*Graphical Abstract

Formation of Fulvene in the Reaction of C₂H with 1,3-Butadiene

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Abstract

Products formed in the reaction of C₂H radicals with 1,3-butadiene at 4 Torr and 298 K are probed using photoionization time-of-flight mass spectrometry. The reaction takes place in a slow-flow reactor, and products are ionized by tunable vacuum-ultraviolet light from the Advanced Light Source. The principal reaction channel involves addition of the radical to one of the unsaturated sites of 1,3-butadiene, followed by H-loss to give isomers of C₆H₆. The photoionization spectrum of the C₆H₆ product indicates that fulvene is formed with a branching fraction of (57 ± 30)%. At least one more isomer is formed, which is likely to be one or more of 3,4-dimethylenecyclobut-1-ene, 3-methylene-1-penten-4-yne or 3-methyl-1,2-pentadien-4-yne. An experimental photoionization spectrum of 3,4-dimethylenecyclobut-1-ene and simulated photoionization spectra of 3-methylene-1-penten-4-yne and 3-methyl-1,2-pentadien-4-yne are used to fit the measured data and obtain maximum branching fractions of 74%, 24% and 31%, respectively, for these isomers. An upper limit of 45% is placed on the branching fraction for the sum of benzene and 1,3-hexadien-5-yne. The reactive potential energy surface is also investigated computationally. Minima and first-order saddle-points on several possible reaction pathways to fulvene + H and 3,4-dimethylenecyclobut-1-ene + H products are calculated.

Keywords: Combustion Chemistry; Astrochemistry; Fulvene; Benzene; Polycyclic Aromatic Hydrocarbons; Photoionization

1. Introduction

There are many parallels between combustion chemistry and the chemistry of planetary atmospheres and interstellar space. In these environments, reactions of radicals with hydrocarbons lead to molecular-weight growth and formation of polycyclic aromatic hydrocarbons (PAHs). Further, it is often the same radicals that are thought to be responsible for these important processes in such varied environments. PAHs are significant in astrochemistry because they are complex molecules whose formation may give us clues to the chemistry of a prebiotic Earth.[1, 2] In combustion, the mechanism of PAH formation is investigated in order to curtail it, because PAHs and soot emitted from combustion engines[3-5] are significant pollutants.

Benzene (C_6H_6), the simplest closed-shell aromatic ring, is likely to be a key primary reactant in PAH chemistry and it has been detected in the circumstellar envelopes,[6, 7] the atmosphere of Titan[2, 8] and in numerous combustion and flame studies[9, 10]; thus, many reactions have been postulated to explain its formation. In addition, it is vital to know the pre-cyclization chemistry as well as the critical ring-forming reactions to understand the generation of PAHs.[4] In combustion environments, propargyl (C_3H_3) recombination is generally thought to be one of the main benzene formation pathways.[4, 11-13] However, several studies have shown that benzene is a minor, or non-existent, product of propargyl recombination at low temperatures and pressures.[12, 14] The $C_3H_3 + C_3H_3$ route to C_6H_6 can only proceed by relatively inefficient radiative association in the very low pressures of astrochemical environments and so alternative mechanisms must be invoked. Another popular candidate for benzene formation is the reaction between the 1,3-butadien-1-yl radical ($n-C_4H_5$) and acetylene (C_2H_2), which undergoes an addition-elimination reaction to yield $C_6H_6 + H$. [3, 4, 15] However, there are conflicting accounts of the importance of C_4H_5 in benzene formation, not the least of which is that 1,3-butadien-2-yl ($i-C_4H_5$) is more stable than $n-C_4H_5$, but it is preferable to have the latter for facile benzene formation.[4] In 1989 Westmoreland *et al* outlined 18 suggested pathways to benzene formation in combustion.[9] Despite all current and past efforts, even the most rigorous combustion models available are unable to accurately predict concentrations of species such as C_6H_6 , C_5H_6 , and C_8H_6 . [16] For example, the concentrations of 1-butyne (CH_3CH_2CCH), 2-butyne (CH_3CCCH_3), 1,3-butadiene ($CH_2CHCHCH_2$), C_4H_5 , C_4H_4 , C_4H_3 and 1,3-butadiyne (C_4H_2) from a butanol flame experiment are not well replicated by the associated model and the authors of this study state that this discrepancy arises because the base C_4 chemistry has not been thoroughly

1 validated for recombination reactions that lead to highly unsaturated C_4 and larger
2 hydrocarbons.[16]

3 A promising species in the search for cyclization reactions is the ethynyl radical
4 (C_2H), which is abundant in many astronomical environments.[17-19] The C_2H radical
5 readily undergoes barrierless addition-elimination reactions with unsaturated
6 hydrocarbons.[20] The fact that these reactions are barrierless is important in low temperature
7 astrochemical environments, where entrance barriers are difficult or impossible to overcome.
8 Reactions of C_2H have been implicated in the generation of long chain polyynes that have
9 been detected in the interstellar medium (ISM).[6, 21, 22] Moreover, the eliminated moiety in
10 the addition-elimination reactions of this radical is often a hydrogen atom, meaning that C_2H
11 reacting with C_4H_6 yields isomers of $C_6H_6 + H$. Thus, C_2H has been suggested by Kaiser and
12 co-workers to be a critical species in benzene formation in the ISM.[23] Although in
13 combustion environments C_2H is present at concentrations that are too small to make a
14 substantial contribution to soot formation, C_2H is formed *via* several reactions: between the
15 hydroxyl radical (OH) and C_2H_2 to form water (H_2O) and C_2H ,[4] between C_3H_3 and oxygen
16 atoms (O) to form formaldehyde (CH_2O) + C_2H , between C_3H_3 and methyl radicals (CH_3) to
17 form ethyl radicals (C_2H_5) + C_2H [24], or between C_3H_3 and methylene radicals (CH_2) to form
18 ethene (C_2H_4) + C_2H . [11] In addition, C_2H can be formed by the reaction of hydrogen atoms
19 (H) with C_2H_2 at higher temperatures.[5, 25]

20 Recently, Mebel and co-workers have carried out an extensive *ab initio* investigation
21 into the reactions of C_2H with unsaturated hydrocarbons, including all isomers of C_4H_6 (1,3-
22 butadiene,[23] 1,2-butadiene,[20] 1-butyne and 2-butyne[26]). In a combined crossed-
23 molecular beams and computational study, Jones *et al.* suggested that benzene is formed in
24 the reaction between C_2H and 1,3-butadiene,[23] at kinetic energies higher than thermal. In
25 the crossed-molecular beams experiment products were ionized by electron impact at 80 eV,
26 and isomer identification was achieved by examination of product translational energy
27 distributions. The experimental part of the study indicated a branching fraction for benzene of
28 30%, with the other 70% of products being 1,3-hexadien-5-yne. The theoretical study found a
29 benzene branching fraction between 40% and 20% at collision energies between 0 kJ mol^{-1}
30 and 45 kJ mol^{-1} . To our knowledge, this is the only experimental report of the products of the
31 $C_2H + 1,3\text{-butadiene}$ reaction, and therefore it is valuable to investigate this reaction *via*
32 additional methods.

33 The reaction of the cyano radical (CN), which is isoelectronic with C_2H , with 1,3-
34 butadiene has also been studied.[27] Previous studies of the reactions of the isoelectronic C_2H

1 and CN radicals with unsaturated hydrocarbons have shown that they react similarly, both in
2 terms of reaction rate and major products.[28-31] Thus, one might expect the outcome of the
3 CN + 1,3-butadiene reaction to provide clues to the C₂H + 1,3-butadiene reaction mechanism.
4 CN + 1,3-butadiene proceeds *via* addition and H-elimination to yield isomers of C₅H₅N.
5 Crossed-molecular beams experiments suggest a maximum of 3%–6% pyridine and 94%–
6 97% 1-cyano-1,3-butadiene is formed under single collision conditions. Rice-Ramsperger-
7 Kassel-Marcus (RRKM) calculations predict only 0.02% pyridine formation at 0 eV collision
8 energy, with a maximum of 6% at the limits of the errors of the calculations.[27] If C₂H +
9 1,3-butadiene were analogous to CN + 1,3-butadiene, one might expect a small branching
10 fraction for benzene, with the remainder of the products being 1,3-hexadien-5-yne.

11 Despite the likely importance of C₂H reactions with C₄H₆ isomers, very few other
12 studies examining them have been published. The reasons for this are manifold, including the
13 technique chosen to produce the C₂H radical. Generally, in flow tube experiments, C₂H is
14 formed *via* 193 nm photolysis of C₂H₂, or occasionally 193 nm photolysis of
15 trifluoromethylacetylene (CF₃CCH). Recent work in our group has employed 193 nm
16 photolysis of C₂H₂ and CF₃CCH to determine the products and rates of reactions of C₂H with
17 acetylene,[32] ethene,[33] propene,[33] butenes,[34] allene[35] and propyne,[35] among
18 others. However, polyunsaturated and acetylenic C₄ (and higher) hydrocarbons tend to absorb
19 strongly at 193 nm, so there are concurrent photodissociation yields of radicals that can
20 interfere with the reaction of interest or give rise to secondary reactions that complicate the
21 analysis. Our group has reported one experimental study of C₂H with an isomer of C₄H₆,
22 specifically 1-butyne,[36] which employed 193 nm photolysis of C₂H₂ to generate the
23 radicals and in which the contribution of products due to 1-butyne photolysis was carefully
24 examined and accounted for. Clearly a method that avoids photodissociation of the molecular
25 co-reactant is preferable. At 300 K, 1,3-butadiene absorbs strongly at 193 nm, but only
26 weakly at 248 nm. Consequently, for the experimental work here, a different C₂H precursor
27 was synthesized, bromoacetylene (BrC₂H), which photolyses efficiently at 248 nm to give Br
28 + C₂H.[37] Details of the synthetic method are given in the Experimental section.

29 Determining the ratio between straight chain and cyclic isomer products of the title
30 reaction is valuable for understanding astrochemical and combustion chemistry. By
31 synthesizing bromoacetylene, an excellent C₂H precursor when photolysed at 248 nm,
32 problems with interfering dissociative products of the 1,3-butadiene are minimized.
33 Obtaining product masses is achieved by tunable synchrotron ionization, time-of-flight mass
34 spectrometry. This method is a powerful multiplexed technique that allows the identification

of the product isomers formed. In the following sections, the experimental techniques are described and the recorded reaction spectra are presented. These results are followed by a discussion of the extracted branching fractions and possible reaction pathways, calculated at the CBS-QB3 level. Finally, the implications of current results for our understanding of astrochemical and combustion environments are discussed.

2. Experimental Details

The experimental technique comprises several components. Synthesized BrC_2H gas is mixed with 1,3-butadiene and flowed through a quartz tube housed in a vacuum chamber. Photodissociation of BrC_2H forms $\text{Br} + \text{C}_2\text{H}$, which react with the closed-shell 1,3-butadiene. Gases exit the reactor through a pinhole and are ionized with tunable vacuum ultra-violet light in a differentially pumped chamber. The mass-analysis of the products is carried out using a time-of-flight mass-spectrometer. Details of the spectrometer and the synthesis procedure will be given in the following sections. In addition, the computational methodologies employed for supporting interpretation of the data are also described.

2.1 Multiplexed Photoionization Mass Spectrometer

The $\text{C}_2\text{H} + 1,3\text{-butadiene}$ reaction takes place in a laser photolysis, slow flow reactor coupled to a multiplexed photoionization mass spectrometer at the Advanced Light Source of Lawrence Berkeley National Laboratory. Comprehensive details of the experimental apparatus are given elsewhere[38-40] and only an overview is presented here. The reactions occur inside a quartz tube with 1.05 cm inner diameter at 4 Torr (533 Pa) and 298 K. The gas flow consists of small amounts of the C_2H radical precursor, BrC_2H , and 1,3-butadiene in a large excess of helium buffer gas. Dilutions of BrC_2H and 1,3-butadiene in helium are prepared in stainless steel cylinders with a total pressure of 2000 Torr. The gases are mixed *in situ* at the entrance of the reactor using calibrated mass flow controllers. The total flow is 100 sccm (standard cubic centimeters per minute), sufficient to completely replenish the gas in the reactor tube between consecutive laser pulses (4 Hz repetition rate). Reactor pressure is maintained with a butterfly valve after the reactor under active feedback control.

A uniform initial concentration of C_2H radicals is produced in the axial and radial directions of the reactor tube by 248 nm photolysis of BrC_2H using the unfocused beam of an excimer laser. The typical photolysis fluence inside the reaction flow tube is $\sim 70 \text{ mJ cm}^{-2}$ in a 20 ns pulse. There is effectively no attenuation of the photon flux along the length of the flow tube due to absorption, as verified by the stable concentrations of products of photolytically-initiated reactions. The initial BrC_2H and 1,3-butadiene number densities are both 6.5×10^{13}

1 cm^{-3} in a total gas density of $1.3 \times 10^{17} \text{ cm}^{-3}$. Depletion of the BrC_2H signal at $t=0$ when the
2 laser fires is not apparent in the time profile for this species above the signal-to-noise ratio
3 and therefore the percentage depletion of the radical precursor is estimated to be $<1\%$. Zhang
4 *et al* employed 193 nm BrC_2H photodissociation in a crossed-molecular beams experiment
5 and indicated that approximately 6% of the BrC_2H is decomposed into $\text{Br} + \text{C}_2\text{H}$ with a laser
6 fluence of $\sim 400 \text{ mJ cm}^{-2}$. [41] The absorbance of 248 nm light by BrC_2H is reported to be
7 around 30 times lower than that of 200 nm light. [42] Due to the absence of absorption data at
8 193 nm, the assumption is made that the absorbance at 193 nm is similar to 200 nm.
9 Correcting for the laser fluence and different cross-section at 200 nm and 248 nm, an estimate
10 of 0.035% for percentage of BrC_2H that photodissociates at 248 nm is calculated. Thus, an
11 estimate for the number density of the C_2H radicals of $\sim 2 \times 10^{10} \text{ cm}^{-3}$ is derived.

12 A portion of the gas escapes from the flow tube through a 650 μm diameter pinhole in
13 the side of the tube into a chamber at a pressure of 10^{-5} Torr. The nearly effusive beam from
14 this pinhole is skimmed by a 1.5 mm diameter skimmer before entering a differentially
15 pumped ionization region. The gas beam is crossed by tunable synchrotron undulator vacuum
16 ultraviolet (VUV) radiation that is dispersed by a 3 m monochromator (Chemical Dynamics
17 Beamline at the Advanced Light Source of Lawrence Berkeley National Laboratory). The
18 monochromatic VUV radiation energy is calibrated using known atomic resonances of Xe; at
19 the conditions employed in these experiments the VUV light has a bandwidth of 20 meV. The
20 VUV photon flux at each photon energy is measured using a calibrated photodiode (SXUV-
21 100 International Radiation Detectors, Inc.). The masses of all cations formed in the
22 ionization region are monitored with an orthogonal acceleration time-of-flight mass
23 spectrometer equipped with a micro-channel plate detector. Mass spectra are taken at
24 intervals of 20 μs , from -20 ms to 130 ms relative to photolysis. By additionally scanning the
25 photon energy, time- and photon energy-resolved mass spectra are recorded, leading to a
26 three-dimensional matrix of data consisting of ion intensity as a function of m/z (mass-to-
27 charge ratio), reaction time, and photon energy.

28 The data can be examined in three ways: m/z vs. kinetic time, m/z vs. photon energy and
29 photon energy vs. kinetic time. Photoionization spectra are constructed by integrating the data
30 first over the desired m/z range and then over a suitable time window that corresponds to
31 production of the species of interest in the reaction. Background contributions are removed
32 by subtraction of the average pre-photolysis signal taken in the 20 ms before the
33 photodissociation laser pulse. Finally, these background-subtracted signals are normalized for
34 the VUV photon flux at each photon energy. Full time- and photon-energy-dependent spectra

are collected three times to check for consistency, with 200 laser pulses at each VUV photon energy.

2.2 Bromoacetylene Synthesis

The C_2H precursor in our experiment was bromoethyne (bromoacetylene, BrC_2H), which was synthesized according to the methodology of Bashford *et al.*[43] Synthesis was carried out in a triple-necked round-bottomed flask in a temperature-controlled water bath, connected to a water-cooled condensing column and a phosphorus pentoxide drying column. 10 g (50% w/w) sodium hydroxide solution was placed in the flask. The synthesis apparatus was purged of air using a helium flow and covered in aluminum foil to prevent any photolytic decomposition of the BrC_2H product. 15 g of 1,2-dibromoethylene and 18 ml of ethanol were injected into the flask. The flask was then heated to 85°C for one hour, whilst maintaining a slow helium flow. Reaction products were collected in a liquid nitrogen cooled cold trap.

Purification of BrC_2H was carried out using three cold traps, covered in aluminum foil, attached in series and connected to a rotary pump, which attained a pressure of 100 mTorr. The temperatures of the three successive cold fingers were -65°C , -115°C and -196°C . The impure product was pumped through the traps and was isolated in pure form at -115°C and then allowed to sublime into a stainless steel cylinder with internal Teflon coating. Helium was added to the cylinder to make a 5% mixture of BrC_2H ; a dilute mixture is used to reduce the rate of degradation and polymerization.

The vapor pressure of BrC_2H was measured to be greater than 100 Torr at 298 K. A very high degradation rate is observed when exposed to light in solid state, and there is a high degradation rate at elevated temperatures, even in gaseous phase. Oxygen reacts extremely violently with BrC_2H and induces explosive polymerization.[43] The purity of the sample was checked with time-of-flight mass spectrometry using the Multiplexed Photoionization Mass Spectrometer (see Section 2.2) and the mass spectrum showed very little impurity.

2.3 Computational Methodology

Identification of the isomers produced in the reaction relies on fitting the measured product photoionization spectra to known spectra of the pure compounds. In cases where these spectra have not been measured, due to the instability of the molecules, the spectra are simulated using computational methods. The photoionization spectrum of a molecule is computed by integrating the Franck-Condon factors between the vibrational modes of the ground and ionic states.[44] Employing the Gaussian 09 suite of programs[45], adiabatic ionization energies (AIEs) are calculated using the CBS-APNO or CBS-QB3 composite methods.[46] The geometries, harmonic vibrational modes and force constants for the

molecules of interest are calculated at the B3LYP/cc-pVTZ level, and photoelectron spectra are simulated making use of the built-in Franck-Condon overlap feature of Gaussian 09.[47, 48] Note that this method is based on the assumption of direct ionization to the lowest-lying cationic state and does not describe autoionizing and shape resonances, dissociative ionization, and ionization to excited cationic states. Where applicable, the semiempirical method of Bobeldijk *et al* [49] is used to estimate the absolute photoionization cross sections. Photoionization spectra used in the following analysis, simulated or experimental, are given in the Supporting Information.

Minima and first-order saddle points on the $C_2H + 1,3$ -butadiene potential energy surface (PES) are explored using the M06-2X method[50] with a 6-31G* basis set, with energies calculated using the CBS-QB3 composite method.[51, 52] The quantum-chemical calculations are performed using Gaussian09.[45]

3. Results

3.1. Experimental Results

$C_2H + 1,3$ -butadiene reaction data were recorded over the 8.2 – 11.5 eV photon energy range, the -20 – 130 ms kinetic time range and up to 160 atomic mass units. Figure 1 shows the background-subtracted product mass spectrum integrated over the 8.2 – 11 eV photon energy range as a function of kinetic time, along with the one-dimensional mass spectrum resulting from integration of the time-dependent spectrum over the 0 – 100 ms range. Four main peaks are present in the background subtracted mass spectrum, at $m/z = 39$, 50, 52 and 78, corresponding to molecular formulae C_3H_3 , C_4H_2 , C_4H_4 and C_6H_6 , respectively. The peak at $m/z = 79$ is approximately 8% of the magnitude of the peak at $m/z = 78$, 6.1% of which is due to the presence of $^{12}C_5^{13}CH_6$ at the natural abundance. The remaining 1.9% is likely due to detection of C_6H_7 , the reaction adduct, which may undergo radiative or collisional stabilization.

Figure 1. Top panel is the background subtracted time-dependent mass spectrum integrated over the 8.2 – 11 eV photon energy range with the radical precursor BrC_2H and the closed-shell reactant 1,3-butadiene present in the flow tube. The products that are dependent on the photolysis laser pulse ($t = 0$) appear in the spectrum. Bottom panel shows a one-dimensional mass spectrum integrated over the 0 – 100 ms time range.

Mass spectra were also recorded at a single photon energy of 10.6 eV with only BrC_2H or only 1,3-butadiene in the flow. These data inform us of any direct photolysis products of the reactants, or secondary reactions involving these photolysis products that do not require both reactants entrained in the flow. One-dimensional mass spectra recorded with only BrC_2H or 1,3-butadiene entrained in the flow are given in the Supplementary Information and compared to a spectrum recorded when both reactants were entrained in the flow; these mass spectra are not background subtracted. When only BrC_2H is present in the flow, a peak at $m/z = 50$, due to detection of a species with molecular formula C_4H_2 , is observed. When only 1,3-butadiene is present in the flow, four peaks appear in the spectrum: at $m/z = 39$, $m/z = 50$, $m/z = 52$ and $m/z = 78$ due to detection of species with the molecular formulae C_3H_3 , C_4H_2 , C_4H_4 and C_6H_6 , respectively. The background subtracted temporal evolutions of these four signals, at $m/z = 39$, 50 , 52 and 78 , are examined and shown in Figure 2. In Figure 2, the solid black and dotted blue lines show the evolution of the signal when only BrC_2H and only 1,3-butadiene, respectively, are present in the flow and the dashed red line is the time profile of the signal when both reactants are present.

Figure 2 (a) shows that $m/z = 39$ is solely due to 1,3-butadiene photolysis. The depletion rate of the $m/z = 39$ concentration when both reactants are present (dashed red line) is faster due to the fact that there are more species in the flow that can react with the radical. The peak at $m/z = 50$ is predominantly due to photolysis of BrC_2H , with a very small contribution from 1,3-butadiene photolysis, Figure 2 (b). The component of the $m/z = 50$

1 signal that is due to 1,3-butadiene photolysis has a slower rise time than that for the total
2 signal when both reactants are present and the signal due to BrC_2H photolysis. This slower
3 rise time suggests that the source of this species is a secondary reaction rather than primary
4 photolysis of 1,3-butadiene. Figure 2 (c) shows that the peak at $m/z = 52$ is primarily due to
5 photolysis of 1,3-butadiene, yet the concentration of this species increases when both
6 reactants are entrained in the flow. The relative areas of the peaks at $m/z = 52$ with only 1,3-
7 butadiene in the flow and with both reactants in the flow reveals that approximately 73% of
8 the products at this mass arise from photolysis of 1,3-butadiene. Possible sources of the
9 remaining 27%, which arises only when both reactants are present, will be discussed later.
10 The time profiles for $m/z = 78$ shown in Figure 2 (d) reveal that the majority of the signal,
11 approximately 90%, only appears when both reactants are present in the flow. When only
12 1,3-butadiene is present, a small signal appears at $m/z = 78$ that has a very slow rise time that
13 accounts for no more than 10% of the total when both reactants are present. This signal is
14 likely due to the recombination of C_3H_3 radicals ($m/z = 39$) that are formed by 1,3-butadiene
15 photolysis, a process that has been observed before,[53] or a reaction of C_3H_3 with 1,3-
16 butadiene. Nevertheless, it is clear that formation of C_6H_6 ($m/z = 78$) is the predominant
17 reaction channel in the $\text{C}_2\text{H} + 1,3\text{-butadiene}$ reaction.

Figure 2. Background subtracted time profiles for $m/z = 39$, 50, 52 and 78 with only BrC_2H and He in the flow (solid black line), with only 1,3-butadiene and He in the flow (dotted blue line) and with both BrC_2H and 1,3-butadiene (and He) in the flow (dashed red line).

The peak at $m/z = 50$ has been identified by its photoionization spectrum as 1,3-butadiyne[54] (C_4H_2), Figure 3 (a). Upon photolysis of BrC_2H , 1,3-butadiyne forms by

1 reaction of the photolytically produced C_2H radical with the radical precursor *via* the
 2 mechanism outlined in Scheme 1, Figure 4.[55] The peaks at $m/z = 39$ and 52 have been
 3 identified as propargyl radicals[56] (C_3H_3), Figure 3 (b), and vinyl acetylene[54] (C_4H_4),
 4 Figure 3 (c), respectively. Few studies have dealt with the fate of 1,3-butadiene following
 5 excitation at 248 nm. However, numerous studies explored the excitation and photolysis of
 6 1,3-butadiene in the 193 nm – 220 nm range, from which it is found that the primary
 7 dissociative channel leads to formation of $C_3H_3 + CH_3$. [14, 57-60] In addition to $C_3H_3 + CH_3$,
 8 the following minor photolysis channels have also been reported in the 193 – 220 nm energy
 9 range: $C_4H_5 + H$, $C_4H_4 + H_2$, $C_2H_3 + C_2H_3$ and $C_2H_2 + C_2H_4$ with varying relative ratios.[14,
 10 59, 60] The 1,3-butadiene cross-section for absorption at 248 nm is nearly two orders of
 11 magnitude smaller than at 193 nm and certain channels are energetically inhibited, such as
 12 formation of two vinyl radicals (C_2H_3) by cleavage of the central C-C bond. It has been
 13 shown that in the 220 nm – 260 nm range, photolysis of 1,3-butadiene leads to formation of
 14 CH_3 radicals (in conjunction with C_3H_3) with a branching of 75%.[61] Propargyl radicals are
 15 formed in conjunction with CH_3 (Scheme 2, Figure 4), although methyl is not detected in our
 16 experiment. The absence of CH_3 signal is likely due to the fact that the photoionization cross-
 17 section of CH_3 is much smaller than that of propargyl radicals; at 10.413 eV, for example, it
 18 is around 4 times lower.[56] In addition, the mass discrimination factor of the mass-
 19 spectrometer means detection of species with $m/z = 39$ is nearly twice as likely as species
 20 with $m/z = 15$. [56] The majority of the signal at $m/z = 52$, vinyl acetylene, is due to 1,3-
 21 butadiene photolysis, Scheme 3 in Figure 4, or secondary reactions of photolysis products,
 22 but a small additional amount is due to the presence of both BrC_2H and 1,3-butadiene in the
 23 flow. Vinyl acetylene could potentially be a product of $C_2H + 1,3$ -butadiene reaction *via* a
 24 mechanism of addition and β -C-C bond scission to yield vinyl acetylene + C_2H_3 , Scheme 4 in
 25 Figure 4. However, vinyl radicals ($m/z = 27$) are not observed above the background level in
 26 the mass spectra, perhaps because they rapidly dissociate or react.

Figure 3. Photoionization spectra of the species detected at (a) $m/z = 50$, (b) $m/z = 39$ and (c) $m/z = 52$. The red solid lines show the photoionization spectra of (a) 1,3-butadiyne, (b) propargyl and (c) vinyl acetylene.

1

Scheme 1

Scheme 2

Scheme 3

Scheme 4

2

3 Figure 4. Scheme 1: Reaction mechanism for formation of 1,3-butadiyne *via* photolysis of BrC_2H at 248 nm to
 4 give $\text{C}_2\text{H} + \text{Br}$, followed by reaction of the C_2H with BrC_2H and Br elimination. Photolysis of 1,3-butadiene by
 5 248 nm light to give $\text{C}_3\text{H}_3 + \text{CH}_3$ (Scheme 2) and vinyl acetylene + H_2 (Scheme 3). Scheme 4: Possible reaction
 6 mechanism for production of vinyl acetylene + vinyl radicals from the reaction of C_2H with 1,3-butadiene.

7 The current experiment shows the predominant channel in the $\text{C}_2\text{H} + 1,3\text{-butadiene}$
 8 reaction to be addition of the radical to one of the unsaturated carbon sites of 1,3-butadiene
 9 followed by H-loss to give C_6H_6 . The fact that the amount of vinyl acetylene ($m/z = 52$)
 10 detected increases by 27% when both BrC_2H and 1,3-butadiene are present in the flow
 11 suggests that a pathway to vinyl acetylene (C_4H_4) + vinyl radicals (C_2H_3) may also represent
 12 a small fraction of the reactivity. In addition, the peak at $m/z = 79$ has an area that is 1.9%

larger than expected from $^{12}\text{C}_5^{13}\text{CH}_6$ alone, suggesting that some reactive intermediates are stabilized radiatively or by collisions. Based solely on the peak areas of these respective signals, and not accounting for the absolute photoionization cross-sections of the constituent species, the process that results in $m/z = 78$ accounts for 96% of reactivity, that resulting in vinyl acetylene ($m/z = 52$) accounts for 4% and the proportion of intermediates that are stabilized is 0.2%.

To identify isomers formed, the measured photoionization spectrum of the products at $m/z = 78$ is examined. As shown earlier, there is a contribution to the peak at $m/z = 78$ when only 1,3-butadiene is present in the flow, arising from C_3H_3 recombination. This C_3H_3 recombination accounts for less than 10% of the total signal at $m/z = 78$ when both reactants are present in the flow. The photoionization spectrum of the products of C_3H_3 recombination is given in the Supplementary Information[62] and is compared to the product photoionization spectrum of $m/z = 78$ obtained here. The onset and shape of the spectrum of the products of C_3H_3 recombination is significantly different to that of the products with $m/z = 78$ in this experiment. Correcting the spectrum for the products of the $\text{C}_2\text{H} + 1,3\text{-butadiene}$ reaction for the 10% contribution from C_3H_3 recombination has a negligible effect on the shape of the measured spectrum. Nevertheless, this corrected spectrum is used in the following analysis. The onset of the measured photoionization spectrum of the products of $\text{C}_2\text{H} + 1,3\text{-butadiene}$ with $m/z = 78$ is at 8.36 eV, which matches exactly with the ionization onset of fulvene.[63] Indeed, the measured photoionization spectrum can be reproduced by the experimentally measured photoionization spectrum of fulvene[36] up to a photon energy of ≈ 8.85 eV, Figure 5 (a). From the deviation of the measured signal from the fulvene photoionization spectrum above 8.85 eV, it is evident that additional isomers must contribute to the overall signal. There are three isomers of C_6H_6 that have ionization onsets in the 8.85 eV region; these are 3,4-dimethylenecyclobut-1-ene (8.8 eV[63]), 3-methylene-1-penten-4-yne (no experimental value available, calculated in this work using the CBS-APNO methodology to be 8.89 eV[64]) and 3-methyl-1,2-pentadien-4-yne (no experimental value available, calculated in this work using the CBS-APNO methodology to be 8.90 eV[64]). It seems likely that one or more of these isomers is formed.

A good fit to the measured photoionization spectrum can be obtained with a weighted contribution of the experimentally measured photoionization spectra of fulvene[36] and 3,4-dimethylenecyclobut-1-ene,[36] as shown in Figure 5 (b). Adjusting the scaling factors for the absolute photoionization cross-sections of these two isomers yields branching ratios of 51% fulvene and 49% dimethylenecyclobut-1-ene. Alternatively, if a contribution from 3-

1 methylene-1-penten-4-yne is included in addition to fulvene, as shown in Figure 5 (c), a good
2 fit of the measured spectrum can be obtained up to a photon energy of around 9.5 eV. The
3 photoionization spectrum of 3-methylene-1-penten-4-yne has not been measured
4 experimentally and so a simulated spectrum reported by Soorkia *et al*[36] is used in the
5 current analysis. These simulations often reproduce the experimental spectra for the transition
6 from the ground electronic state of the neutral to the ground electronic state of the cation.
7 However, excited electronic states of the cation and autoionization are not considered in the
8 calculation and so the simulated spectrum may not have the same shape as the real spectrum
9 at higher photon energies. For this reason it is difficult to determine whether the deviation of
10 the fit from the measured spectrum in Figure 5 (c) at 9.5 eV is due to formation of other
11 isomers with higher ionization energies or due to photo-excitation to excited electronic states
12 of 3-methylene-1-penten-4-yne. Finally, a good fit to the measured spectrum can also be
13 obtained if a contribution of 3-methyl-1,2-pentadien-4-yne is included, in addition to the
14 fulvene component, Figure 5 (d). An experimental photoionization spectrum of 3-methyl-1,2-
15 pentadien-4-yne is not available and so was simulated using the methodology outlined in the
16 Experimental section. Using fulvene and 3-methyl-1,2-pentadien-4-yne, the fit begins to
17 deviate from the data at around 9.75 eV, which could be due to excited electronic states of the
18 3-methyl-1,2-pentadien-4-yne cation or additional isomers being formed.

Figure 5. Black open circles show the measured photoionization spectrum for the product of the $C_2H + 1,3$ -butadiene reaction at $m/z = 78$. The dark blue dotted line shows the photoionization spectrum for fulvene, which fits the measured spectrum up to a photon energy of 8.85 eV, as shown in (a). In (b), the dashed green line shows the experimental photoionization spectrum of 3,4-dimethylenecyclobut-1-ene and the solid red line shows the fit to the data, constructed by adding weighted contributions of the fulvene and 3,4-dimethylenecyclobut-1-ene spectra. The fit in (c), shown by the solid red line, is constructed by adding a contribution of 3-methylene-1-penten-4-yne, the photoionization spectrum shown by the pale blue line, to the fulvene component. The fit in (d), shown by the solid red line, is constructed by adding a contribution of 3-methyl-1,2-pentadien-4-yne, the photoionization spectrum shown by the orange dot-dashed line, to the fulvene component.

Benzene has vertical ionization energy of 9.244 eV.[63] There is not a distinct rise in the measured photoionization spectrum at 9.244 eV, thus, it seems that benzene is not a major product of the title reaction. 1,3-hexadien-5-yne has an ionization energy of 9.2 eV[63], very close to that of benzene. Reasonable fits to the measured photoionization spectrum can be made with weighted contributions of both of these isomers, but only benzene will be discussed further, given its significance in combustion and astrochemical environments. However, since two possible combinations of isomers can reproduce the data, the maximum branching fraction extracted is for a sum of benzene and 1,3-hexadien-5-yne. As shown in Figure 6, a fit to the measured spectrum can be obtained with a combination of the

experimental PI spectrum of fulvene,[36] the simulated spectrum of 3-methylene-1-penten-4-yne and the experimental PI spectrum of benzene.[54] The scaling factors for each PI curve that give the best fit to the data are adjusted for the absolute photoionization cross-section of each species, yielding a maximum possible branching for the sum of benzene and 1,3-hexadien-5-yne.

Figure 6. Black open circles show the measured photoionization spectrum of the C_6H_6 products of the $C_2H + 1,3$ -butadiene reaction at 4 Torr and 298 K. Dark blue dashed line shows the experimental photoionization spectrum of fulvene. Pale blue dotted line shows the simulated photoionization spectrum of 3-methylene-1-penten-4-yne. Green dot-dashed line shows the experimental photoionization spectrum of benzene. The solid red line shows a fit to the data constructed using an appropriately weighted sum of each of these calibration photoionization spectra (dark blue, pale blue and green lines).

It is clear from the product photoionization spectrum that the dominant product of the $C_2H + 1,3$ -butadiene reaction is fulvene. The identity of the other isomers formed includes one or a combination of 3,4-dimethylenecyclobut-1-ene, 3-methylene-1-penten-4-yne and 3-methyl-1,2-pentadien-4-yne. Using the experimental or simulated photoionization spectra available at this time, the measured product PI spectrum can be reproduced by the sum of the PI spectra of each isomer multiplied by a scaling factor. The scaling factors need to be adjusted for the absolute photoionization cross-section of each isomer. An uncertainty of 50% is estimated for the cross-sections calculated using the semi-empirical method of Bobeldjik *et al.*[49] and an uncertainty of 20% is estimated for the absolute cross-section of benzene, which has been experimentally measured. Adjusting the scaling factors for the absolute photoionization cross-section of each isomer, a branching fraction for the fulvene product with an associated error and maximum possible branching fractions for 3,4-dimethylenecyclobut-1-ene, 3-methylene-1-penten-4-yne and 3-methyl-1,2-pentadien-4-yne

are calculated and given in Table 1. Also shown in Table 1 is the maximum possible branching fraction for the sum of benzene and 1,3-hexadien-5-yne, given the significance of the benzene molecule in a variety of environments. The ground state reaction exothermicities for formation of each proposed isomer + H from $C_2H + 1,3\text{-butadiene}$, calculated at the CBS-QB3 level of theory, are also given in Table 1.

Table 1. Branching fraction for fulvene and upper limits for the branching fractions for 3,4-dimethylenecyclobut-1-ene, 3-methylene-1-penten-4-yne, 3-methyl-1,2-pentadien-4-yne and the sum of benzene and 1,3-hexadien-5-yne derived from fitting the measured photoionization spectrum of $m/z = 78$ in the reaction of $C_2H + 1,3\text{-butadiene}$. Also given are the CBS-QB3 ground state reaction exothermicities for forming the specific product isomer + H from $C_2H + 1,3\text{-butadiene}$.

Product Isomer	Branching Fraction / %	Reaction Exothermicity (including H atom co-product) ^a / kJmol^{-1}
Fulvene	57 ± 30	-247
3,4-dimethylenecyclobut-1-ene	<74	-123
3-methylene-1-penten-4-yne	<24	-101
3-methyl-1,2-pentadien-4-yne	<31	-59
Benzene	<45	-384
1,3-hexadien-5-yne		-116

^aAll reaction exothermicities are ground state and calculated at the CBS-QB3 level of theory.

The results strongly indicate that under the conditions of this experiment (4 Torr and 298 K), fulvene has a branching fraction of $(57 \pm 30)\%$. The maximum branching fractions for the other possible cyclic isomers, 3,4-dimethylenecyclobut-1-ene and benzene, are estimated to be 74% and 45%, respectively. What is intriguing about these values is that the branching fraction for fulvene and the maxima for 3,4-dimethylenecyclobut-1-ene and benzene are significant, and could potentially account for nearly all products formed, suggesting that cyclization reactions can compete favorably with direct H-loss to give straight-chain isomers. The reaction of $C_2H + 1,3\text{-butadiene}$ may be a significant source of cyclic molecules in combustion and astrochemical environments.

Since the reactions take place in a collisional environment, it is necessary to verify that collisions with species other than He in the flow do not alter the product distribution. To verify that H-assisted isomerization, or any other secondary process, does not change the isomer distribution, the signal rise time of the fulvene product is compared to the signal rise time for the $m/z = 78$ peak at all photon energies. By integrating the data over the 8.2 – 8.6 eV photon energy range the temporal behavior of the fulvene component can be examined

without contribution from other product isomers. It is found that the rise time of the fulvene product after the laser pulse is the same as the rise time for the peak as a whole, Figure 7, confirming that fulvene formation is not a result of H-assisted isomerization from another product, at least not on the millisecond time scale. The initial C_2H concentration (and hence the H atom concentration) is estimated to be $2 \times 10^{10} \text{ cm}^{-3}$, so the characteristic time for H-atom assisted isomerization even for an unrealistically large rate coefficient of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ would be in excess of 50 ms. In addition, the photoionization spectrum was examined in 5 ms intervals over the 0 – 100 ms kinetic time range; the shape of the spectrum, and therefore the isomer distribution, remained the same over the entire range. Another point to address is the possibility of unimolecular isomerization of the C_6H_6 product. Isomerization of the closed-shell products formed by the H-loss involves prohibitively high energetic barriers and does not occur in the current experiment at 298 K.

Figure 7. Large red circles show the time profile of the C_6H_6 product integrated over the 8.2 - 10.5 eV range. Small black circles show the time profile of the fulvene product, which is obtained by integrating over the 8.2 – 8.6 eV range. Although the signal-to-noise of the fulvene-only signal is low, the risetime is consistent with that of the sum of all C_6H_6 isomers and is inconsistent with contributions from H-atom assisted isomerization. The laser fires at $t=0$.

3.2 Computational Results

A quantum chemical investigation of possible reaction mechanisms resulting in fulvene and 3,4-dimethylenecyclobut-1-ene was carried out. The principal aim of the quantum chemical calculations is to uncover reaction pathways to fulvene and 3,4-dimethylenecyclobut-1-ene formation that may be able to compete with the pathways to 1,3-hexadien-5-yne and benzene formation outlined by Jones *et al.* Structures of stationary points and transition states were determined at the M06-2X/6-31G* level and energies computed using the CBS-QB3 composite method. These calculations do not attempt to predict the products of the title reaction quantitatively, but they do provide auxiliary information to the experimental results obtained. Four energetically possible pathways to fulvene formation and four pathways to 3,4-dimethylenecyclobut-1-ene formation in the $C_2H + 1,3$ -butadiene

reaction were found. Schematics of the energy profile of these pathways as a function of the reaction coordinate are given in Figure 8 and Figure 9.

Figure 8. Schematic of the potential energy profile showing the enthalpy vs reaction coordinate, illustrating four possible reaction pathways to fulvene formation in the $C_2H + 1,3$ -butadiene reaction.

C_2H can add to either the terminal or central unsaturated carbon atoms of 1,3-butadiene, leading to two structurally different encounter complexes, termed E1 and E2, respectively. E1 and E2 have energies of -286 kJ mol^{-1} and -213 kJ mol^{-1} relative to the asymptote for the infinitely separated reactants. Transformation of E1 to E2 and vice versa can occur *via* a 3-membered-ring isomer, as shown schematically in Figure 10. In addition, E1 could directly lose an H atom to yield 1,3-hexadien-5-yne or 1,2-hexadien-5-yne and E2 could lose an H atom to yield 3-methylene-1-penten-4-yne. Alternatively, isomerization of E1 or E2 *via* H-shifts or cyclization could occur. The simplest pathway to fulvene formation that was found involves cyclization of E1 *via* a low barrier that is 90 kJ mol^{-1} above the energy of E1, a single H-shift and H-loss to yield fulvene + H, denoted by the thick black line in Figure 8. Three other possible fulvene-formation pathways were also determined that involve isomerization of E1 *via* H-shift as their first step; these pathways are denoted by the green, blue and red curves in Figure 8 and correspond to 2,1-, 2,3- and 1,3-H-shifts,

respectively. These three alternate pathways involve an additional H-shift step *via* transition states that lie high in energy compared to E1 and also to the barriers involved in the first pathway described. Consequently, it seems very likely that the simplest pathway, involving cyclization prior to H-shift, would be more likely to account for the fulvene formation in the $C_2H + 1,3$ -butadiene reaction than the pathways involving H-shift prior to cyclization.

Figure 9. Schematic of the potential energy profile showing the enthalpy vs reaction coordinate, illustrating four possible reaction pathways to 3,4-dimethylenecyclobut-1-ene formation in the $C_2H + 1,3$ -butadiene reaction.

Four energetically possible reaction pathways to 3,4-dimethylenecyclobutene-formation were also found, two from addition of the C_2H radical to the terminal carbon atom and two from addition of the radical to the central carbon atom of 1,3-butadiene, Figure 9. All routes to 3,4-dimethylenecyclobutene that have been calculated involve a primary H-shift isomerization of E1 or E2 followed by cyclization, a secondary H-shift and finally H-loss. E1 can undergo 4,1- or 2,1-H-shift to yield straight-chain radicals that can undergo cyclization reactions to give the 4-membered ring backbone of 3,4-dimethylenecyclobut-1-ene. The cyclic intermediate then undergoes a secondary H-shift, followed by H-loss. The 2,1-H-shift has a very high barrier, lying only 12 kJ mol^{-1} below the energy of the separated reactants and so it is postulated that this route is unlikely to play an important role in 3,4-

dimethylenecyclobut-1-ene formation compared to the pathway that involves 4,1-H-shift. E2 could isomerize *via* a shift of the H that was originally bound to the central carbon atom on which the radical addition took place to the neighboring terminal position. Alternatively, one of the H atoms bound to the terminal carbon furthest from the site of radical addition could shift to the opposite terminal position. The radicals resulting from these H-shifts could then undergo a cyclization isomerization and a secondary H-shift, followed by H-loss.

4. Discussion

To understand the experimental results obtained in this study of the $C_2H + 1,3$ -butadiene reaction, it is helpful to put them in the context of the PES considering multiple C_4H_6 isomers. Despite the fact that the isomeric form of the reactant C_4H_6 dictates where the C_6H_7 surface is accessed, which may influence the product distributions, these starting points are inherently connected, as illustrated in Figure 10. Only the simplest inter-conversions (fewest steps) between the primary adducts are given in Figure 10, although others exist. CBS-QB3 energies for each transition state involved in the transformations shown in Figure 10 have been calculated relative to the $C_2H + 1,3$ -butadiene ground state asymptote. Conversion of the initial adduct of terminal addition of C_2H on 1,3-butadiene (E1) to the initial adduct of terminal addition on 1,2-butadiene (E3) occurs *via* a single H-shift with a transition state that lies 23.6 kJmol^{-1} below the asymptote for the separated $C_2H + 1,3$ -butadiene reactants. The dominant products of the $C_2H + 1,2$ -butadiene reaction are predicted by Jamal *et al* to be 3-methylene-1-penten-4-yne + H.[20] However, CH_3 -loss is also predicted by Jamal *et al* to occur in the $C_2H + 1,2$ -butadiene reaction, giving isomers of C_5H_4 with a branching fraction between 9 and 16% of the reactivity.[20] The fact that C_5H_4 is not detected above the signal-to-noise ratio in the current experimental study of the $C_2H + 1,3$ -butadiene reaction implies that the inter-conversion *via* a H-shift from the initial adduct of the $C_2H + 1,3$ -butadiene terminal addition to the initial adduct of the $C_2H + 1,2$ -butadiene terminal addition is unfavorable. Conversion of E1 and E2 to the initial adducts of the $C_2H + 1$ -butyne or 2-butyne reactions involves at least two H-shifts and so one might expect these conversions to be less favorable than to the initial adducts of the $C_2H + 1,2$ -butadiene reaction. Indeed, the $C_2H + 2$ -butyne and $C_2H + 1$ -butyne reactions are predicted by Jamal *et al* to yield high branching fractions of C_5H_4 isomers,[26] and the experimental study of the $C_2H + 1$ -butyne reaction by Soorkia *et al* found a branching of 56% for C_5H_4 ,[36] whereas no C_5H_4 isomers are detected in this study. In summary, it seems that E1 and E2 do not isomerize to explore the areas of the C_6H_7 PES accessed in the $C_2H + 1,2$ -butadiene, 1-butyne

and 2-butyne reactions. These insights indicate that isomerizations of the adducts E1 and E2 *via* H-shift are not favorable under the current conditions.

Figure 10. Schematic of the addition reactions of C_2H on the unsaturated sites of 1,3-butadiene, 1,2-butadiene, 1-butyne and 2-butyne. The most facile inter-conversions between the initial adducts are shown. Transition state energies relative to the infinitely separated C_2H and 1,3-butadiene reactants are in kJ mol^{-1} . Also given are the energies of the infinitely separated C_2H and 1,2-butadiene, 1-butyne and 2-butyne relative to the infinitely separated C_2H and 1,3-butadiene in kJ mol^{-1} .

Mebel and co-workers have published *ab initio* investigations of the C_2H reaction with all non-cyclic isomers of C_4H_6 (1,3-butadiene, 1,2-butadiene, 1-butyne and 2-butyne).[20, 23, 26] All of the branching ratios reported in each of those papers are given in Table 2. The experimentally obtained branching fractions in the $C_2H + 1\text{-butyne}$ reaction reported by Soorkia *et al.*[36] are also given in Table 2. The results of Soorkia *et al* were obtained by employing the same experimental apparatus as in the present study. The branching fractions for the $C_2H + 1\text{-butyne}$ reaction reported by Soorkia *et al*[36] are significantly different from the *ab initio* results of Jamal *et al.*[26] In another computational

study by Mandal *et al.*, [65] the experimental findings of Soorkia *et al* are corroborated and reaction pathways to each detected isomer are found. Unfortunately, overall branching fractions are not given in the publication of Mandal *et al.*

Table 2. Previously published experimental and theoretical branching fractions for the products of C₂H reactions with 1,3-butadiene, 1,2-butadiene, 1-butyne and 2-butyne.

Product Channel	C ₂ H + 1,3-butadiene[23] (Experiment and theory, Jones <i>et al</i>)	C ₂ H + 1,2-butadiene[20] (Theory, Jamal <i>et al</i>)	C ₂ H + 2-butyne[26] (Theory, Jamal <i>et al</i>)	C ₂ H + 1-butyne[26] (Theory, Jamal <i>et al</i>)	C ₂ H + 1-butyne[36] ^f (Experiment, Soorkia <i>et al</i>)
Benzene + H	40 ^a -20 ^b , 30 ^{b,c}	0	0 ^e	0 ^e	<10
1,3-hexadien-5-yne + H	60 ^a -80 ^b , 70 ^{b,c}	0	0	3.6 ^a -2.4 ^d	-
3-methylene-1-penten-4-yne + H	0 ^e	90.8 ^a -83.68 ^d	0.4 ^a -0.5 ^d	57 ^a -36 ^d	2.4
Penta-1,4-diyne + CH ₃	0 ^e	6.98 ^a -11.86 ^d	98.6 ^a -97.7 ^d	0 ^e	-
1,2-pentadien-4-yne + CH ₃	0 ^e	1.78 ^a -3.38 ^d	0	32.9 ^a -42.6 ^d	56
1,4-hexadiyne + H	0 ^e	0.10 ^a -0.26 ^d	0 ^e	0 ^e	-
3-methyl-1,4-pentadiyne + H	0 ^e	0.06 ^a -0.32 ^d	0 ^e	0 ^e	-
Diacetylene + C ₂ H ₅	0 ^e	0.12 ^a -0.18 ^d	0	4.2 ^a -15.5 ^d	-
2,3-hexadien-5-yne + H	0 ^e	0.04 ^a -0.1 ^d	0	1.3 ^a -1.2 ^d	8.4
3-methyl-1,2-pentadien-4-yne + H	0 ^e	0.02 ^a -0.08 ^d	1.0 ^a -1.7 ^d	0	-
1,3-hexadiyne + H	0 ^e	0	0	0.9 ^a -1.8 ^d	4.2
Methyldiacetylene + CH ₃	0 ^e	0 ^e	0 ^e	0.03 ^a -0.2 ^d	14
Fulvene + H	0 ^e	0 ^e	0	0	5.4
3,4-Dimethylenecyclobut-1-ene + H	0 ^e	0 ^e	0	0	9.6
1,2,3,4-hexatetraene + H	0 ^e	0	0 ^e	0 ^e	-
1,2-hexadien-5-yne + H	0 ^e	0	0 ^e	0 ^e	-
1,2-hexadien-4-yne + H	0 ^e	0	0 ^e	0 ^e	-

^aAt zero collision energy, ^bAt 45 kJmol⁻¹ collision energy, ^cExperimental value, ^dAt 29 kJmol⁻¹ collision energy, ^eNot specified so assumed to be zero. ^fCalculated from the relative $m/z = 64:m/z = 78$ peak areas in reference [36] and corrected for the isomeric composition of each peak and the estimated photoionization cross-section of each isomer that are reported in the paper.

The experimentally derived branching ratios in the $C_2H + 1,3$ -butadiene reaction presented here, particularly the high branching fraction for fulvene, are not in agreement with the experimental and computational results published by Jones *et al.*[23]. Some possible reasons for these disagreements are discussed here, and, clearly, there are still unanswered questions in $C_2H + C_4H_6$ reaction systems that merit further investigation. Firstly, the branching fractions of $(70 \pm 10)\%$ and $(30 \pm 10)\%$ for 1,3-hexadien-5-yne and benzene, respectively, in the $C_2H + 1,3$ -butadiene reaction reported by Jones *et al.*[23] were obtained employing a crossed-molecular-beams technique. In this technique the reaction between the radical and reactant takes place in a single-collision environment at elevated collision energy. Although their collision energy of 45 kJmol^{-1} , translates to a thermal energy of 5400 K, the excess energy is likely rapidly randomized within the initial C_6H_7 reactive complex. In contrast, in the current study the reactions take place in a collisional environment and at 298 K. Excess translational or internal energy of the C_2H reactant is collisionally relaxed prior to reaction with 1,3-butadiene, and collisional redistribution of energy in the C_6H_7 complex is also possible. The distribution of angular momentum states in the C_6H_7 may also be substantially different in the two experiments. In the crossed-molecular beams investigation of Jones *et al.*, products are ionized *via* electron impact at 80 eV, the angularly resolved TOF spectra are recorded and a product translational energy distribution in the center-of-mass frame is calculated. The identification of the isomers is carried out by fitting the experimental data to modeled distributions that are obtained by forward convolution. The molecular beam experiments are particularly selective for benzene, the most exothermic channel, because it can appear at energies that are closed for other reaction products. The identification of isomers in the present study is spectroscopic, and the identification of fulvene by its photoionization spectrum is independent of the energy disposal in the reaction. The present experiments can detect fulvene with particular selectivity because it has the lowest photoionization energy of the C_6H_6 isomers and appears at photon energies where other reaction products are absent. It is not specified in the publication of Jones *et al.* whether inferior fits resulted from using isomers other than benzene and 1,3-hexadien-5-yne. As the reported maximum benzene yields are consistent with the benzene yields observed in the molecular beam experiments, the major discrepancy with the Jones *et al.* report is the fraction of fulvene. A composite photoionization spectrum has been simulated that is composed of 70% 1,3-hexadien-5-yne and 30% benzene (Figure 11), the branching fractions reported by Jones *et al.*[23]. It is clear from the comparison of this simulated composite spectrum and the actual spectrum measured in this experiment, also shown in Figure 11, that the product

1 branching fractions resulting in the onset and shape of the measured spectrum are
2 unequivocally different to the values observed by Jones *et al.*

3
4 Figure 11. Black circles show the measured photoionization spectrum for the products with $m/z = 78$ in the
5 current experiment. Red triangles show a simulated spectrum with a composition of 70% 1,3-hexadien-5-yne
6 and 30% benzene, the branching fractions reported by Jones *et al.*[23] Both spectra are normalized to the same
7 maximum value.

8 Jones *et al* also report a computational investigation into the $C_2H + 1,3$ -butadiene
9 reaction that corroborates their experimental components.[23] The computational branching
10 fractions are reported from 0 – 45 kJ mol^{-1} collision energy. At lower collision energies,
11 which would be more comparable to the current flow tube conditions, they predict that the
12 benzene product increases in relative yield compared to the 1,3-hexadien-5-yne, (branching
13 given in Table 2). Jones *et al* outline two possible pathways to benzene formation, which are
14 shown in Figure 12: cyclization of the initial adduct followed by H-shift or H-shift followed
15 by cyclization, both followed by H-loss to yield benzene; all values in Figure 12 are
16 reproduced from that paper. Jones *et al* state that 99% of the benzene molecules are formed
17 by the first pathway. 1,3-hexadien-5-yne can be formed *via* direct H-loss from the adduct
18 formed by terminal addition of C_2H to 1,3-butadiene *via* a transition state that lies 13 kJ mol^{-1}
19 higher in energy than the separated 1,3-hexadien-5-yne + H products. Jones *et al* do not
20 mention the possibility of any products other than benzene or 1,3-hexadien-5-yne and so it is
21 difficult to know if formation of any other isomers was considered. From the computational
22 studies carried out and presented here, the transition state with the highest energy in the
23 proposed fulvene-formation pathway lies at -116 kJ mol^{-1} relative to the asymptote for the
24 reactants, whereas the highest energy transition state on the 1,3-hexadien-5-yne -formation
25 pathway of Jones *et al* lies at -103 kJ mol^{-1} , a difference of 13 kJ mol^{-1} . It may be that this
26 fulvene formation path may be able to effectively compete with the proposed 1,3-hexadien-5-
27 yne formation path by Jones *et al*, and with the lower-energy benzene formation pathway

1 shown in Figure 12, depending on the entropy of each transition state and the effect of the
2 collisional stabilization in our experiment.

3
4 Figure 12. Minima and first-order saddle points on two possible reaction pathways to benzene formation in the
5 $C_2H + 1,3\text{-butadiene}$ reaction. Values and structures are from the publication by Jones *et al.*[23] The thick black
6 line shows the pathway that accounts for 99% of benzene products, according to Jones *et al.*, and the thin red
7 line shows the pathway that accounts for the remaining 1% of benzene products.

8 All of the proposed 3,4-dimethylenecyclobut-1-ene pathways involve preliminary H-
9 shifts, which, due to the lack of C_5H_4 products detected in the current experiment, have been
10 postulated to be unfavorable, as discussed earlier. Furthermore, the assignment of 3,4-
11 dimethylenecyclobutene is less definitive than the observation of fulvene formation (see
12 above). Consequently, in the case of the 3,4-dimethylenecyclobut-1-ene product, further
13 experimental or theoretical work would be particularly valuable to corroborate its formation.
14 It is possible that lower energy pathways to both fulvene and 3,4-dimethylenecyclobut-1-ene
15 exist that have not been found in the present calculations.

16 Although we observe no spectroscopic evidence for benzene, the signal-to-noise ratio
17 in the photoionization spectrum indicates that benzene could account for a maximum of 45%
18 of products of the $C_2H + 1,3\text{-butadiene}$ reaction under the current conditions. The maximum
19 branching fraction of 45% is in fair agreement with the branching fractions measured (30% at

45 kJmol⁻¹ collision energy) and predicted (40% at 0 kJmol⁻¹ collision energy) by Jones *et al.*[23] Given the significance of benzene in PAH chemistry in both astrochemical and combustion environments, it is important to identify reactions that are likely or unlikely to form benzene. Jones *et al* propose that the C₂H + 1,3-butadiene reaction is a likely candidate for benzene production in the interstellar medium. However, the experimental evidence presented here suggests that the C₂H + 1,3-butadiene reaction may also contribute significantly to yields of the 5-membered ring species fulvene in such environments. It would be very interesting to search for the major product of the C₂H + 1,3-butadiene reaction, fulvene, in the interstellar medium as this molecule possesses a substantial dipole moment[66] and may be present as a result of the title reaction where C₂H radicals are abundant, for example in circumstellar shells.

One factor that would assist greatly in the interpretation of the photoionization spectrum would be accurate absolute photoionization spectra for 3,4-dimethylenecyclobut-1-ene, 3-methylene-1-penten-4-yne and 3-methyl-1,2-pentadien-4-yne. Alternatively, the system could be studied using different experimental methodologies, or current methodology could be augmented with a secondary component for identification. A full time-dependent, multi-well master equation investigation of this system, which includes the new pathways presented here, would be very valuable, particularly given the significance of the title reaction in formation of cyclic molecules in astrochemical and combustion environments.

5. Conclusion

The reaction of C₂H with 1,3-butadiene was investigated using a slow flow reactor at 4 Torr and 298 K coupled with synchrotron photoionization time-of-flight mass spectrometry. The primary channel in the reaction is H-loss from the adduct to yield C₆H₆. No signal is observed from the C₅H₄ + CH₃ channel, which is prominent when C₂H reacts with other C₄H₆ isomers, implying that the title reaction does not access the entrance channels involved in reaction with the other C₄H₆ isomers. The measured photoionization spectrum of this C₆H₆ product reveals that fulvene is formed with branching fraction of (57 ± 30)%. From the deviation of the measured spectrum from that of fulvene, it seems very likely that additional isomers of C₆H₆ are formed. Using the currently available calibration photoionization spectra for each isomer, maximum branching fractions for 3,4-dimethylenecyclobut-1-ene, 3-methylene-1-penten-4-yne and 3-methyl-1,2-pentadien-4-yne are calculated to be 74%, 24% and 31%, respectively. The upper limit of the branching fraction for the sum of benzene and 1,3-hexadien-5-yne under the current conditions is 45%. The observation of fulvene as the

major product of the title reaction is not in good agreement with the interpretation of Jones *et al.*, [23] suggesting that further investigation of the $C_2H + 1,3$ -butadiene reaction would be valuable to better understand formation of cyclic species in combustion and astrochemical environments.

Several energetically feasible reaction pathways to fulvene and 3,4-dimethylenecyclobut-1-ene from the $C_2H + 1,3$ -butadiene reactants have been determined using quantum chemical methods. For fulvene formation a route involving relatively low energy transition states has been calculated, which may be able to effectively compete with the benzene-formation pathway calculated by Jones *et al.* [23] under the current conditions. Given the potentially significant reaction channels and the disagreement encountered between studies thus far, a full time-dependent multi-well master equation calculation and further experimental investigation of the $C_2H + 1,3$ -butadiene system would be extremely valuable.

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