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Abstract

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Keywords

propene, spectrometry, reaction, synchrotron, photoionization, product, branching, fractions, ch, mass, GeoQuest

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Product Branching Fractions of the CH + Propene Reaction from Synchrotron Photoionization Mass Spectrometry

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ABSTRACT

The CH ($X^2\Pi$) + propene reaction is studied in the gas phase at 298 K and 4 Torr (533.3 Pa) using VUV synchrotron photoionization mass spectrometry. The dominant product channel is the formation of C_4H_6 (m/z 54) + H. By fitting experimental photoionization spectra to measured spectra of known C_4H_6 isomers, the following relative branching fractions are obtained: 1,3-butadiene (0.63 ± 0.13), 1,2-butadiene (0.25 ± 0.05) and 1-butyne (0.12 ± 0.03) with no detectable contribution from 2-butyne. The CD + propene reaction is also studied and two product channels are observed that correspond to C_4H_6 (m/z 54) + D and C_4H_5D (m/z 55) + H, formed at a ratio of 0.4 (m/z 54) to 1.0 (m/z 55). The D elimination channel forms almost exclusively 1,2-butadiene (0.97 ± 0.20) whereas the H elimination channel leads to the formation of deuterated 1,3-butadiene (0.89 ± 0.18) and 1-butyne (0.11 ± 0.02); mass spectra of undeuterated species are used in the fitting of the measured m/z 55 (C_4H_5D) spectrum. The results are generally consistent with a CH cycloaddition mechanism to the C=C bond of propene, forming 1-methylallyl followed by elimination of a H atom via several competing processes. The direct detection of 1,3-butadiene as a reaction product is an important validation of molecular weight growth schemes implicating the CH + propene reaction, for example those reported recently for the formation of benzene in the interstellar medium (B. M. Jones *et al.*, *Proc. Nat. Acad. Sci.* **2011**, *108*, 452–457).

KEYWORDS: radical, gas-phase, photoionization, synchrotron, propene, methylidyne, mass spectrometry.

1. INTRODUCTION

The highly reactive methylidyne (CH) radical affects the chemistry of energetic gas-phase environments including combustion¹⁻³, interplanetary atmospheres⁴⁻⁶ and the interstellar medium.⁷ In order to accurately model these systems, detailed chemical data are needed in the form of reaction rate coefficients and product branching fractions. Our purpose here is to determine total product branching fractions and provide mechanistic details for the CH ($X^2\Pi$) + propene reaction. The present work builds on a series of previous product detection studies of the CH radical with small, unsaturated hydrocarbons: acetylene (C_2H_2), ethylene (C_2H_4), allene (C_3H_4 , CH_2CCH_2) and propyne (C_3H_4 , CH_3CCH).⁸ Recent works have also investigated the CH reaction with the carbonyl-containing species acetaldehyde⁹ and acetone¹⁰ as well as the cyclic nitrogen-containing species pyrrole.¹¹ Primarily, the isomer-resolved products detected in these studies can be rationalized by a reaction entrance channel characterized by CH addition to π -bond(s) of the co-reactant, although other processes, including insertion into C-H σ -bonds, could not be unequivocally ruled out.

The experimental study of Goulay *et al.* found that, at 298 K and 4 Torr, CH + C_2H_4 produces 70% allene and 30% propyne. The CD + C_2H_4 results suggest that of the possible D-loss and H-loss channels, the former leads to allene and the latter to propyne.⁸ These results conform with a cycloaddition mechanism of CH to the C=C bond. For the CH + allene reaction, the main product isomers were 23% 1,2,3-butatriene and 77% vinylacetylene, and these products can also be explained by invoking a cycloaddition mechanism to a C=C bond as the entrance channel.⁸ In other studies, Kaiser and coworkers have examined CH + C_2H_4 and some partially deuterated analogues using crossed molecular beam experiments at nominal collision energies of 17–18 kJ mol⁻¹ and report that allene is the main product under single collision conditions. In the CD + C_2H_4 case, D-elimination was found to be exclusive and this is supportive of a cycloaddition entrance channel.¹²

In all of these cases the dominant product channels are characterized by loss of an H-atom, following CH addition, forming a general pattern of $\text{CH} + \text{C}_x\text{H}_y \rightarrow \text{C}_{x+1}\text{H}_y + \text{H}$ for the reaction of CH with small unsaturated hydrocarbons. To date, detailed product detection studies for the CH + propene reaction have not been reported. The quantitative isomer-resolved studies of this reaction presented here offer important evidence supporting this general scheme for the reactivity of CH radicals with unsaturated hydrocarbons.

The CH + propene rate constant has been measured by Daugey *et al.* using Laval nozzle expansions and LIF techniques to monitor the disappearance of the CH at temperatures over the 77 – 170 K range.¹³ The reported rate constants are close to the gas-kinetic limit with a slight negative temperature dependence, increasing from $3.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 170 K to $4.45 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 77 K. Smith *et al.* predict the reaction to be rapid at temperatures of the interstellar medium (i.e., 10-20 K).¹⁴ At 2 Torr and 298 K, Loison and Bergeat measured a CH + propene rate constant of $4.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ also using LIF to monitor the disappearance of CH.¹⁵ These rate constants are indicative of a reaction devoid of any significant entrance barrier and that the reaction proceeds at efficiencies approaching unity.

The Loison and Bergeat study also determined total H-atom product yields using resonance LIF measurements. In the case of CH + propene a yield of 0.78 ± 0.10 (1 std. dev) was reported for $\text{C}_4\text{H}_6 + \text{H}$, indicating other active product channels. In the same study, CH reactions with C_2H_2 , C_2H_4 and methylacetylene and allene were all found to yield H elimination fractions >90%, consistent with our previous product detection studies.⁸ The reaction with *trans*-2-butene demonstrated a lower H-atom yield of (0.69 ± 0.12) . From these studies there is no direct information about the non-H-elimination product channels or the isomeric composition of the H-elimination co-products.

A recent computational study on the CH + propene reaction reported a potential energy diagram generated from B3LYP/6-311G(d,p) optimized structures and G3B3 single point energies.¹⁶ This study considered two entrance pathways for this reaction: (i) cycloaddition and (ii) insertion (into a C-H σ -bond) (see Scheme 1). Each entrance pathway leads to distinct intermediate C₄H₇ isomers. Based predominantly on thermodynamic arguments, as rate constants were not calculated, they predict that 1,3-butadiene + H and C₂H₄ + vinyl (C₂H₃) will be the dominant products with minor contributions from cyclic C₄H₆ isomers and “almost negligible” amounts of 1,2-butadiene + H, CH₃ + propyne, 2-butyne + H and CH₃ + allene. Due to the high energy of the CH radical, there are many products and reactions pathways that are energetically accessible so experimentally verified, isomer-specific, product data are essential to understand the mechanisms of this reaction and to test the computational predictions.

Scheme 1.

In the current paper we report the products of the CH + propene reaction studied at 298 K and 4 Torr. The products are detected using mass spectrometry and quantitative information regarding isomer populations is determined using synchrotron photoionization spectroscopy. Using this strategy it is found that C₄H₆ + H appears to be the dominant exit-channel with several isomers populating the C₄H₆ signal. We also report on the CD + propene

reaction, using the products associated with H- and D-loss to extract further mechanistic detail.

2. EXPERIMENTAL METHODS

Details of the multiplexed synchrotron photoionization mass spectrometry apparatus used in these experiments are described in depth in several recent articles.^{11,17,18} The experiment comprises a reaction flow tube coupled to a photoionization mass spectrometer. The flow tube is a 62 cm long quartz tube with 1.05 cm inner diameter. The gas pressure within the reaction tube is typically 4 Torr (533 kPa) with a total gas flow of 100 sccm. At 298 K, these conditions correspond to a bulk gas flow velocity of 4 m s⁻¹. The CH/CD radical precursor (bromoform (tribromomethane) and *d*₁-bromoform, $\sim 4 \times 10^{13}$ molecule cm⁻³), reaction gas (propene, 2.1×10^{14} molecule cm⁻³), and excess He buffer gas are supplied to the reactor via separate mass-flow controllers. In other studies of the CH radical, a small amount of N₂ is added to the flow to quench any vibrationally excited CH radicals. This was explored in these studies and no difference was observed between the photoionization spectra with and without N₂ in the flow, so N₂ was not added for the majority of the experiments. The pressure within the reaction flow-tube is maintained at 4 Torr (533.3 Pa) using a butterfly valve that throttles a Roots pump. At 298 K and 4 Torr the total flow density is 1.3×10^{17} molecule cm⁻³. Within the flow-tube, radical reactions are initiated by multiple photon photolysis of bromoform using a pulsed excimer laser operating on KrF (248 nm), generating CH radicals uniformly throughout the reactor. The photolysis fluence is typically ~ 50 mJ/cm². At ~ 30 cm along the flow tube a 650 micron diameter pinhole allows a small portion of the reacted gas mixture to escape into a vacuum chamber. This gas is sampled by a skimmer creating a near-effusive beam of molecules that is subsequently intersected by the quasi-continuous vacuum-ultraviolet (VUV) synchrotron radiation of the Chemical Dynamics Beamline^{19,20} at the Advanced Light Source. Ions formed in this region are then detected as a function of their

mass-to-charge (m/z) ratio using a 50 kHz pulsed orthogonal-acceleration time-of-flight mass spectrometer. All detected ions are time-tagged relative to the excimer laser pulse and accumulated in a multi-hit time to digital converter. In this way, complete mass spectra are collected as a function of reaction time in 20 μ s intervals. The excimer laser is operated at 4 Hz, allowing sufficient time between laser pulses to completely refresh the gas mixture before the next laser pulse. The photon energy of the synchrotron radiation can also be scanned, in this study from 9.0 – 10.5 eV in steps of 0.025 eV, and this ultimately provides a three-dimensional data set of time-resolved mass spectra as a function of photoionization energy. All data are normalized for variations in the ALS photocurrent using a NIST-calibrated photodiode (SXUV-100, International Radiation Detectors Inc.). Pre-photolysis background signal is subtracted from the final data set, so the resulting signal represents the change in intensity after photolysis. The CH + propene and CD + propene photoionization data sets are the average of three scans and the photoionization spectra are shown with 2σ error bars around the average value.

Gases and reagents are obtained from commercial sources and used without further purification: propene ($\geq 99\%$), He (99.999%), *d*-bromoform (99.5%), bromoform ($>99\%$).

3. RESULTS

Figure 1. The CH + propene product mass spectrum integrated over 0 – 80 ms and from 9 – 10.5 eV.

CH + propene

The product mass spectrum of the CH + propene reaction, integrated over the 0 – 80 ms time period and over 9 – 10.5 eV photon energy is shown in Figure 1. The dominant peak appears at m/z 54 and corresponds to C_4H_6 cations arising from $CH + C_3H_6 \rightarrow C_4H_6 + H$. The main product isomers contributing to this signal will be discussed below. Also apparent in the spectrum is a peak at m/z 55 that comprises a small ^{13}C contribution from C_4H_6 and other contributions that likely arise from dissociative photoionization at the higher energy end of this photon energy range, of a larger m/z brominated species. Furthermore, the kinetic trace of the m/z 55 product channel does not decay as would be expected from a C_4H_7 radical. Low intensity peaks at m/z 39, 52 and 53 could signify other product channels from the title reaction. To check for this, the concentration of propene in the flow was changed over an order of magnitude range. These product mass spectra, acquired at 10.5 eV photon energy, are shown in the Supporting Information (Figure S1). None of these three m/z signals

significantly tracked with the changing conditions, unlike the m/z 54 signal, so they do not appear to arise directly from the CH + propene reaction.

Other thermodynamically accessible product channels, including the $C_2H_4 + C_2H_3$ channel postulated to be dominant by Li *et al.*¹⁶, are not observed. No signal was observed at m/z 28 for photon energies up to 10.575 eV (the adiabatic ionization energy (AIE) for ethene is 10.51 eV²¹) indicating no significant ethene production. The AIE of the vinyl radical (C_2H_3) is reported as 8.506 eV²² and a lack of signal at m/z 27 at the photon energies employed here suggests that it is not a significant product. Other possible closed-shell products mentioned in the introduction include allene (m/z 40, AIE 9.69 eV²³) and propyne (m/z 40, AIE 10.36 eV [NIST recommended value]) – these would be CH_3 elimination co-products – but there are only small counts detected at m/z 40 despite scanning the photon energy well over their respective AIEs. There is also no evidence of CH_3 (m/z 15) detection (AIE 9.85 eV). Ultimately, there does not appear to be any significant product channel other than the observed H-loss co-products at m/z 54. In the Loison and Bergeat study, the CH + propene H-atom reaction yield is reported as (0.78 ± 0.10) (1 std. dev) product fraction. It is not apparent where these additional product channels would arise. Within the S/N of the experiment and depending on photoionization cross section values for each species, the product branching limit of these unobserved species is estimated at <5% of the total product yield. One possible explanation is that the remaining fraction may be distributed across several different mass channels and the corresponding product ion signals are weak and not detectable in our experiment.

From the photolysis of bromoform, there are recorded carbon-bearing products other than CH, including $CHBr_2$ and $CHBr$.²⁴ In particular the $CHBr$ singlet carbene could react with propene with competitive kinetics. However, $CHBr$ is reportedly produced at very low yields via 248 nm photolysis of bromoform.^{24,25} The possible interference of $CHBr$ to product

detection studies of CH is considered in more detail in a recent article¹⁰ but we expect that here its influence is included within the uncertainties of the reported product branching ratios.

The m/z 54 reaction product

The m/z 54 signal dominates the product mass spectrum and arises from the $C_4H_6 + H$ product channel. The measured photoionization spectrum for m/z 54, integrated between 0 and 80 ms after photolysis, is shown in Figure 2. There are four plausible C_4H_6 isomers that may contribute to this m/z 54 signal: 1,3-butadiene, 1,2-butadiene, 1-butyne and 2-butyne. At the photon energy resolution of this experiment, we are not able to distinguish cis/trans isomers. Other structural isomers of C_4H_6 , for example cyclic species considered by Li *et al.*¹⁶, correspond to considerably less exothermic product channels and are excluded as discussed below. For the purpose of fitting the m/z 54 photoionization spectrum to apportion individual contributions from the main product isomers, the absolute photoionization spectra of these butadiene and butyne species are required and are included as Supporting Information (Figure S2). Figure S2(a) contains the absolute photoionization spectrum of 1,3-butadiene²³ and 1,2-butadiene (measured in this study) and Figure S2(b) contains the absolute photoionization spectra of 1-butyne and 2-butyne²⁶. Comparison of the spectra for the butadienes with those for the butynes reveals some marked differences; most notably that the butynes both have large photoionization cross-section values at a few tens of meV after their AIEs. The spectacularly fast-rising cross section of 2-butyne, attributed to a shape resonance, is discussed in detail by Xu *et al.*²⁷ In comparison, 1-butyne does not share such a rapid increase but nevertheless bears strong photoionization cross-section values soon after the ionization onset, particularly compared to the butadienes. These four C_4H_6 isomers have well separated AIEs and the general morphologies of their spectra are markedly different. Thus, extracting the C_4H_6 isomer branching ratios is tractable by fitting the experimental m/z 54 photoionization spectrum to a linear combination of the individual isomer spectra.

The experimental m/z 54 trace from the CH + propene reaction, shown in Figure 2, was fit to weighted sums of these four absolute photoionization data using a least-squares fitting routine. The resulting product branching fractions for the isomers, as deduced from the respective fit coefficients, are shown in Table 1. The curve resulting from the fit is shown in Figure 2 and compares well with the experimental data. Table 1 also lists experimental and calculated AIEs (using the CBS-QB3 method^{28,29} implemented with Gaussian 09³⁰) for these isomers and the two cyclic C₄H₆ species mentioned earlier. The most dominant product isomer is 1,3-butadiene contributing 0.63 ± 0.03 of the product followed by 1,2-butadiene at 0.25 ± 0.05 and 1-butyne at 0.12 ± 0.02 where these uncertainties are the 2 standard deviations from the fit. However an estimate of the upper limit to the uncertainty is $\pm 20\%$ of the final product branching fractions, due primarily to the uncertainties in the absolute photoionization cross-section values, and these values are reported, correspondingly, in Table 1.

Considering the large photoionization cross-section value of 2-butyne, detection efficiencies of this species will be relatively very high. It is clear from the experimental trace that there is no onset of ion signal around the 2-butyne AIE (9.59 eV) so we can confidently assert that this C₄H₆ isomer is not a reaction product. The cyclic C₄H₆ species, 1- and 3-methylcyclopropene, have AIEs that are predicted to be close to that of 1,3-butadiene. However, the experimentally determined photoionization spectrum of 1,3-butadiene appears to match the experimental data around the onset region and there does not appear to be any inconsistency that would suggest contributions from the cyclic isomers to the measured product signal.

C₄H₆ isomer	AIE_{exp} (eV)^c	AIE_{CBS-QB3} (eV)	Fitted Branching Fraction^b
1,3-butadiene	9.082	9.07	0.63 ± 0.13
1,2-butadiene	9.23	9.24	0.25 ± 0.05
1-butyne	10.20	10.21	0.12 ± 0.03
2-butyne	9.59	9.60	0.00^a
1-methylcyclopropene	-	9.12	-
3-methylcyclopropene	-	9.06	-

Table 1. Adiabatic ionization energies and fitted product branching fractions for the *m/z* 54 photoionization spectrum shown in Figure 2. ^bUncertainties are ±20% as discussed in the text. ^aValue reached the lower limit during fitting, ^cReference ³¹.

Figure 2. The photoionization spectrum of m/z 54 from the CH + propene reaction (data points). The solid line is the fitted spectrum using absolute photoionization spectra for individual C_4H_6 isomers and is the sum of the weighted contributions from 1,3-butadiene (dotted line), 1,2-butadiene (dashed line) and 1-butyne (dotted and dashed line); the fitted parameters are shown in Table 1.

CD + propene

To provide deeper insight into the reaction mechanism leading to the formation of the detected C_4H_6 products, the CD + propene reaction was also investigated. The product mass spectrum, integrated between 0 and 80 ms after photolysis, is shown in Figure 3. The main peaks of interest are m/z 54 and m/z 55 that correspond to CD addition to propene followed by D- and H-elimination, respectively. Other peaks appear at m/z 56 which, similar to m/z 55 in the CH + propene case (Figure 1), is principally populated from a dissociative ionization

process of a heavier mass species occurring at the higher end of this photon energy range. Peaks at m/z 52 and 53 do not scale with the reactants and m/z 42 is an artifact of the propene signal background subtraction.

Figure 3 The CD + propene product mass spectrum integrated over 0 – 80 ms and from 9 to 10.5 eV.

In order to ascertain quantitatively the ratio of D-loss to H-loss, the isomeric compositions of m/z 54 (C_4H_6) and m/z 55 (C_4H_5D) are required so that appropriate corrections for photoionization cross-section can be made. Also, by revealing the dominant isomers on these mass channels a general mechanism can be formulated.

Figure 4a shows the H-elimination channel photoionization spectrum at m/z 55 corresponding to $C_4H_5D + H$. The signal displays an onset near 9.0 eV. This spectrum was fitted in the same way as the data in Figure 2 from the CH + propene reaction. It is important to note that absolute photoionization spectra of the undeuterated species are used in the fitting routine. Person and Nicole have shown that several undeuterated and deuterated isotopologues of small hydrocarbons, including propene, have similar absolute photoionization spectra.³² We anticipate that any effects on the absolute photoionization

spectra that arise from deuteration of the C_4H_6 isomers here will be small compared to the $\pm 20\%$ uncertainty in reported branching fractions. The results of the fit indicate the isomer branching fractions for H-loss of (0.89 ± 0.01) for 1,3-butadiene and (0.11 ± 0.01) for 1-butyne. With the overall $\pm 20\%$ uncertainty these results are reported as 1,3-butadiene (0.89 ± 0.18) and 1-butyne (0.11 ± 0.02) . The resulting curve produced from these fitted parameters is shown in Figure 4a and compares well with the experimental data.

Figure 4. Photoionization spectra of the dominant product channels of CD + propene. (a) The m/z 55 photoionization spectrum from H-elimination (diamonds) and the fitted spectrum (solid line: 0.89 fraction 1,3-butadiene and 0.11 fraction 1-butyne,

see text) (b) The m/z 54 photoionization spectrum from D-elimination (squares) and the fitted spectrum (solid line: 0.97 fraction 1,2-butadiene and 0.03 fraction 1-butyne, see text).

The m/z 54 product signal corresponds to C_4H_6 from the $C_4H_6 + D$ product channel. Shown in Figure 4b is the m/z 54 photoionization spectrum with an onset of ion signal around 9.25 eV. The best fit of this spectrum to C_4H_6 isomers corresponds to branching fractions of (0.97 ± 0.15) for 1,2-butadiene and (0.03 ± 0.23) for 1-butyne. The resulting curve from these fitted values, dominated overwhelmingly by the 1,2-butadiene contribution, is also shown in Figure 4b and again the comparison of the fitted spectrum and the data is reasonably good. From these results it is apparent that the sole path to 1,2-butadiene is via D-elimination whereas the sole path to 1,3-butadiene is via H-elimination. This result has some interesting relevance when establishing a mechanism for this reaction as described below.

To establish quantitatively the partitioning between H- and D-elimination channels the measured signals must be corrected for the photoionization cross-sections of the major isomers contributing to each channel. The product mass spectra used for this analysis are summed over 10.35, 10.375 and 10.40 eV where the photoionization cross-section values of 1,3-butadiene, 1,2-butadiene and 1-butyne are known; these photon energies include the three measured products. The product mass spectrum and the integrated ion signal are shown in the Supporting Information (Figure S3). The relative signal strengths are $\sim 0.3 (m/z\ 54) : 1.0 (m/z\ 55)$. Correcting for the average cross section values using branching fractions obtained from the fits in Figure 4, this corrects to $\sim 0.4 (m/z\ 54) : 1.0 (m/z\ 55)$. From this, the final branching fractions for the CD + propene reaction are 0.28 1,2-butadiene and <0.01 1-butyne from D-elimination and 0.63 1,3-butadiene and ~ 0.08 1-butyne from H-elimination. These results are

quite similar to the results for the undeuterated CH + propene reaction shown in Table 1 and suggests that isotope effects on product branching are small.

H-assisted isomerization

The issue of H-assisted isomerization warrants discussion as our product detection could be influenced by isomerization of less stable C₄H₆ isomers into more stable ones facilitated by secondary H-atom reactions in the flow.³³ The energy calculations of the CH + propene reaction of Li *et al.* show that pathways leading to the numerous C₄H₆ isomers have thermodynamic barriers of 1—4 kcal/mol on their respective exit channels with respect to the various C₄H₆ + H product energies. This suggests that the rate constants for H + C₄H₆ should be slower than the gas-kinetic rate and detectable via kinetic measurements on the present apparatus. However, the *m/z* 54 product kinetic profiles did not change significantly when the propene concentration was changed by over a factor of 5. Furthermore, from the CD + propene experiment the almost pure 1,2-butadiene (*m/z* 54) kinetic signal displayed no decay that would suggest significant secondary reactions were occurring. It is thus likely that the exothermic H-assisted isomerization, 1,2-butadiene + H → 1,3-butadiene + H, is not significantly affecting the product branching fractions reported in this study.

4. DISCUSSION

Figure 5. Mechanism for CD + propene via a C=C π cycloaddition entrance channel leading to distinct isomers 1,2-butadiene and 1,3-butadiene- d_1 via D- or H-loss, respectively.

The results presented here show that the 1,3-butadiene isomer of C_4H_6 is the major product of the CH + propene reaction and that non-negligible quantities of 1,2-butadiene and 1-butyne are also formed. Revealingly, the CD + propene results show strong partitioning of the H-elimination and D-elimination channels (in a $\sim 3:1$ ratio, respectively) to distinct product isomers. Because there is only one D-atom and six H-atoms in the C_4H_6D radical intermediate, the mechanism leading to the formation of undeuterated 1,2-butadiene must be rather direct so as restrict the opportunity for D-atom scrambling. A suggested mechanism, outlined in Figure 5, involves direct cycloaddition of the CD radical to the double bond of propene, followed by ring opening to form deuterated 1-methylallyl ($CH_3CHCDCH_2$). This intermediate can be followed by prompt elimination of a D-atom to form undeuterated 1,2-butadiene, and our labeling results show this occurs with a ~ 0.28 branching fraction. An alternative 1-methylallyl dissociation pathway is H-elimination from the methyl group to form 1,3-butadiene- d_1 . This is also shown in Figure 5 and is consistent with the results in Figure 4b for the H-elimination product, occurring with a branching fraction of ~ 0.63 . In the computational study of Li *et al.*, the direct H-elimination from the methyl group of 1-

methylallyl is not calculated. They do calculate a pathway connecting 1-methylallyl to 1,3-butadiene + H but it first undergoes a 1,2-H atom shift from the methyl group to the adjacent carbon, forming 3-buten-1-yl ($\text{CH}_2\text{CHCH}_2\text{CH}_2$), which subsequently eliminates H from the internal CH_2 group to form 1,3-butadiene.

It should be noted that, on their own, the deuterium-labeling studies do not distinguish between 1,3-butadiene- d_1 produced directly from 1-methylallyl via methyl group H-elimination or from the 1,2-H shift via 3-buten-1-yl followed by H-elimination. In order to directly compare the energetics of these processes we draw on the calculations of Miller, who extensively explored the C_4H_7 linear-chain energy landscape using the G3//B3LYP method.³⁴ Using these calculated stationary points, the lowest energy pathways from the 1-methylallyl intermediate are reproduced in Figure 6 (we note that this is essentially the same figure that appears in the 1-methylallyl photodissociation study of Bach and co-workers³⁵). Figure 6 includes data for both the *Z* and *E* isomers where relevant, but the closeness of these stereoisomer energies is such that our analysis does not allow us to resolve them. The energy of CH + propene is ~125 kcal/mol above the minimum energy for 1-methylallyl (zero energy in Figure 6), well above all barriers presented in Figure 6. The 1,2 H-atom shift that isomerizes 1-methylallyl to 3-buten-1-yl has a barrier of 48.2 kcal/mol. Alternatively, direct H-elimination from the methyl group of 1-methylallyl proceeds via a barrier of 45.3 kcal/mol to form 1,3-butadiene. Comparison of the barrier heights involved in these two processes favors direct H-elimination by ~3 kcal/mol. Furthermore, direct H-elimination from the methyl group is likely to be entropically favored compared to the more geometrically constrained 1,2 H-atom shift transition state. In photolysis studies ($\lambda=415$ nm, 68.8 kcal/mol) of 1-methylallyl, H-elimination was found to be a major channel and in the deuterium-labeled case of $\text{CD}_2\text{CDCDCH}_3$, the loss of an H-atom is almost exclusive.³⁵ With these issues

considered, it is likely that direct H-elimination from the methyl group can compete, and in fact perhaps dominate, as the main 1-methylallyl $\rightarrow$ 1,3-butadiene + H pathway.

Figure 6. Calculated relative enthalpies (kcal/mol) for the E isomers for some of the lowest energy isomerization and dissociation pathways from the 1-methylallyl radical (values sourced from Miller ³⁴). Values in parentheses are for the Z isomers. The CH + propene limit is at +125 kcal/mol relative to 1-methylallyl.¹⁶ The hydrogen in blue would originate from the CH radical in accord with the scheme in Figure 5.

Figure 6 shows that the formation of 1,2-butadiene is significantly less exothermic than the 1,3-butadiene product channel (by ~ 12 kcal/mol). The Miller study places the product channel transition state between 1-methylallyl and 1,2-butadiene + H at 58.8 kcal/mol, ~ 13.5 kcal/mol higher than the barrier to direct formation of 1,3-butadiene. With the high energy of the CH radical ($\Delta H_f = 142$ kcal/mol ³⁶), these pathways are energetically accessible; the Li *et al.* study places the CH + propene energy at 125 kcal/mol relative to 1-methylallyl.¹⁶ Although a less exothermic reaction channel when compared to 1,3-butadiene

+ H, observation of a significant yield of 1,2-butadiene + D (from the CD + propene reaction) is consistent with traversal through this direct channel of H/D elimination from 1-methylallyl.

Small amounts of 1-butyne were detected in the present experiments, convincingly from H-loss (Figure 4a) and less so from D-loss (Figure 4b). The observation of deuterated 1-butyne from H-loss in the CD + propene experiments is consistent with the pathway from 1-methylallyl depicted in Figure 6, via a relatively high barrier (65.1 kcal/mol relative to 1-methylallyl) for a 1,2 H-atom shift to form 1-buten-2-yl followed by elimination of a terminal methylene H-atom yielding 1-butyne + H. This high barrier between 1-methylallyl and 1-buten-2-yl, along with the unfavorable entropic factors that accompany this 1,2-H atom transfer, are somewhat difficult to reconcile with the moderate 0.12 branching fraction of 1-butyne. Furthermore, from 1-buten-2-yl there are also pathways to other product channels (not depicted in Figure 6) including allene + CH₃³⁴ that are not detected in our experiment. Also, as mentioned above, there is no clear evidence of H-assisted isomerization that could produce 1-butyne from 1,2-butadiene. So it appears that an unknown reaction pathway may lead to the formation of 1-butyne, that may not include 1-buten-2-yl, and such a pathway would also have to be consistent with the CD + propene result that shows most of the 1-butyne is formed from H elimination (not D elimination).

Alternative reaction entrance pathways, other than the C=C π cycloaddition, are C—H σ insertion channels. The CD + propene results suggest that such mechanisms do not need to be invoked to explain our results. As shown in Scheme 1(ii), C—H insertion would lead to a $\text{—C}\cdot\text{HD}$ moiety, regardless of which C—H bond was attacked. From these intermediates the almost-pure 1,2-butadiene + D product fraction is difficult to justify, offering compelling evidence that the dominant entrance channel for the reaction is via π cycloaddition. The 1,3-butadiene-*d*₁ result is also consistent with this but, in this case, there are other possibilities. The σ insertion by CD into a C—H bond, either at the —CH_3 group or the =CH_2 group of

propene, followed by H-elimination, could plausibly lead to 1,3-butadiene- d_1 , which is detected, and so cannot be ruled out.

5. CONCLUSION

Under the conditions of this experiment (4 Torr, 298 K), the CH + propene reaction is found to lead to two major product channels, 1,3 butadiene + H (0.63 ± 0.13 branching fraction) and 1,2-butadiene + H (0.25 ± 0.05 branching fraction). The quoted uncertainties are $\pm 20\%$. In addition, a small portion of 1-butyne + H is produced (0.12 ± 0.02 branching fraction). From investigations into the CD + propene reaction both H-elimination and D-elimination channels are detected and produce unique products, eliminating the possibility of H-atom scrambling in the C_4H_6D intermediate. From this C_4H_6D intermediate, the D-loss channel produced almost exclusively 1,2-butadiene while H-loss produced mostly 1,3-butadiene with small amounts of 1-butyne. The results from the CD + propene study were found to be generally consistent with a cycloaddition entrance channel forming 1-methylallyl, followed by either direct D-elimination or H-elimination from the CH_3 group of the intermediate. However, a CD insertion process into a C-H σ -bond to form 1,3-butadiene- d_1 could not be unequivocally ruled out. A Rice-Ramsperger-Kassel-Marcus/Master Equation analysis would be helpful to verify if the stationary points in Figure 6 are sufficient to explain the product branching fractions observed in this study.

These conclusions have important implications to the modeling of radical + hydrocarbon systems, especially that the CH + propene reaction is a potential source of 1,3-butadiene. For example, recent studies of the 1,3-butadiene + phenyl reaction reveal that a bicyclic 1,4-dihydronaphthalene species is produced, indicating an important early pathway to building larger polyaromatic hydrocarbons species in hydrocarbon-rich systems in diverse environments including the interstellar medium or combustion processes.^{37,38} Another recent study implicates 1,3-butadiene in the formation of benzene in the interstellar medium via

reaction with the C_2H radical.⁷ Furthermore, the modeling contained in that study concluded that neutral-neutral chemistry is the dominant source of benzene in the Taurus Molecular Cloud (TMC-1). The postulated chemical mechanism relies on $CH + C_3H_6 \rightarrow 1,3\text{-butadiene} + H$ reaction which is then followed by $1,3\text{-butadiene} + C_2H \rightarrow c\text{-}C_6H_6 + H$.⁷ Our results reported here provide the first direct evidence that 1,3-butadiene is the dominant product of the $CH +$ propene reaction, in support of this assumption. Interestingly, the significant branching fraction for production of 1,2-butadiene may warrant further investigation into its role in the chemistry of hydrocarbon-rich environments.

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SUPPORTING INFORMATION AVAILABLE

Additional Figures are provided in Supporting Information, as mentioned in the text, in addition to the complete author list for Ref [30]. This information is available free of charge for the Internet at <http://pub.acs.org>.

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