7 Schematic profile of the potential energy surface (UB3LYP/6-311 + G** + ZPVE) for the C_2H + allene reaction.³⁵ Only the most favorable exit channels are displayed.

4.2 Implication for Titan's atmosphere

In a collaborative work between Leone and coworkers³³ and Smith and coworkers³¹ on the reaction of the C_2H radical with unsaturated hydrocarbons, the authors point out that the studied reactions must be added to the models of Titan's atmosphere. The present work elaborates the mechanism of the formation of polyynes and substituted polyynes through reaction of the ethynyl radical with propyne and allene at room temperature. However, some caution is required, as it is known that extrapolation of data obtained at high temperatures to low temperatures is often inaccurate. The rate coefficients for the reactions of the ethynyl radical with allene and propyne increase slightly when the temperature is lowered. This behavior is typical of reactions proceeding without any activation barrier. A recent study of the deuterium kinetic isotope effect of the reaction of C_2H with C_2H_2 has been performed by the Leone group.⁵⁶ The kinetic isotope effect for substitution of all the hydrogen atoms by deuterium atoms stays constant and is very small between 100 and 300 K. The same experiment in a temperature range of 296–700 K⁵⁵ shows the same behavior. These results are consistent with addition of the ethynyl radical into the $C\equiv C$ bond of the acetylene molecule as the rate-limiting step and suggest that the entrance channel stays the same to very low temperatures. It is then reasonable to assume that the mechanisms discussed above are similar to the mechanisms occurring at the lower temperatures relevant to Titan's atmosphere and that the product isomer ratios might transfer to lower temperature with some success. Considering the abundances of propyne, allene, and C_2H in Titan's atmosphere, it is reasonable to assume the presence of methyldiacetylene, ethynylallene and 1,4-pentadiyne in Titan's atmosphere in non-negligible amounts. Further reactions of C_2H with long carbon chains formed by this chemical scheme

can lead to the formation of C_6H_2 and C_7H_4 with several possible isomers.

5. Conclusion

The direct observation of polyyne formation by the reaction of the ethynyl radical with propyne and allene has been performed. Branching ratios for the isomers of general formula C_5H_4 have been estimated for both reactions. The C_5H_4 product channel in the reaction of propyne with the ethynyl radical produces mainly methyldiacetylene by direct addition of the radical on the carbon–carbon triple bond of propyne. Ethynylallene is found to be a secondary product. On the other hand, the reaction of the ethynyl radical with allene produces ethynylallene and 1,4-pentadiyne by addition of the radical on the outer carbons and methyldiacetylene by addition of the radical to the central carbon of allene. These results are in agreement with previous theoretical calculations and experimentally unravel the reaction mechanism. The product branching ratio for the formation of diacetylene by reaction of propyne with the ethynyl radical is found to be higher than 50% and lower than 70%. Our results, in agreement with theoretical calculations by Stahl *et al.*,³⁵ suggest that $C_5H_4 + H$ are the major products of the reaction of allene with the ethynyl radical. These product branching ratios are of central importance for the understanding of the chemistry of gas phase media.

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