



HAL
open science

Reactions of Atomic Carbon with Butene Isomers: Implications for Molecular Growth in Carbon-Rich Environments

Jérémy Bourgalais, Michael Spencer, David L. Osborn, Fabien Goulay,
Sébastien D. Le Picard

► **To cite this version:**

Jérémy Bourgalais, Michael Spencer, David L. Osborn, Fabien Goulay, Sébastien D. Le Picard. Reactions of Atomic Carbon with Butene Isomers: Implications for Molecular Growth in Carbon-Rich Environments. *Journal of Physical Chemistry A*, 2016, 120 (46), pp.9138–9150. 10.1021/acs.jpca.6b09785 . hal-01437440

HAL Id: hal-01437440

<https://univ-rennes.hal.science/hal-01437440>

Submitted on 10 Jul 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Reactions of Atomic Carbon with Butene Isomers: Implications for Molecular Growth in Carbon-Rich Environments

J. Bourgalais¹, Michael Spencer,² David L. Osborn,³ F. Goulay^{2,*} and S. D. Le Picard^{1,*}

¹*Institut de Physique de Rennes, Département de Physique Moléculaire, Astrophysique de Laboratoire, UMR*

CNRS 6251, Université de Rennes 1, Campus de Baulieu, 35 042 Rennes Cedex, France

²*Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, USA*

³*Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, California 94551, USA*

Corresponding Author:

*Fabien.Goulay@mail.wvu.edu

*Sebastien.le-picard@univ-rennes1.fr

ABSTRACT

Product detection studies of C(³P) atom reactions with butene (C₄H₈) isomers (but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene) are carried out in a flow tube reactor at 353 K and 4 Torr under multiple collision conditions. Ground state carbon atoms are generated by 248 nm laser photolysis of tetrabromomethane, CBr₄, in a buffer of helium. Thermalized reaction products are detected using synchrotron tunable VUV photoionization and time of flight mass spectrometry. The temporal profiles of the detected ions are used to discriminate products from side or secondary reactions. For the C(³P) + *trans*-but-2-ene and C(³P) + *cis*-but-2-ene reactions, various isomers of C₄H₅ and C₅H₇ are identified as reaction products formed via CH₃- and H-elimination. Assuming equal ionization cross sections for all C₄H₅ and C₅H₇ isomers, C₄H₅:C₅H₇ branching ratios of 0.63:1 and 0.60:1 are derived for the C(³P) + *trans*-but-2-ene and the C(³P) + *cis*-but-2-ene reactions, respectively. For the C(³P) + but-1-ene reaction, two reaction channels are observed: the H-elimination channel, leading to the formation of the ethylpropargyl isomer, and the C₃H₃ + C₂H₅ channel. Assuming equal ionization cross sections for ethylpropargyl and C₃H₃ radicals, a branching ratio of 1:0.95 for the C₃H₃ + C₂H₅ and H + ethylpropargyl channels is derived. The experimental results are compared to previous H-atom branching ratios and used to propose the most likely

mechanisms for the reaction of ground state carbon atoms with butene isomers.

I. INTRODUCTION

Carbon is the fourth most abundant element in the universe and unbounded carbon atoms have been detected in a wide range of environments, from interstellar media (dense and diffuse clouds, protoplanetary nebulae, circumstellar envelopes...)¹⁻⁵ to planetary atmospheres (e.g. Mars, Venus, Titan),⁶⁻⁸ and plasmas.⁹⁻¹¹ In these environments, their barrierless reactions¹²⁻³⁵ with abundant saturated and unsaturated hydrocarbons, nitrogen bearing molecules, and small free radicals are expected to initiate the growth of complex molecules^{9,36,37} even at very low temperatures.^{12-14,33,34} Consequently, carbon atom reactions are expected to play a role in the formation of polycyclic aromatic hydrocarbons (PAHs), aerosols, and soot.^{9,36,37} Improving the accuracy of models trying to reproduce the chemistry of such environments requires a better understanding of the mechanisms of elementary reactions between carbon atoms and abundant hydrocarbons. This goal can be achieved by probing the products of these reactions experimentally and theoretically over a wide range of physical conditions.

Most of the previous research on C(³P) reactivity focused on reactions with hydrocarbons containing fewer than 4 carbon atoms, investigated using various experimental techniques such as crossed molecular beams,^{16,19-21,27,35,38,39} flow tubes,^{23,26,31,40} or CRESU experiments,^{13,14,41} often coupled with *ab initio* calculations.^{18,24,25} The accepted dominant reaction mechanism derived from these experiments is addition of the C(³P) to the hydrocarbon followed by the loss of a hydrogen atom or methyl group to form an open-shell molecule.^{23,40} For large unsaturated hydrocarbons such as butene isomers (C₄H₈), exit channels other than H-atom or CH₃ loss may become accessible.²³

Butene is one of the smallest hydrocarbons with structural isomers and is a good archetype molecule for the study of gaseous fuel reactivity. It is a negligible component in

1 gasoline but is produced during the combustion of larger hydrocarbons.⁴²⁻⁴⁴ The high
2 temperature (>1200 K) pyrolysis of butene isomers leads to the formation of reactive free
3 radicals such as methyl (CH₃), propargyl (C₃H₃) and allyl (C₃H₅) and ultimately to the
4 formation of larger molecules such as benzene and C₅H₆ isomers.⁴⁵ Under plasma conditions,
5 butene is known to decompose easily into CH_x and C₂H_x (x=1,2,3) species and is used as a
6 source of carbon atoms.⁴⁶ Butene isomers are also believed to play a role in the
7 photochemistry of organic molecules in planetary atmospheres (*e.g.* Titan).^{47,48} They are
8 expected to react rapidly with atoms such as C, O, or N and with small hydrocarbons radicals
9 such as CH or C₂H. Although rate constants and product distributions of butene reactions
10 have been shown to depend on the specific butene isomer,⁴⁹ computational model of these
11 environments do not consider isomeric C₄H₈ structures, likely leading to uncertainties in the
12 derived abundances of large species. Atkinson & Aschmann⁴⁹ determined rate constants for
13 the reactions of OH radical with but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene and isobutene at
14 295±1 K to be (3.13±0.16)×10⁻¹⁰ cm³ molecules⁻¹ s⁻¹, (5.60±0.13) ×10⁻¹⁰ cm³ molecules⁻¹ s⁻¹,
15 (6.39±0.13) × 10⁻¹⁰ cm³ molecules⁻¹ s⁻¹ and (5.13±0.24) × 10⁻¹⁰ cm³ molecules⁻¹ s⁻¹,
16 respectively. Loison *et al.*⁵⁰ investigated the lighter products formed by the reaction of OH
17 radicals with *trans*-but-2-ene, and but-1-ene in a fast flow reactor at room temperature. The
18 branching fractions for the H-atom abstraction channel were measured to be 8±3% for OH +
19 but-1-ene, and 3±1% for OH + *trans*-but-2-ene. More recently Bouwman *et al.*⁵¹ investigated
20 C₂H radical reactions with butene isomers (but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene and
21 isobutene) in a Laval expansion at 79 K. They found similar rate constants for all reactions
22 (*ca.* 2 × 10⁻¹⁰ cm³ molecules⁻¹ s⁻¹) in agreement with previous measurements performed at
23 room temperature,^{52,53} but observed an isomer dependence of the reaction products. It is
24 worth noting that this work also showed that the C₂H + C₄H₈ reactions contribute to
25 molecular weight growth with formation of larger species (4-penten-1-yne, 3-penten-1-yne,
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55

2-methyl-1-buten-3-yne, 4-methyl-3-penten-1-yne) through methyl radical elimination in addition to H-atom elimination.

The reaction kinetics of $C(^3P) +$ butene isomers was first studied by Haider & Husain¹² at room temperature in a slow flow reactor. They measured overall rate constants for reactions with but-1-ene, *cis*-but-2-ene and *trans*-but-2-ene of $(4.3 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(3.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(2.9 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. More recently, Loison & Bergeat²³ measured an overall rate coefficient for the $C(^3P) +$ *trans*-but-2-ene reaction of $(1.9 \pm 0.6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is a factor of 1.5 smaller than the value of Haider & Husain. Loison & Bergeat²³ suggest the initial formation of a triplet $H_3C-HC\bullet\bullet C=CH-CH_3$ adduct. From this intermediate, the accessible exothermic channels are $H + C_5H_7$ and $CH_3 + C_4H_5$ through isomerization and C-H or C-C bond breaking, respectively. In addition Loison & Bergeat measured an absolute atomic hydrogen branching fraction of 0.33 ± 0.08 using H-atom resonance fluorescence. The authors stress the fact that the isomerization of the initial reaction adduct ($H_3CHCCCHCH_3$) may greatly affect the final isomer distribution. Subsequently, Li *et al.*⁵⁴ performed a theoretical study of the ground state carbon atom reaction with *trans*-but-2-ene by probing the complex triplet potential energy surface. They predict two major products: dimethylpropargyl ($H_3CHCCCCH_3$) and a methylpropargyl isomer (CH_3CHCCH), in agreement with Loison and Bergeat.²³ The authors confirm a barrierless association reaction followed by isomerization and dissociation of the initial adduct. The large reaction rate coefficient measured at room temperature is therefore expected to remain high at low temperatures, making this reaction of interest for both interstellar medium and plasma assisted combustion chemistry.

The role of the $C(^3P) +$ butene reactions in gas phase environments depends on the importance of the H elimination exit channel relative to elimination of larger hydrocarbon

1
2
3 radicals, as well as on the isomeric structure of the final products. If C_5H_7 isomers are
4
5 produced, the reactions will contribute to the formation of long linear carbon chains in carbon
6
7 rich environments. If C_4H_5 isomers are formed, the reactions could play a role in the chemical
8
9 scheme leading to the formation of aromatic rings.^{55,56} C_4H_5 -isomers (*i*- C_4H_5 and
10 methylpropargyl isomers) have been observed both in fuel-rich flames⁵⁷ and as $C(^3P)$ +
11 propene reaction products.^{26,57} The reaction of acetylene (C_2H_2) with the *i*- C_4H_5 isomer is
12 suggested as a possible route to benzene (*c*- C_6H_6) formation under certain flame conditions.⁵⁸
13
14
15
16
17
18

19 The reaction would initially form fulvene (*c*- $C_5H_4=CH_2$) which could then convert to benzene
20 by H-atom-assisted isomerization.⁵⁹ The role of the methylpropargyl isomers (CH_3CHCCH
21 and CH_3CCCH_2) in ring formation processes is still unknown and requires further
22 investigation. For instance, CH_3CHCCH , is completely absent from flame models whereas
23 CH_3CCCH_2 is suggested to form toluene C_7H_8 ($C_6H_5-CH_3$) or benzyl radical C_7H_7 (C_6H_5-
24 CH_2) by reaction with the propargyl radical (CH_3CCH_2).⁶⁰
25
26
27
28
29
30
31

32 In this work we present an investigation of the products formed by reactions of triplet
33 ground state carbon atoms $C(^3P)$ with three butene isomers : but-1-ene, *cis*-but-2-ene and
34 *trans*-but-2-ene. In order to probe the reaction products, experiments are performed in a flow
35 tube reactor under multiple collision conditions²⁶ (353 K & 4 Torr) at the Advanced Light
36 Source (ALS) synchrotron of Lawrence Berkeley National Laboratory. Detection of the
37 products in the flow is carried out using tunable Vacuum Ultraviolet (VUV) photoionization
38 and time of flight mass spectrometry. Kinetic traces and photoionization spectra supported by
39 thermodynamic and Franck-Condon factor calculations of the C_4H_5 and C_5H_7 species have
40 been used to infer the primary products of the reactions.
41
42
43
44
45
46
47
48
49
50
51
52

53 II. EXPERIMENTAL PROCEDURE

54 A description of the apparatus has been given elsewhere^{61,62} and only a brief overview
55 is presented here. Reactions are performed in a quartz flow tube with a length of 62 cm and
56
57
58
59
60

1
2
3 1.05 cm inner diameter. The gas pressure inside is typically 4 Torr with a total gas flow of
4
5 250 sccm (standard cubic centimeters per minute). All experiments are carried out at 353 K
6
7 corresponding to a total number density of $1.09 \times 10^{17} \text{ cm}^{-3}$ and a slow flow velocity ($\sim 10 \text{ m s}^{-1}$).
8
9 The buffer gas (helium), carbon atom precursor (CBr_4) and reagent gas (butene isomers)
10
11 are metered by mass-flow controllers. Reagent gases and the precursor were used without
12
13 further purification: but-1-ene ($> 99\%$, Aldrich), *cis*-but-2-ene ($> 99\%$, Aldrich), *trans*-but-2-
14
15 ene ($> 99\%$, Aldrich) & CBr_4 (99%, Aldrich). CBr_4 was introduced in the reactor with a
16
17 typical density of $\sim 4 \times 10^{12} \text{ cm}^{-3}$, by flowing a small amount of He over solid CBr_4 upstream
18
19 of the reaction tube. At ~ 30 cm along the tube, a $650 \mu\text{m}$ pinhole allows a small portion of
20
21 the gas mixture to expand into a vacuum chamber. There, a skimmer generates a beam of
22
23 molecules entering a differentially pumped ionization chamber in which molecular and
24
25 atomic species are ionized by quasi-continuous VUV synchrotron radiation. Ions formed are
26
27 detected using an orthogonal-acceleration time-of-flight mass spectrometer pulsed at 50 kHz.
28
29 All detected ions are time-tagged relative to the excimer laser pulse (at $t=0$) operating at 10
30
31 Hz and accumulated in a transient digitizer to collect complete mass spectra as a function of
32
33 time. It should be noted that the operation frequency of the laser allows sufficient time
34
35 between laser pulses to completely refresh the gas mixture. The total ion detection time-
36
37 window is 50 ms, beginning 10 ms before the laser pulse. Time-and energy-resolved mass
38
39 spectra are obtained by averaging at least 500 laser shots at each photon energy. All data are
40
41 normalized to account for variations in VUV photon flux using a NIST-calibrated photodiode
42
43 (SXUV-100, International Radiation Detectors, Inc.). At each mass-to-charge (m/z) ratio, the
44
45 average signal present before the laser pulse is subtracted from the time dependent data. The
46
47 photoionization spectra at a given m/z ratio are obtained by integrating the data set over the
48
49 desired mass and time windows. The ionizing photon energy is scanned from 7.4 to 9.0 eV in
50
51 steps of 0.025 eV. Kr or Ar is used in a gas filter to absorb higher energy photons at
52
53
54
55
56
57
58
59
60

1
2
3 harmonics of the undulator energy. Up to three independent datasets are recorded for each
4
5 reaction and averaged. The photon energy resolution is determined to be of the order of 40
6
7 meV by measuring an atomic resonance of Xe.

8
9
10 Carbon atoms were generated by 248 nm photolysis of CBr₄, using a pulsed excimer
11
12 (KrF) laser operating at 10 Hz. The laser power output is typically 266 mJ per pulse (20 ns),
13
14 with a fluence inside the reaction flow tube of ~20-50 mJ cm⁻². The multiphoton
15
16 photodissociation of CBr₄ at 248 nm eliminates multiple halogen atoms, leading to the
17
18 formation of carbon atoms⁶² and CBr radicals.^{63,64} Under our experimental conditions 20% of
19
20 the introduced CBr₄ is photodissociated. Shannon et al.⁶³ determined a C(¹D)/C(³P) ratio
21
22 following CBr₄ photodissociation at 266 nm of 0.15 ± 0.04 at 296 K. Molecular nitrogen is
23
24 known to efficiently quench C(¹D) atoms through C(¹D) + N₂ → C(³P) + N₂ with a reaction
25
26 rate coefficient of $k = 5.3 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$.⁶⁵ In order to avoid potential chemical
27
28 interferences from the reaction between C(¹D) and butene, the present experiments were
29
30 performed using a large excess of N₂ ($1.8 \times 10^{16} \text{ cm}^{-3}$). In the present experimental conditions
31
32 (353 K & 4 Torr), for known densities of reactant (C₄H₈ ~ 10^{14} cm^{-3}) and considering a C(³P)
33
34 + C₄H₈ reaction rate constant of $k = 1.9 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$,²³ the characteristic decay
35
36 times are calculated to be five times shorter for C(¹D) reaction with molecular nitrogen than
37
38 for the C(³P) reaction with butene isomers. Consequently, in the following sections the
39
40 influence of C(¹D) atoms reactions with butene isomers is neglected. In addition, due to the
41
42 high efficiency of C(³P) fine structure relaxation by collision with He, the spin-orbit level
43
44 population distribution of ground state carbon atoms, C(³P_{0,1,2}) in the flow tube are expected
45
46 to be thermalized.^{13,66} The impact of CBr reactions with butene on product identification is
47
48 discussed in the Results section. Finally, it is worth noting that the absorption cross-section of
49
50 1-butene was measured to be $6.8 \times 10^{-21} \text{ cm}^2$ at 220 nm,⁶⁷ likely leading to negligible
51
52 dissociation of the butene isomers at the longer wavelength used here.
53
54
55
56
57
58
59
60

III. COMPUTATIONAL METHODS

Electronic structure calculations of the neutral C_5H_7 species and their cations are carried out using the Gaussian09 package employing the B3LYP/CBSB7 method to obtain optimized geometries. Theoretical calculations with the same methods were applied for C_4H_5 isomers in a previous study.²⁶ Heats of reaction and adiabatic and vertical ionization energies are obtained using the CBS-QB3 composite method. All the vibrational frequencies are real, indicating that the optimized geometries represent minima on the potential energy surface. Photoionization spectra of C_5H_7 isomers are calculated at 298 K using the G09 package within the Franck–Condon approximation.⁶⁸ The simulated factors are convolved with a 40 meV (FWHM) Gaussian response function and integrated to simulate direct photoionization spectra.

IV. RESULTS

Table 1 reports the optimized structures for seven C_5H_7 isomers together with their computed ionization energies. Because the cationic form of the cyclic isomer cannot be optimized, the value reported is the vertical ionization energy. As mentioned above, C_4H_5 isomers have been investigated in a previous study.²⁶

Table 1 Optimized structures (B3LYP/CBSB7 method) and adiabatic ionization energies (CBS–QB3 method)(vertical for the $c-C_5H_7$) of C_5H_7 isomers

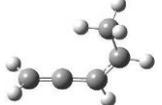
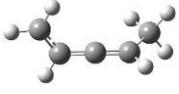
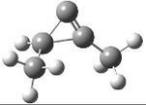
| Isomer | Optimized structure | Ionization energy (eV) | Isomer | Optimized structure ^a | Ionization energy (eV) |
|-------------------|---|------------------------|-------------------|---|------------------------|
| Trans C_5H_7 |  | 7.10 | Ethylpropargyl |  | 7.88 |
| Cis C_5H_7 |  | 7.19 | Trans 3- C_5H_7 |  | 7.40 |
| Dimethylpropargyl |  | 7.41 | Cis 3- C_5H_7 |  | 7.41 |
| $c-C_5H_7$ |  | 8.19 | | | |

Table 2 presents computed enthalpies of reaction at 298 K for all the predicted reaction channels and investigated C₄H₈ isomers. All of the reaction channels are found to be exothermic. The difference between isomers is outside the error of the method which is ~5 kJ mol⁻¹ on averaged prediction of Δ_fH°(298.15 K) for CBS-X methods.⁶⁹ Within these uncertainties, the enthalpies of reaction displayed in Table 2 for the C(³P) + *trans*-C₄H₈ reaction are similar to those calculated by Li et al. (G3B3//B3LYP/6-311G(d,p)).⁵⁴ These values are all lower than the enthalpies calculated by Loison and Bergeat based on experimental enthalpies of formation.²³

Table 2 ΔH_r (298 K)^a (kJ.mol⁻¹) for possible reaction channels of C(³P) + C₄H₈.

| Channels | <i>Trans</i> -C ₄ H ₈ | <i>Cis</i> -C ₄ H ₈ | 1-C ₄ H ₈ |
|--|---|---|---------------------------------|
| <i>Trans</i> -C ₅ H ₇ + H | -204.52 | -209.75 | -215.00 |
| <i>Cis</i> -C ₅ H ₇ + H | -207.13 | -212.37 | -217.62 |
| <i>Dimethylpropargyl</i> + H | -209.75 | -215.00 | -220.24 |
| <i>Ethylpropargyl</i> + H | -199.26 | -204.51 | -209.75 |
| 3-C ₅ H ₇ + H | -201.89 | -207.13 | -212.37 |
| <i>c</i> -C ₅ H ₇ + H | -49.82 | -55.06 | -60.30 |
| <i>i</i> -C ₃ H ₅ + CH ₃ | -243.84 | -249.08 | -254.32 |
| CH ₃ CHCCH + CH ₃ | -238.59 | -243.84 | -249.08 |
| CH ₃ CCCH ₂ + CH ₃ | -249.08 | -254.32 | -259.57 |
| C ₃ H ₃ +C ₃ H ₅ | -236.64 | -247.66 | -247.14 |

^aCBS-QB3

^b*Cis* and *Trans*

Photoion spectra were recorded with and without CBr₄ and with or without the photolysis laser pulse. In the absence of butene in the reactor flow, no ion signals were detected at *m/z* 15, 53 and 67, corresponding to the expected C(³P) + butene product masses (CH₃, C₄H₅ and C₅H₇). The reactivity of CBr radicals with butene isomers has to be considered to ensure that products formed at *m/z* 53 and 67 do not originate from reactions involving CBr. The rate coefficient of *trans*-C₄H₈ reaction with CBr has been determined by Ruzsicska et al.⁷⁰ to be 1.23×10⁻¹¹ cm³ molecules⁻¹ s⁻¹, which is fifteen times lower than that of the C(³P) reaction with butene.²³ Consequently, under the present experimental conditions, CBr + butene products are formed more slowly than the C(³P) + butene products. Previous

investigations on the C(³P) + ethylene and C(³P) + propylene reactions have shown that such slower secondary processes and side reactions with characteristic times of the order of few hundreds of microseconds can be discriminated against primary processes by inspecting the product time traces.²⁶ Furthermore, for all the results presented below, the contributions from slow reactions or subsequent reactions are minimized by integrating mass spectra only over the 0–1 ms time range.

In the sections below, we analyze mass spectra and photoionization spectra obtained upon irradiation of a mixture of CBr₄ with three different butene isomers: but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene. Photoionization spectra acquired at 4 and 8 Torr do not show significant differences. In the following section only spectra recorded at 4 Torr are presented. Comparing photoionization spectra to previous results or to calculated photoionization spectra identifies the isomeric structure of the reaction products.

The time behavior of the non-normalized ion signal after the laser pulse is used to discriminate between C(³P) reaction products and products from side reactions as well as to infer product branching fractions. The signals S_i for the main products are fitted using Eq. 1 corresponding to a pseudo-first order model of sequential reactions.⁷¹

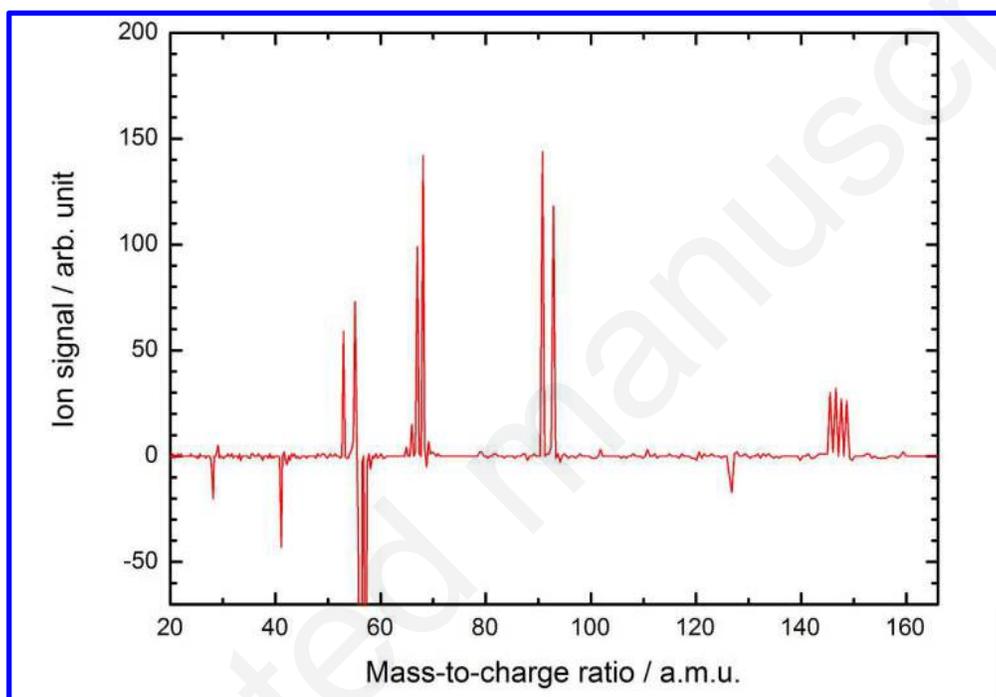
$$S_i(t) = \frac{(S_i \cdot k_{1,i})}{(k_{2,i} - k_{1,i})} \left(e^{-k_{1,i}t} - e^{-k_{2,i}t} \right) \quad \text{Eq.1}$$

The coefficients $k_{1,i}$ and $k_{2,i}$ are the pseudo first order rate constants for the formation and loss of the product i . S_i is proportional to the amount of reactants consumed to form product i . Branching ratios are obtained from the ratio of the S_i values for two different channels assuming equal ionization cross sections.

A. C(³P) + *trans*-but-2-ene

55 FIG. 1 displays the mass spectrum obtained following photolysis of a mixture of CBr₄
56 and *trans*-but-2-ene in helium and nitrogen. The data are recorded at 9.0 eV photon energy.
57

1
2
3 The negative signals at *m/z* 28, 41, 56 and 127 are due to imperfect subtraction of ion signal
4 from butene or from impurities present in the reaction flow. Over the short reaction window
5 (1 ms), the main ion signals are observed at *m/z* 53, 55, 67, 68, 91, 93, 146, 147, 148 & 149.
6
7
8 Products at *m/z* 91 & 93 are identified to be C⁷⁹Br and C⁸¹Br, formed by photodissociation of
9
10 CBr₄ at 248 nm.
11
12
13



36 FIG. 1. Mass spectrum obtained by photolysis of a CBr₄ and *trans*-but-2-ene mixture in
37 helium at 9.0 eV photon energy integrated over the 0–1 ms time range.
38
39

40
41
42 FIG. 2 shows the normalized averaged kinetic traces of *m/z* 146/148 (red circles) and
43 *m/z* 147/149 (blue squares) together with modeled C₄H₇Br (red line) and C₄H₈Br (blue line)
44 temporal traces. The *m/z* 147/149 and *m/z* 146/148 temporal profiles are modeled using the
45 following scheme:
46
47
48



The metastable $C_5H_8Br^*$ at m/z 147/149 is formed by the $CBr + C_4H_8$ reaction (R1b) ($k_{1a+1b}=1.23\times 10^{-11}$ cm³ molecules⁻¹ s⁻¹)⁷⁰ and decays ($k_2=500$ s⁻¹) to give $C_5H_7Br + H$ (R2).

The temporal profile for C_5H_7Br at m/z 146/148 signal is the sum of the contributions from $CBr + C_4H_8$ (R1a) and C_5H_8Br decomposition to $C_5H_7Br + H$ (R2). The data are best reproduced with branching ratios of 0.5–0.6 for reaction R1a and 0.5–0.4 for reaction R1b.

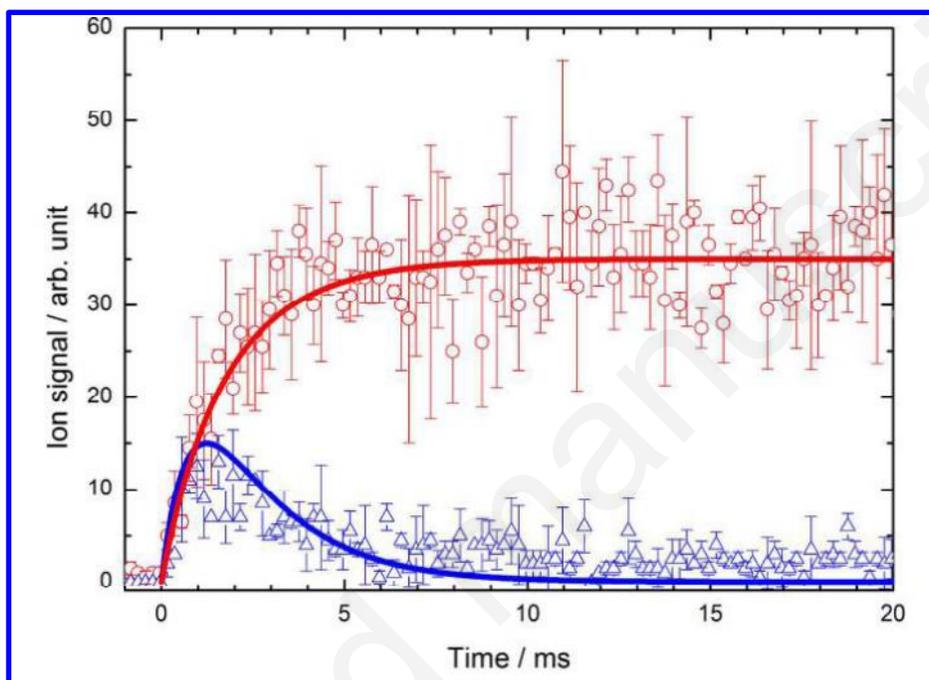
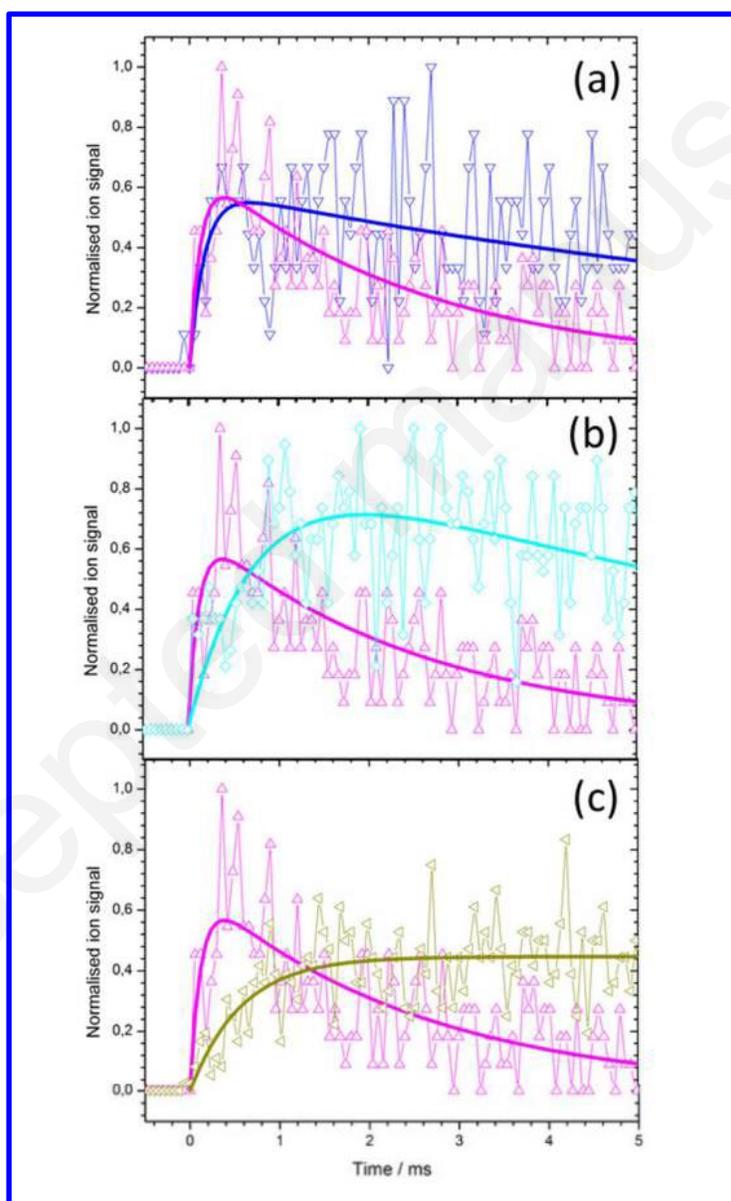


FIG. 2. Normalized averaged kinetic traces of m/z 146/148 (red circles) and m/z 147/149 (blue squares) obtained by photolysis of a CBr_4 and *trans*-but-2-ene mixture in helium, at 9.0 eV photon energy. The thick lines are modeled traces for C_5H_7Br (red line) and C_5H_8Br (blue line).

FIG. 3 shows the normalized temporal traces of (a) m/z 53 (C_4H_5 , blue down triangles) and 67 (C_5H_7 , purple triangles), (b) m/z 55 (C_4H_7 , cyan diamonds) and 67 (purple triangles), and (c) m/z 68 (C_5H_8 , dark yellow left triangles) and 67 (purple triangles). Thick blue, cyan and purple lines are double exponential fits to m/z 53, 55 and 67, respectively. The thick dark yellow line is a single exponential fit to m/z 68. According to these kinetic traces, m/z 53 & 67 are likely to be formed by the fast $C(^3P) + C_4H_8$ reaction, as suggested by the

1
2
3 350 μs time constant of the observed rise, corresponding to a large value of $k_{1\text{st}} (\geq 3\,500\text{ s}^{-1})$.
4
5 The diffusion corrected^{72,73} pseudo first order rate ($\sim 9,000\text{ s}^{-1}$) is still lower than the predicted
6
7 one ($19,000\text{ s}^{-1}$), likely due to the instrument response function. Here we assume that the
8
9 rising edges of these two signals represent creation of C_4H_5 and C_5H_7 . By contrast, the
10
11 kinetic traces of m/z 55 & 68 show a slower increase ($k_{1\text{st}} \sim 1\,000\text{ s}^{-1}$), suggesting that they are
12
13 formed by reactions slower than $\text{C}(\text{}^3\text{P}) + \text{C}_4\text{H}_8$.
14



55
56
57
58
59
60

FIG. 3. Normalized kinetic traces obtained by photolysis of a CBr_4 and *trans*-but-2-ene mixture in helium, at 9.0 eV photon energy of (a) m/z 53 (blue down triangles) & 67 (purple

1
2
3 triangles) (b) m/z 55 (cyan diamonds) & 67 (purple triangles) and (c) m/z 68 (dark yellow left
4 triangles) & 67 (purple triangles). Thick blue, cyan & purple lines are double exponential fits
5 to m/z 53, 55 & 67 respectively. The thick dark yellow line is a single exponential fit to m/z
6
7
8
9
10 68.

11
12 From the above analysis, C_5H_7 and C_4H_5 isomers are likely to be the primary products
13 of the $C(^3P) +$ butene reaction through H-elimination and CH_3 -elimination. The branching
14 ratio between these two channels can be estimated directly from the values of S'_i obtained
15 from the fit of the temporal traces corrected by the relative ionization cross sections and the
16 mass discrimination factor. As these cross sections are unknown, they are assumed to be
17 equal. Consequently, the ratio of the S'_i values gives only an estimate of the H- vs. CH_3 -loss
18 branching. The fit of the m/z 53 and 67 temporal signals suggests a 0.63:1 C_4H_5/C_5H_7
19 branching ratio. No data were recorded at photon energies above the IE of methyl radical
20 (9.83 eV),⁷⁴ although it is expected it is formed.
21
22
23
24
25
26
27
28
29
30
31

32
33 FIG. 4 displays the m/z 53 photoionization spectrum obtained by irradiating the CBr_4
34 and *trans*-but-2-ene mixture at 248 nm. The data are integrated over the 0-40 ms time range
35 and displayed from 7.4 to 9.0 eV photon energy. Within the experimental uncertainty, the
36 absence of an ion signal onset at 7.55 eV suggests that the *i*- C_4H_5 isomer is not formed by the
37 $C(^3P) +$ *trans*-but-2-ene reaction.⁵⁷ The ion onset at 7.9 eV suggests the presence of one or
38 both of the methylpropargyl isomers (IE = 7.94 eV for H_2CCCCH_3 and IE = 7.95 eV for
39 $HCCCHCH_3$).⁵⁷ Within the experimental photon energy resolution (40 meV) it is not possible
40 to differentiate between the two methylpropargyl isomers. FIG. 4 also displays the integrated
41 Franck-Condon factor simulations for the *i*- C_4H_5 (dashed cyan line) and methylpropargyl
42 isomers (dashed and dotted blue & dotted green lines). The spectra for each isomer are
43 normalized to unity at 9.0 eV, because the simulated spectra are constant above this photon
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

energy. The thick red line is the simulated spectrum of the methylpropargyl isomer H_2CCCCH_3 normalized to the experimental data. The data are well reproduced with no contribution from $i\text{-C}_4\text{H}_5$. The absence of the $i\text{-C}_4\text{H}_5$ isomer and the formation of one or both methylpropargyl isomers differs from previous studies on C_4H_5 formation.^{26,57}

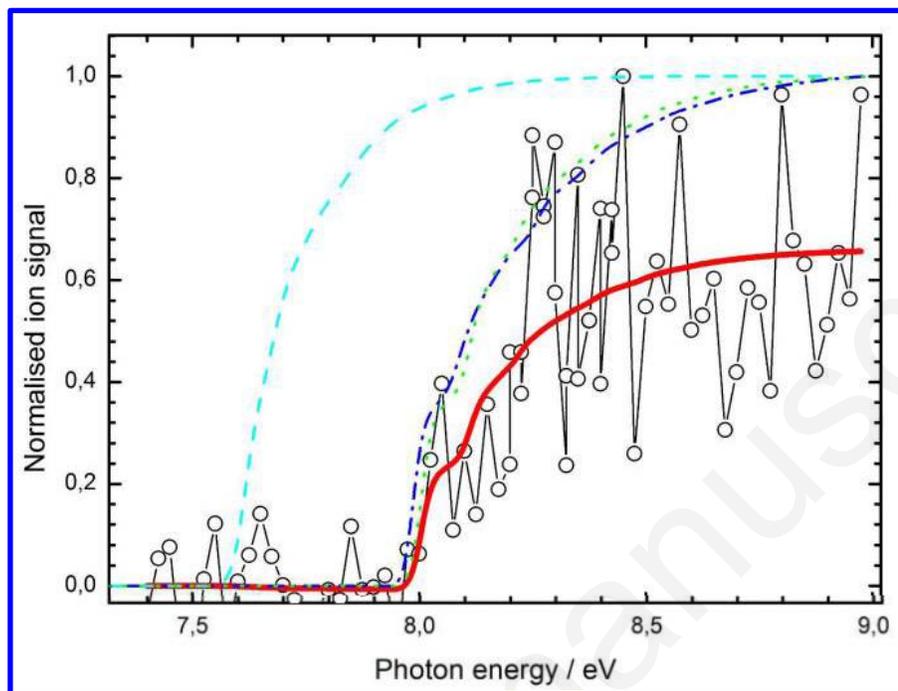


FIG. 4. Photoionization spectrum of m/z 53 obtained by photolysis of a CBr_4 and *trans*-but-2-ene mixture in helium integrated over the 0-40 ms time range and displayed from 7.4 to 9.0 eV photon energy. The lines are the integrated Franck-Condon factor simulations for $i\text{-C}_4\text{H}_5$ (dash cyan line) and methylpropargyl isomers (H_2CCCCH_3 dashed-dotted blue line & HCCCHCH_3 dotted green lines). The thick red line is the integrated Franck-Condon factor simulation of H_2CCCCH_3 normalized to the experimental data.

Due to small signal-to-noise-ratio in the photoionization spectrum at m/z 67 it is not possible to infer the contribution from the various C_5H_7 isomers. The faster decay of this signal compared with $m/z = 53$ makes the C_5H_7 spectra much noisier. However, the detection of ion signal above 7.5 eV is consistent with the possible formation of the dimethylpropargyl isomers as suggested by Bergeat & Loison²³ and Li *et al.*⁵⁴

1
2
3 In FIG. 3, the decay rate of the m/z 67 signal (428 s^{-1}) is greater than that of the m/z
4 53 signal (42 s^{-1}). From the product identification above, these signals are likely to be due to
5 ionization of dimethylpropargyl and methylpropargyl. The presence of a methyl group on
6 either terminal carbon of the propargyl radical may result in hyperconjugation⁷⁵ between the
7 partially filled p orbital and the σ orbital from a C–H bond in beta position. Although
8 hyperconjugation stabilizes the radical site, it weakens the methyl C–H bond, facilitating H-
9 abstraction by Br or H atoms. The large difference in decay rate between the two radicals
10 could be due to the dependence of the hyperconjugation strength on the isomeric structure of
11 the substituted propargyl radical and the number of methyl groups. Abstraction of a H-atom
12 from dimethylpropargyl is consistent with the detection of a signal at m/z 66 with a slow
13 formation rate (not shown). Within the experimental signal-to-noise, no signal is detected at
14 m/z 52.

15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30 Photoionization spectra were also recorded for secondary products, m/z 55 and 68
31 (not shown here). The presence of an ion onset at ca. 7.5 eV for m/z 55 suggests the
32 contribution of one or two 1-methylallyl isomers (C_4H_7).⁷⁶ They are likely formed by
33 abstraction of an H atom from butene by reactive species such as Br, CBr, or H.⁷⁶ The
34 presence of an ion onset at 8.8 eV in the photoionization spectrum for m/z 68 suggests its
35 identification as isoprene.⁵⁴

36 37 38 39 40 41 42 43 **B. $\text{C}(^3\text{P}) + \text{cis-but-2-ene}$**

44
45
46 The mass spectrum registered (not shown here) following photolysis of a CBr_4 and *cis-but-2-*
47 *ene* mixture in helium and nitrogen leads to the observation of the same four major peaks m/z
48 53, 55, 67 & 68 as for *trans-but-2-ene*. FIG. 5 shows the normalized temporal traces of (a)
49 m/z 53 (blue down triangles) and 67 (purple triangles) (b) m/z 55 (cyan diamonds) and 67
50 (purple triangles) and (c) m/z 68 (dark yellow left triangles) and 67 (purple triangles). Thick
51 blue, cyan and purple lines are double exponential fits to m/z 53, 55 and 67 respectively. The
52
53
54
55
56
57
58
59
60

thick dark yellow line is a single exponential fit to m/z 68. The first-order rise of m/z 53 and 67, around $3\,000\text{--}4\,000\text{ s}^{-1}$, suggests that they are primary reaction products as for the reaction of C^3P with *trans*-but-2-ene. The first-order rise coefficients of m/z 55 and 68, are 1230 and 1386 s^{-1} , suggesting products formed by secondary or slower reactions. The fit of the m/z 53 and 67 signals from FIG. 5 lead to a 0.60:1 $\text{C}_4\text{H}_5/\text{C}_5\text{H}_7$ branching ratio.

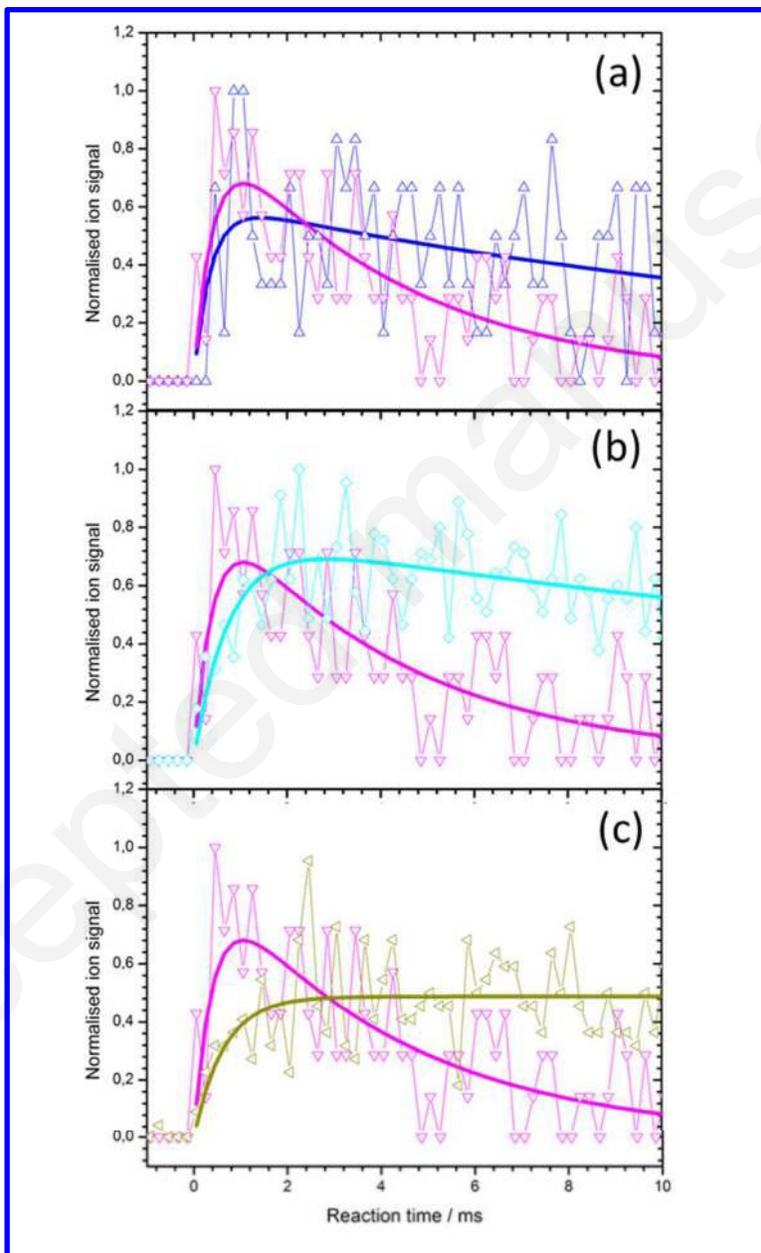


FIG. 5. Normalized kinetic traces obtained by photolysis of a CBr_4 and *cis*-but-2-ene mixture in helium, at 9.0 eV photon energy of (a) m/z 53 (blue down triangles) & 67 (purple triangles)

(b) m/z 55 (cyan diamonds) & 67 (purple triangles) and (c) m/z 68 (dark yellow left triangles) & 67 (purple triangles). Thick blue, cyan & purple lines are double exponential fits to m/z 53, 55 & 67 respectively. The thick dark yellow line is a single exponential fit to m/z 68.

FIG. 6 displays the m/z 53 photoionization spectrum obtained by irradiating a CBr_4 and *cis*-but-2-ene mixture at 248 nm. The data are integrated over the 0-40 ms time range and displayed from 7.4 to 8.8 eV photon energy. Similar to the results for *trans*-but-2-ene, there is no evidence for *i*- C_4H_5 isomer, and clear evidence for one or both methyl propargyl isomers.

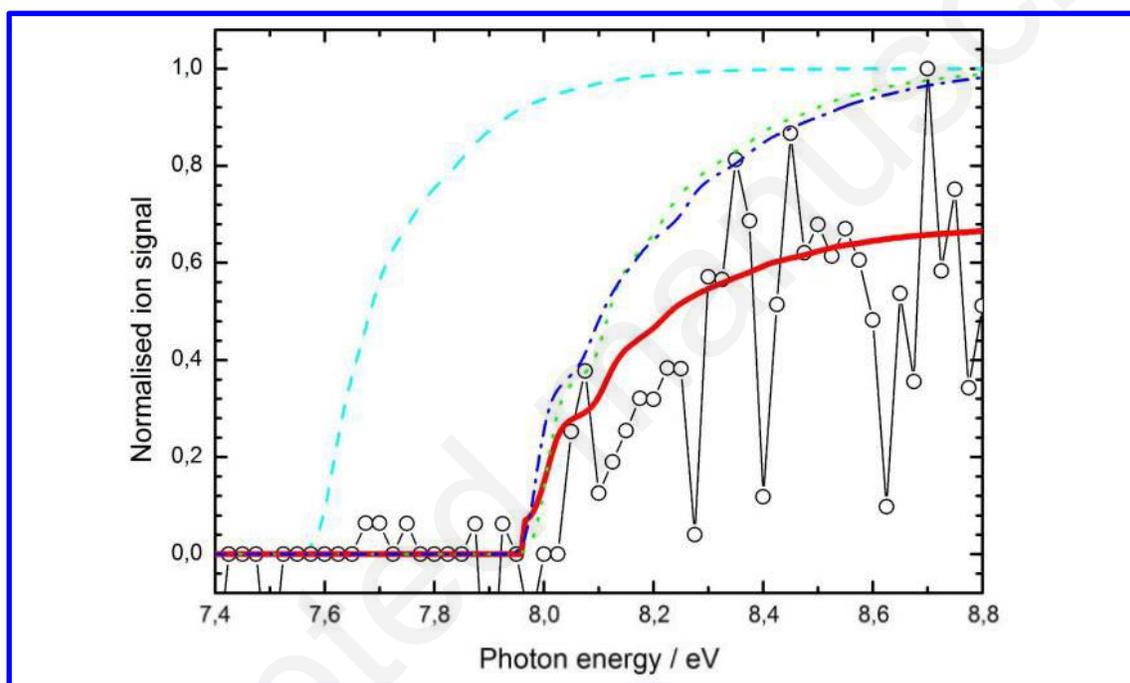
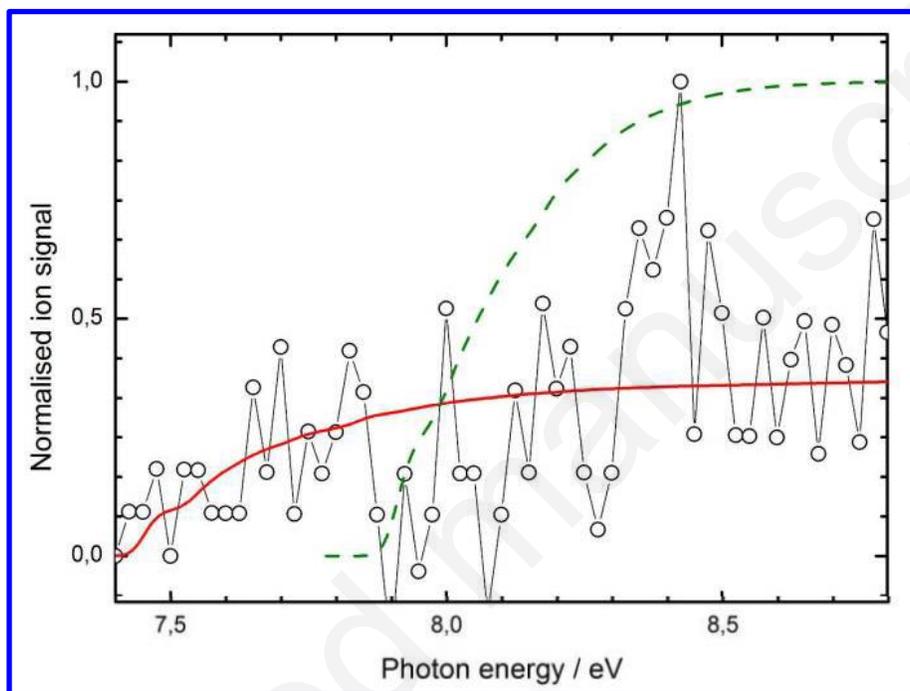


FIG. 6. Photoionization spectrum of m/z 53 obtained by photolysis of a CBr_4 and *cis*-but-2-ene mixture in helium integrated over the 0-40 ms time range and displayed from 7.4 to 8.8 eV photon energy. The lines are the integrated Franck-Condon factor simulations for *i*- C_4H_5 (dash cyan line) and methylpropargyl isomers (H_2CCCCH_3 dashed-dotted blue line & HCCCHCH_3 dotted green lines). The thick red line is the integrated Franck-Condon factor simulation of H_2CCCCH_3 normalized to the experimental data.

FIG. 7 displays the m/z 67 photoionization spectrum obtained by irradiating a CBr_4 and *cis*-but-2-ene mixture at 248 nm. The red solid line represents the normalized integrated

1
2
3 Franck Condon factors of the dimethylpropargyl isomer while the dashed line is that of the
4 ethylpropargyl isomer. The relatively good match between the dimethylpropargyl simulated
5 spectrum and experimental spectrum suggests that dimethylpropargyl is formed by the
6
7
8
9
10 reaction. Due to the low signal however, it is not possible to determine the contribution from
11
12 the ethylpropargyl isomer to the signal.



13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
FIG. 7. Photoionization spectrum of m/z 67 obtained by photolysis of a CBr_4 and *cis*-but-2-ene mixture in helium integrated over the 0-40 ms time range and displayed from 7.4 to 8.8 eV photon energy. The thick red line and the dash green line are the integrated Franck-Condon factor simulation for dimethylpropargyl (red line) and ethylpropargyl (green line) respectively.

50 51 52 53 54 55 56 57 58 59 60 C. $\text{C}(^3\text{P}) + \text{but-1-ene}$

FIG. 8 displays a time resolved mass spectrum obtained by photolysis of a CBr_4 and but-1-ene mixture in helium and nitrogen at 9.0 eV photon energy from -2.5 to 35 ms relative to the laser pulse. The main time-resolved signals are observed at m/z 39, 55, 66, 67 and 68. By contrast with experiments performed with *cis*- and *trans*-but-2-ene, m/z 53 is not

observed, and signals at m/z 29 and 39 appear after the photolysis laser pulse. Experiments performed while doubling the concentrations of all the reactants (not shown here) led to similar kinetic traces. As for the reaction with *trans*-C₄H₈, signals at m/z 55 and 68 are identified as methylallyl and isoprene. Signal at m/z 29, 39 and 67 are likely to originate from ionization of C₂H₅, C₃H₃, and C₅H₇ respectively, corresponding to the C₃H₃ + C₂H₅ and H + C₅H₇ exit channels of the C(³P) + but-1-ene reaction. Signal at m/z 66 could come from abstraction of a hydrogen atom from m/z 67 as discussed in Section IV A. The signal at m/z 39 is clearly identified as propargyl radical due to an ion onset at the propargyl ionization energy (IE=8.70 eV) and clear autoionization resonances.⁷⁷ It should be noted, that when the concentration of butene is increased, the signal at m/z 29 is not observed anymore, while the signal at m/z 39 is still present. This is likely due to fast reaction of the C₂H₅ radical, produced by the C(³P) + butene reaction, with butene. This is consistent with the fact that C₂H₅ reactions with hydrocarbons are expected to be faster than reactions with the resonance stabilized propargyl (C₃H₃) radical (see KIDA datasheet at <http://kida.obs.u-bordeaux1.fr/>).

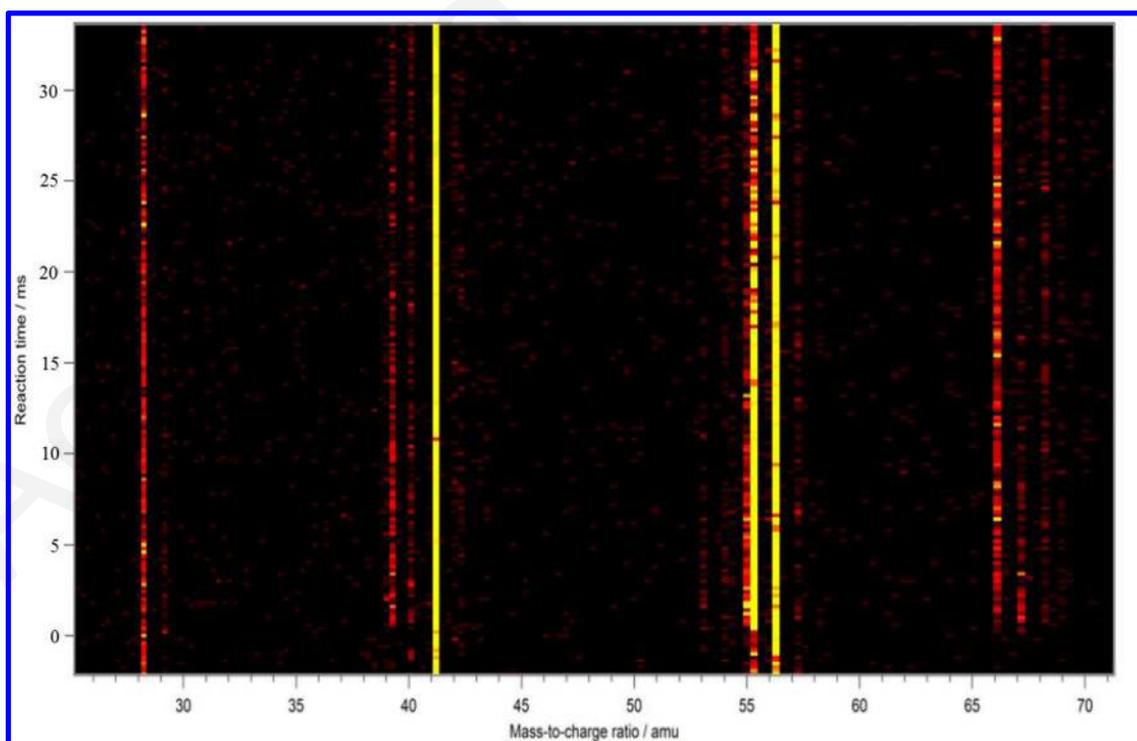


FIG. 8. 3D mass spectrum obtained by photolysis of a CBr₄ and but-1-ene mixture in helium

at 9.0 eV photon energy from -2.5 to 35 ms relatively to the laser pulse.

FIG. 9 displays the m/z 67 photoionization spectrum obtained by irradiating a CBr_4 and but-1-ene mixture in helium and nitrogen at 248 nm. The data are integrated over the 0-40 ms time range and displayed from 7.4 to 8.8 eV photon energy. The green dashed line is the integrated Franck-Condon factor simulation for ethylpropargyl and the thick red line that for dimethylpropargyl. The reasonable match between the integrated Franck-Condon factor simulation for ethylpropargyl and the experimental data suggests that ethylpropargyl is the main C_5H_7 isomer formed by the reaction $\text{C}(^3\text{P}) + \text{but-1-ene}$. The product branching ratio for the $\text{C}_3\text{H}_3/\text{C}_5\text{H}_7$ isomers can be estimated directly from the ratio of their ion signals assuming equal ionization cross sections. The m/z 39 and 67 signals from the mass spectrum lead to a 1:0.95 branching ratio for the $\text{C}_3\text{H}_3 + \text{C}_2\text{H}_5$ and $\text{H} + \text{C}_5\text{H}_7$ exit channels.

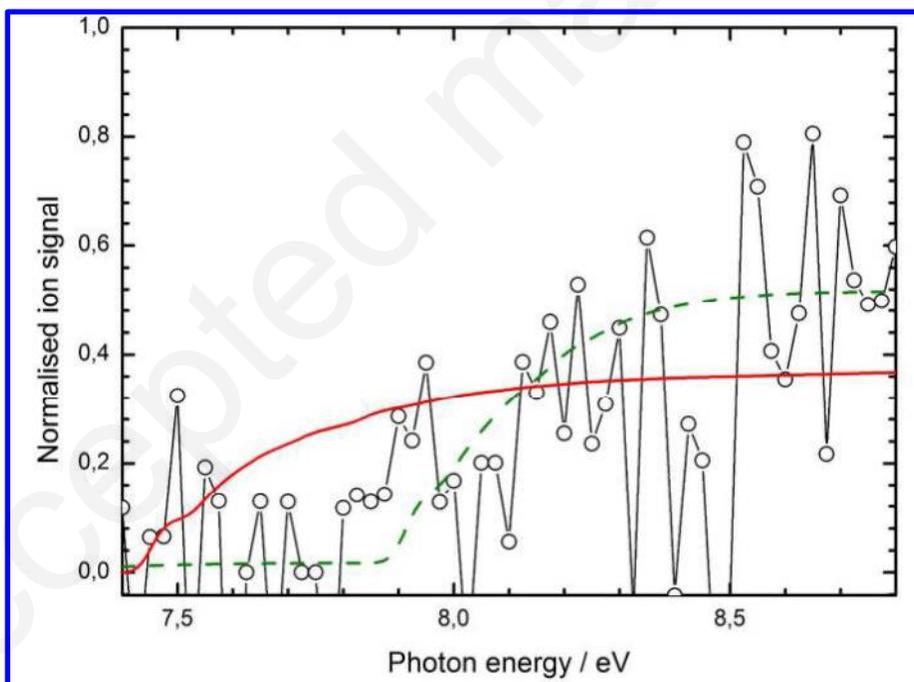


FIG. 9. Photoionization spectrum of m/z 67 obtained by photolysis of a CBr_4 and but-1-ene mixture in helium integrated over the 0-40 ms time range and displayed from 7.4 to 8.8 eV photon energy. The thick red line and the dash green line are the integrated Franck-Condon factor simulation for dimethylpropargyl (red line) and ethylpropargyl (green line)

1
2
3 respectively.
4
5

6 V. DISCUSSION

7 For the C(³P) reactions with the *trans*- and *cis*-but-2-ene isomers, assuming equal ionization
8 cross sections for the C₄H₅ and C₅H₇ isomers, C₄H₅:C₅H₇ branching ratios are found to be
9 0.63:1 and 0.60:1 ratio, respectively. This suggests that the stereoisomery has no effect on the
10 product ratios. The results for the *trans*-but-2-ene isomer differs from the 0.33±0.06 absolute
11 H-atom production branching fraction measured in fast flow reactor monitoring H-atom
12 fluorescence by Loison and Bergeat²³ corresponding to a 1:0.5 C₄H₅:C₅H₇ branching ratio. Li
13 *et al.* propose a possible 1:1 branching fraction based solely on the energetics of the products
14 and transition states.⁵⁴ Previous work on branching fraction for the C(³P) + C₃H₆ reaction led
15 to reasonable agreement between our results using tunable VUV photoionization with time of
16 flight mass spectrometry and those obtained Loison and Bergeat using H atom fluorescence
17 detection.²⁶ The discrepancy reported here could be due to the low signal in the present
18 experiments for the C₅H₇ isomers combined with the assumed equivalence of the
19 photoionization cross section of these isomers. For these reasons the values reported by
20 Loison and Bergeat²³ are likely to be more accurate. For the C(³P) reaction with but-1-ene,
21 the 1:0.95 branching fraction for the C₃H₃:C₅H₇ isomers derived from our experiments
22 suggests similar probability of losing a H or C₂H₅ group from the initial C₅H₈ reaction
23 adduct. No experimental or theoretical values are available for comparison.
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39

40 C₅H₇ production, corresponding to the H elimination channel, is observed for all three
41 C(³P) + butene isomer reactions. In the case of the C(³P) + *trans*-but-2-ene reaction, the
42 theoretical investigation by Li *et al.* suggests that dimethylpropargyl (CH₃CHCCCH₃) is the
43 most likely isomer produced. Although this cannot not be confirmed by the present study for
44 the C(³P) + *trans*-but-2-ene reaction, the fit of the photoionization spectrum presented in FIG.
45 7 is consistent with the formation of the dimethylpropargyl isomer by the C(³P) + *cis*-but-2-
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

nene reaction. Regarding the $C(^3P) + \text{but-1-ene}$ reaction, the photoionization spectrum in FIG. 9 suggests ethylpropargyl as the main product isomer.

FIG. 10 presents a proposed mechanism for the direct formation of the dimethylpropargyl and ethylpropargyl isomers from $C(^3P)$ reactions with the butene isomers. As previously proposed²⁶ the carbon atom is likely to interact with the π -electron system of the unsaturated hydrocarbon to form a 3-carbon ring. In the case of but-2-ene, different stereoisomers of the cyclic intermediate will be formed by reaction with the *cis*- or *trans*-but-2-ene. The strained isomer is likely to have a very short life time ($<1\text{ps}$) as suggested by Loison *et al.*²³ for reaction with butene and Kaiser *et al.* for reaction with ethylene.¹⁶ Upon ring opening it will form a substituted triplet allene-like intermediate. Elimination of a hydrogen atom from one of the C–H groups in alpha position to the triplet carbon leads to the formation of dimethylpropargyl for reaction with *trans/cis*-but-2-ene and ethylpropargyl with but-1-ene. The photoionization spectra at m/z 67 reported here are consistent with the previously discussed mechanism, although a more complex isomerization schemes could lead to other C_5H_7 isomers. The formation of the energetically accessible $\text{HCCC}(\text{CH}_3)\text{CH}_3$ would require a CH_3 transfer after formation of the cyclic intermediate.

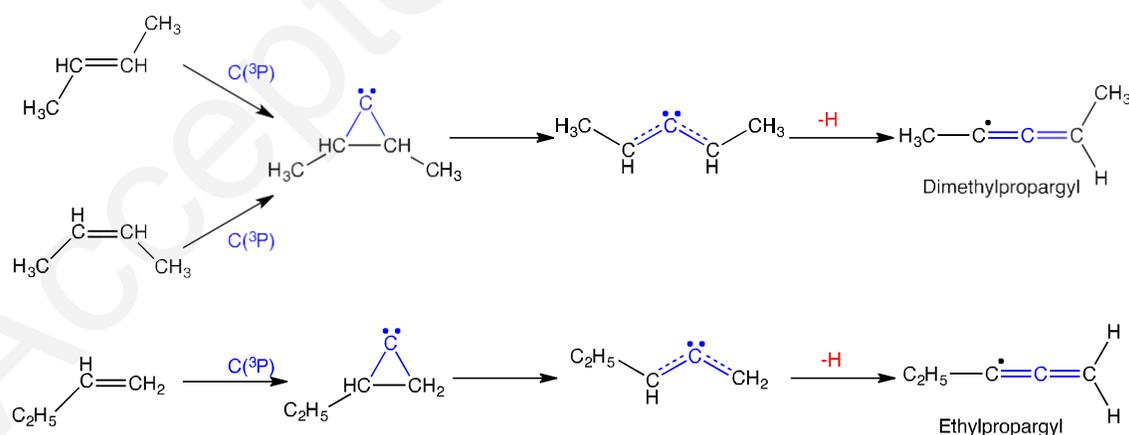


FIG. 10. Proposed mechanisms for the formation of C_5H_7 isomers from $C(^3P)$ reactions with butene isomers.

C_4H_5 isomers are observed for both $C(^3P) + trans-$ and $cis-but-2-ene$ reactions, while they are not detected for the $C(^3P) + but-1-ene$ reaction. The absence of C_4H_5 products in the case of but-1-ene is consistent with the absence of a methyl group on the carbon double bond of the initial reactants. This suggests a rapid dissociation of the acyclic adduct through breaking of the C–H or C–C bonds initially on the C=C group of the reactant without further isomerization. FIG. 11 shows the decomposition of the initial C_5H_8 adduct into ethyl + propargyl.

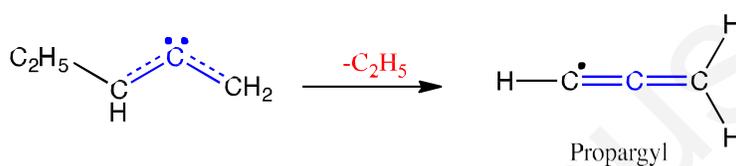
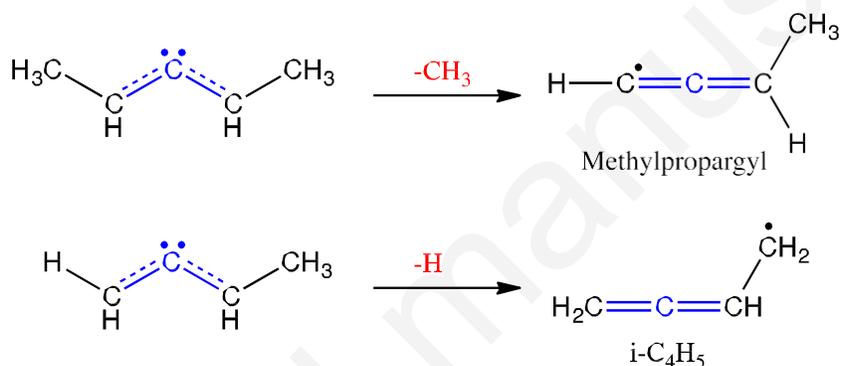


FIG. 11. Formation of propargyl radical from C_2H_5 -loss from the $C(^3P) + but-1-ene$ reaction adducts.

Interestingly, in the case of $C(^3P) + trans-$ and $cis-but-2-ene$ reactions where C_4H_5 is formed, the photoionization spectra, displayed in FIG. 4 and 6, differ significantly from those obtained for the $C + C_3H_6$ reactions by Capron et al.²⁶ or for fuel-rich flames experiments by Hansen et al.⁵⁷ The main difference seems to be due to the absence of the $i-C_4H_5$ isomer (IE=7.55 eV).²⁶ This contrast can be explained by the different loss channels of the intermediates formed by ring opening of the adducts from the $C + propene$ or $C + butene$ reactions. FIG. 12 displays the adduct formed by reaction of carbon atoms with $cis-but-2-ene$ (top) and propene (bottom). In the case of the reaction with propene, the $i-C_4H_5$ isomers are formed directly by elimination of an H-atom from the methyl group.²⁶ In the case of CH_3 loss from the C_5H_8 intermediate, the isomer formed by the most direct pathway is the CH_3CHCCH methylpropargyl isomer. Formation of the $i-C_4H_5$ isomer would require a hydrogen transfer from the methyl group to a carbon in γ position. Although within our experimental energy resolution it is not possible to distinguish between the two methylpropargyl isomers, the detection of one or both of the methylpropargyl isomers is

1
 2
 3 consistent with mechanisms proposed by Loison & Bergeat and Li *et al.* for the C(³P)
 4
 5 reaction with *trans*-but-2-ene. Li *et al.* suggest CH₃CHCCH as a likely candidate for C₄H₅
 6
 7
 8 isomers from C + *trans*-C₄H₈ reaction due to either kinetic or thermodynamic factors. Indeed,
 9
 10 from FIG. 12 formation of CH₃CCCH₂ would require a H-atom transfer to a carbon in β
 11
 12 position. Distinguishing between the two isomers would be of interest as CH₃CHCCH is
 13
 14 completely absent from flames models whereas CH₃CCCH₂ is proposed to form toluene
 15
 16 (C₇H₈) or benzyl radical (C₇H₇) by reaction with another CH₃CCH₂ or with propargyl
 17
 18 radical.⁵⁸
 19
 20
 21
 22
 23
 24
 25
 26
 27
 28
 29
 30
 31
 32



33 FIG. 12. Formation of C₄H₅ isomer from CH₃ or H-loss from the C(³P) + *cis/trans*-but-2-ene
 34
 35 (top) and C + propene (bottom) reaction adducts.²⁹
 36
 37

38 Although carbon atoms may not be formed in standard flames and engines, they are
 39
 40 known to be present in plasma and plasma-assisted environments.⁹⁻¹¹ Similar to the CH
 41
 42 radical, carbon atoms will react with the most abundant fuel molecules through
 43
 44 addition/elimination pathways to form larger molecules. Such mechanisms still need to be
 45
 46 validated, especially for large hydrocarbon molecules used as fuels. Coupling plasmas to
 47
 48 combustion systems has the potential to greatly improve the combustion process through both
 49
 50 an increase in combustion efficiency and a reduction in the emission of pollutants (e.g. NO_x,
 51
 52 CO₂, soot).⁷⁸ Feedback control algorithms using emission concentration as error signals and
 53
 54 applied plasma as control signals could allow the combustion device to run at its stability
 55
 56 limit. The design of such plasma-assisted technologies requires a basic understanding of the
 57
 58
 59
 60

1
2
3 combined combustion and plasma chemistry leading to increased heat release and decreased
4
5 emissions.
6
7

8 Isomers of the C₄H₅ and C₅H₇ hydrocarbon radicals have been detected in standard
9
10 combustion flames where they contribute to the formation of larger molecules, including
11 aromatic hydrocarbons.^{58,79} Their detection from the C(³P) + butene isomers reactions
12
13 suggests that the formation of these radicals will be enhanced under plasma assisted
14
15 combustion conditions potentially changing the molecular growth chemical scheme. The
16
17 estimated branching ratios obtained in the present experiments are important data for the
18
19 design of new combustion models under high-energy conditions such as those found in
20
21 plasma. Ultimately these models will be used to tailor new combustion strategies with lower
22
23 emission and higher efficiency.
24
25

26
27
28 Carbon-containing molecules can take various forms such as carbon chain molecules,
29
30 polycyclic aromatic hydrocarbons (PAHs), carbon clusters and carbonaceous solids.⁸⁰ C(³P)
31
32 atoms have been detected in dense interstellar clouds⁸¹⁻⁸³ where a large fraction of the
33
34 observed interstellar molecules are formed. None of the C₄H₈ isomers however, have been
35
36 observed so far, likely due to their low electric dipole moments ($\leq 0,5$ D). Their predicted
37
38 abundances in astrochemical models, formed through C and C⁺ reactions, seems to be
39
40 sensitive to reactions involving atomic oxygen and nitrogen.⁸⁴ In methane rich atmospheres
41
42 such as Titan's, hydrocarbon formation is initiated by the photochemistry of methane that
43
44 produces more complex and less saturated hydrocarbons.^{47,48,85-88} Although C₄H₈ has not been
45
46 detected in Titan's atmosphere,⁴⁷ Lavvas and coworkers⁴⁸ for instance, included the reaction
47
48 of carbon with 1-butene isomer in their photochemical model of Titan's atmosphere with no
49
50 information on the products. Zhang *et al.*⁶ used a 1D-photochemical model of Titan to
51
52 produce an atomic carbon profile reproducing the atomic carbon emission at 1657Å observed
53
54 by the Cassini Ultra-violet Imaging Spectrograph and stress the need of a full set of
55
56
57
58
59
60

1
2
3 photochemical reactions involving chemical species containing at least three carbon atoms to
4 describe carbon atom chemistry above 600 km. Recently, Dobrijevic and coworkers⁸⁸ derived
5 abundance profiles from a 1D-photochemical model coupling neutral and ion chemistries,
6
7 showing that C₄H₈ (with no isomer distinction) is among the most abundant C₄H_x species
8 above 600 km. Such large hydrocarbons could also play a role in the formation of organic
9 hazes observed in Titan's atmosphere.⁸⁹

10
11
12
13
14
15
16
17 The rate coefficient of the reaction C(³P) trans-but-2-ene was measured by Loison et
18 al. at room temperature ($k = 1.9 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$)²³ and is likely to be of the same
19 order of magnitude for cis-but-2-ene and but-1-ene. A large number of reactions between
20 ground state carbon atoms and small saturated or unsaturated hydrocarbons have been shown
21 to be fast at room temperature^{12,23,33,40,90} with rate coefficients increasing with decreasing
22 temperature.^{13,14,91} Similarly, it is expected that reactions of C(³P) with butene isomers
23 remain fast down to very low temperatures. Furthermore, the present investigation shows that
24 even for such a simple system, the title reaction can form quite a large number of
25 hydrocarbon radicals such as C₄H₅ isomers (H₂CCCCH₃ and/or HCCCHCH₃), propargyl
26 (C₃H₃), dimethylpropargyl and ethylpropargyl. Although the methyl radical is not detected it
27 is expected to be formed by reaction of carbon atoms with trans- and cis-butene. The nature
28 and branching ratios of these radicals are found to depend on the C₄H₈ isomers considered,
29 and are consistent with simple addition/elimination schemes shown in Figs.10 - 12. All these
30 radicals are susceptible to participate in the formation and destruction of other molecules
31 present in these environments. This stresses the importance of including molecular isomer
32 resolution for both reactants and products in interstellar astrochemical and atmospheric
33 photochemical models in order to estimate their abundances as well as their potential
34 importance in chemical schemes leading to the formation and destruction of complex
35 molecules.
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

VI. CONCLUSION

The ground state $C(^3P)$ reactions with butene isomers (but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene) were studied under multiple collision conditions²⁶ at 353 K and 4 Torr using tunable photoionization coupled to time-of-flight mass spectrometry. Products from secondary or side reactions are distinguished from primary products using the temporal profile of the detected ions. The reactions are performed under multiple collision conditions from 4 to 8 Torr with no significant pressure dependence of the product distributions. Although the initial energized adduct is expected to have a very short lifetime (<1 ps),^{16,23} statistical calculations have shown that some of its isomers may have longer lifetime, up to tens of nanoseconds for intermediates of the $C(^3P) + C_2H_2$ reaction for instance.¹⁸ Experimental or theoretical studies over a wider range of pressure are required to fully investigate the effect of collisional quenching on the final product distribution and the role of intersystem crossing.

In the case of $C(^3P) + \textit{trans}$ -but-2-ene and $C(^3P) + \textit{cis}$ -but-2-ene reactions, the observed reaction exit channels are $C_4H_5 + CH_3$ and $C_5H_7 + H$. Assuming similar ionization cross sections for the CH_3 - and H -coproducts, the $C_4H_5:C_5H_7$ branching ratios are 0.63:1 and 0.60:1 for reactions with *trans*- and *cis*-2-butene, respectively. These values differ from the 1:0.5 $CH_3:H$ -loss ratio measured in fast flow reactor²³ or the 1:1 ratio suggested by Li et al.⁵⁴ from the analysis of the C_5H_8 potential energy surface. The difference between the experimental branching ratios is likely to be in part due to the absence of data on the photoionization cross sections for the C_5H_7 and C_4H_5 isomers. Further experimental or theoretical studies are required to obtain C_4H_5 and C_5H_7 photoionization cross-section and therefore more accurate branching ratios.

For the $C(^3P) + \textit{but-1-ene}$ reaction, the observed reaction channels are $C_3H_3 + C_2H_5$ and $C_5H_7 + H$. The measured $C_3H_3:C_5H_7$ signal ratio from the present flow data is found to

1
2
3 be 1:0.95 assuming equal photoionization cross sections for the C₃H₃ and C₅H₇ radicals. No
4
5 C₄H₅ formation is observed for this reaction. The non-detection of C₄H₅ for reaction with but-
6
7 *I*-ene is consistent with direct addition of the carbon atom onto the carbon double bond
8
9
10 followed by rapid ring opening to form a triplet allene-like structure. The most likely fate of
11
12 the energized intermediate is a C–C bond breaking in β position from the carbene center. In
13
14 the case of reaction with but-*I*-ene, this direct addition-elimination mechanism leads to the
15
16 formation of the observed C₂H₅ and C₃H₃ radicals.
17

18
19 Photoionization spectra at the mass of the C₄H₅ isomers for the *trans* and *cis* isomers
20
21 show formation of one or both methylpropargyl isomers and negligible formation of *i*-C₄H₅.
22
23 Within the experimental energy resolution, it is not possible to distinguish between the two
24
25 methylpropargyl isomers. Photoionization spectra at the mass of the C₅H₇ isomers display
26
27
28 very low signal-to-noise ratio and do not allow the unequivocal identification of the formed
29
30 isomers. The detection of signal below 7.8 eV is consistent with the formation of
31
32 dimethylpropargyl for reaction with the *trans* and *cis* isomers. In the case of the reaction with
33
34 but-1-ene, the photoionization spectrum is well reproduced by the simulated spectrum of only
35
36 ethylpropargyl.
37

38
39 Overall, the isomer-resolved product detection for the C(³P) + butene isomer reactions
40
41 is consistent with the addition of the carbon atom to the double bond to form a cyclic
42
43 intermediate. This intermediate is likely to have a very short lifetime and to isomerize
44
45 through ring opening to a triplet allene-like intermediate. The experimental data can all be
46
47
48 explained using direct H-, CH₃-, or C₂H₅-elimination without further isomerization of the
49
50 energized intermediates. Experimental and theoretical determinations of open-shell molecule
51
52 photoionization cross-sections are required in order to improve the accuracy of branching
53
54 ratios inferred from photoionization mass spectrometry studies. The reaction of ground state
55
56 carbon atoms with butene isomers in carbon rich environments such as the ISM or plasma
57
58
59
60

1
2
3 assisted combustion is therefore likely to contribute to the formation of large carbon radicals
4
5 and therefore to molecular growth chemical schemes.
6
7

8 **ACKNOWLEDGEMENTS**

9
10 The Rennes team acknowledges support from the Agence Nationale de la Recherche, contract
11 ANR-11-BS04-024-CRESUSOL-01, the French INSU/CNRS Program “Physique et Chimie
12
13 du Milieu Interstellaire” (PCMI), the Institut National de Physique (INP CNRS), the Région
14
15 Bretagne and the Université de Rennes 1. S.D.L.P. acknowledges financial support from the
16
17 Institut Universitaire de France. Acknowledgement is made to the Donors of the American
18
19 Chemical Society Petroleum Research Fund (PRF#53105-DN16) for partial support of this
20
21 research (F.G. and M.S.). We thank Mr Howard Johnsen for technical support of this
22
23
24
25
26 experiment. D.L.O. and the instrumentation for this work are supported by the Division of
27
28 Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the
29
30 U.S. Department of Energy. Sandia is a multi-program laboratory operated by Sandia
31
32 Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration
33
34
35 under contract DE-AC04-94-AL85000. This research used resources of the Advanced Light
36
37 Source, a DOE Office of Science User Facility, which is supported by the Direct, Office of
38
39 Science, Office of Basic Energy Sciences, the U.S. Department of Energy under contract DE-
40
41 AC02-05CH11231 at Lawrence Berkeley National Laboratory.
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3
4
5
6 **REFERENCES**
7

- 8
9 (1) Ingalls, J. G.; Bania, T. M.; Jackson, J. M. Atomic carbon in the high-latitude molecular
10 cloud MBM-12. *Astrophys. J.* **1994**, *431*, L139-L142.
11
12 (2) Ingalls, J. G.; Chamberlin, R. A.; Bania, T. M.; Jackson, J. M.; Lane, A. P.; Stark, A. A.
13 Atomic carbon in southern hemisphere high-latitude clouds. *Astrophys. J.* **1997**, *479*, 296-
14 302.
15
16 (3) Van der Veen, W.; Huggins, P. J.; Matthews, H. E. Atomic carbon in the circumstellar
17 envelopes of evolved stars. *Astrophys. J.* **1998**, *505*, 749-755.
18
19 (4) Sofia, U. J.; Cardelli, J. A.; Guerin, K. P.; Meyer, D. M. Carbon in the diffuse interstellar
20 medium. *Astrophys. J.* **1997**, *482*, L105-L108.
21
22 (5) Wilson, C. D. Atomic carbon emission from individual molecular clouds in M33.
23 *Astrophys. J.* **1997**, *487*, L49-L52.
24
25 (6) Zhang, X.; Ajello, J. M.; Yung, Y. L. Atomic carbon in the upper atmosphere of Titan
26 *Astrophys. J. Lett.* **2010**, *708*, L18-L21.
27
28 (7) McElroy, M. B.; McConnell, J. C. Atomic carbon in atmospheres of Mars and Venus *J.*
29 *Geophys. Res.* **1971**, *76*, 6674-6690.
30
31 (8) Ajello, J. M.; Gustin, J.; Stewart, I.; Larsen, K.; Esposito, L.; Pryor, W.; McClintock, W.;
32 Stevens, M. H.; Malone, C. P.; Dziczek, D. Titan airglow spectra from the Cassini Ultraviolet
33 Imaging Spectrograph: FUV disk analysis. *Geophys. Res. Lett.* **2008**, *35*, L06102 1-5.
34
35 (9) Belikov, A. E.; Sakhapov, S. Z.; Smith, M. A.; Tikhonov, G. Mass spectrometry of
36 molecules and radicals in glow discharge plasma. *J. Eng. Thermophys.* **2011**, *20*, 42-54.
37
38 (10) Benedikt, J.; Wisse, M.; Woen, R. V.; Engeln, R.; van de Sanden, M. C. M. Role of
39 carbon atoms in the remote plasma deposition of hydrogenated amorphous carbon. *J. Appl.*
40 *Phys.* **2003**, *94*, 6932-6938.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (11) Yu, B. W.; Girshick, S. L. Atomic carbon vapor as a diamond growth precursor in
4 thermal plasmas. *J. Appl. Phys.* **1994**, *75*, 3914-3923.
5
6
7 (12) Haider, N.; Husain, D. Absolute rate data for the reactions of ground-state atomic
8 carbon, $C\ 2p^2(^3P_J)$, with alkenes investigated by time-resolved atomic resonance-absorption
9 spectroscopy in the vacuum ultraviolet *J. Chem. Soc., Faraday* **1993**, *89*, 7-14.
10
11 (13) Chastaing, D.; James, P. L.; Sims, I. R.; Smith, I. W. M. Neutral-neutral reactions at the
12 temperatures of interstellar clouds: Rate coefficients for reactions of atomic carbon, $C(^3P)$,
13 with O_2 , C_2H_2 , C_2H_4 and C_3H_6 down to 15 K. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2247-2256.
14
15 (14) Chastaing, D.; Le Picard, S. D.; Sims, I. R.; Smith, I. W. M.; Geppert, W. D.; Naulin,
16 C.; Costes, M. Rate coefficients and cross-sections for the reactions of $C(^3P_J)$ atoms with
17 methylacetylene and allene. *Chem. Phys. Lett.* **2000**, *331*, 170-176.
18
19 (15) Clary, D. C.; Haider, N.; Husain, D.; Kabir, M. Interstellar carbon-chemistry - Reaction-
20 rates of neutral atomic carbon with organic-molecules *Astrophys. J.* **1994**, *422*, 416-422.
21
22 (16) Kaiser, R. I.; Lee, Y. T.; Suits, A. G. Crossed-beam reaction of $C(^3P_J)$ with $C_2H_2(^1\Sigma^+)$ -
23 Observation of tricarbon-hydride C_3H . *J. Chem. Phys.* **1995**, *103*, 10395-10398.
24
25 (17) Takayanagi, T. Quantum dynamics study on the product branching for the $C(^3P)+C_2H_2$
26 reaction: cyclic- C_3H versus linear- C_3H . *J. Phys. Chem. A* **2006**, *110*, 361-366.
27
28 (18) Mebel, A. M.; Kislov, V. V.; Hayashi, M. Prediction of product branching ratios in the
29 $C(^3P)+C_2H_2 \rightarrow 1-C_3H+H/c-C_3H+H/C_3+H_2$ reaction using ab initio coupled clusters
30 calculations extrapolated to the complete basis set combined with Rice-Ramsperger-Kassel-
31 Marcus and radiationless transition theories. *J. Chem. Phys.* **2007**, *126*, 204310 1-11.
32
33 (19) Kaiser, R. I.; Lee, Y. T.; Suits, A. G. Crossed-beam reaction of carbon atoms with
34 hydrocarbon molecules .1. Chemical dynamics of the propargyl radical formation C_3H_3
35 (X^2B_2), from reaction of $C(^3P_J)$ with ethylene, $C_2H_4(X^1A_g)$. *J. Chem. Phys.* **1996**, *105*, 8705-
36 8720.
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (20) Leonori, F.; Petrucci, R.; Segoloni, E.; Bergeat, A.; Hickson, K. M.; Balucani, N.;
4
5 Casavecchia, P. Unraveling the dynamics of the $C(^3P, ^1D)+C_2H_2$ reactions by the crossed
6
7 molecular beam scattering technique. *J. Phys. Chem. A* **2008**, *112*, 1363-1379.
- 8
9
10 (21) Kaiser, R. I.; Mebel, A. M.; Chang, A. H. H.; Lin, S. H.; Lee, Y. T. Crossed-beam
11
12 reaction of carbon atoms with hydrocarbon molecules. V. Chemical dynamics of n-C₄H₃
13
14 formation from reaction of $C(^3P_J)$ with allene, $H_2CCCH_2(X^1A_1)$. *J. Chem. Phys.* **1999**, *110*,
15
16 10330-10344.
- 17
18 (22) Schranz, H. W.; Smith, S. C.; Mebel, A. M.; Lin, S. H. Prediction of absolute rate
19
20 coefficients and product branching ratios for the $C(^3P)$ plus allene reaction system. *J. Chem.*
21
22 *Phys.* **2002**, *117*, 7055-7067.
- 23
24 (23) Loison, J. C.; Bergeat, A. Reaction of carbon atoms, $C(2p^2, ^3P)$ with C₃H₄ (allene and
25
26 methylacetylene), C₃H₆ (propylene) and C₄H₈ (trans-butene): Overall rate constants and
27
28 atomic hydrogen branching ratios. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5396-5401.
- 29
30 (24) Mebel, A. M.; Kaiser, R. I.; Lee, Y. T. Ab initio MO study of the global potential
31
32 energy surface of C₄H₄ in triplet electronic state and the reactions of $C(^3P_J)$ with C₃H₄ (allene
33
34 and propyne) and $C_2(A^3\Pi_u)$ with $C_2H_4(X^1A^+_{1g})$. *J. Am. Chem. Soc.* **2000**, *122*, 1776-1788.
35
36
37
38
- 39 (25) Kaiser, R. I.; Nguyen, T. L.; Le, T. N.; Mebel, A. M. An ab initio investigation of
40
41 reactions of carbon atoms $C(^3P_J)$ with C₂H₄ and C₃H₆ in the interstellar medium. *Astrophys.*
42
43 *J.* **2001**, *561*, 858-863.
- 44
45 (26) Capron, M.; Bourgalais, J.; Kailasanathan, R. K. A.; Osborn, D. L.; Le Picard, S. D.;
46
47 Goulay, F. Flow tube studies of the $C(^3P)$ reactions with ethylene and propylene. *Phys. Chem.*
48
49 *Chem. Phys.* **2015**, *17*, 23833-23846.
- 50
51 (27) Kaiser, R. I.; Stranges, D.; Bevsek, H. M.; Lee, Y. T.; Suits, A. G. Crossed-beam
52
53 reaction of carbon atoms with hydrocarbon molecules .4. Chemical dynamics of
54
55
56
57
58
59
60

1
2
3 methylpropargyl radical formation, C_4H_5 , from reaction of $C(^3P_J)$ with propylene, C_3H_6
4
5 (X^1A'). *J. Chem. Phys.* **1997**, *106*, 4945-4953.

6
7 (28) Chin, C. H.; Chen, W. K.; Huang, W. J.; Lin, Y. C.; Lee, S. H. Identification of C_4H_5 ,

8
9
10 C_4H_4 , C_3H_3 and CH_3 radicals produced from the reaction of atomic carbon with propene:
11
12 Implications for the atmospheres of Titan and giant planets and for the interstellar medium.
13
14 *Icarus* **2013**, *222*, 254-262.

15
16 (29) Hahndorf, I.; Lee, Y. T.; Kaiser, R. I.; Vereecken, L.; Peeters, J.; Bettinger, H. F.;
17
18 Schreiner, P. R.; Schleyer, P. V.; Allen, W. D.; Schaefer, H. F. A combined crossed-beam, ab
19
20 initio, and Rice-Ramsperger-Kassel-Marcus investigation of the reaction of carbon atoms
21
22 $C(^3P_J)$ with benzene, $C_6H_6(X^1A_{1g})$ and d(6)-benzene, $C_6D_6(X^1A_{1g})$. *J. Chem. Phys.* **2002**,
23
24 *116*, 3248-3262.

25
26 (30) Sun, B. J.; Huang, C. Y.; Kuo, H. H.; Chen, K. T.; Sun, H. L.; Huang, C. H.; Tsai, M.
27
28 F.; Kao, C. H.; Wang, Y. S.; Gao, L. G. *et al.* Formation of interstellar 2,4-pentadiynylidyne,
29
30 $HCCCCC(X^2\Pi)$, via the neutral-neutral reaction of ground state carbon atom, $C(^3P_J)$, with
31
32 diacetylene, $HCCCCH(X^1\Sigma^+)$. *J. Chem. Phys.* **2008**, *128*, 244303 1-16.

33
34 (31) Bourgalais, J.; Capron, M.; Kailasanathan, R. K. A.; Osborn, D. L.; Hickson, K. M.;
35
36 Loison, J. C.; Wakelam, V.; Goulay, F.; Le Picard, S. D. The $C(^3P) + NH_3$ reaction in
37
38 interstellar chemistry. I. Investigation of the product formation channels. *Astrophys. J.* **2015**,
39
40 *812*, 1-12.

41
42 (32) Hickson, K. M.; Loison, J. C.; Bourgalais, J.; Capron, M.; Le Picard, S. D.; Goulay, F.;
43
44 Wakelam, V. The $C(^3P) + NH_3$ reaction in interstellar chemistry. II. Low temperature rate
45
46 constants and modeling of NH , NH_2 , and NH_3 abundances in dense interstellar clouds.
47
48
49
50
51
52 *Astrophys. J.* **2015**, *812*, 1-8.

- 1
2
3 (33) Haider, N.; Husain, D. Kinetic investigation of the reactions of ground-state atomic
4 carbon, $C(2p^2(^3P_J))$, with acetylenes by time-resolved atomic resonance - absorption-
5 spectroscopy in the vacuum ultra-violet *Ber. Bunsen-Ges. Phys. Chem.*
6
7
8
9
10 *Chem. Phys.* **1992**, *176*, 133-150.
- 11
12 (34) Husain, D.; Ioannou, A. X. Collisional removal of atomic carbon, $C 2p^2(^3P_J)$, by
13 aldehydes and ketones, investigated by time-resolved atomic resonance absorption
14 spectroscopy in the vacuum ultra-violet. *J. Photochem. Photobiol., A* **1999**, *129*, 1-7.
- 15
16
17 (35) Geppert, W. D.; Naulin, C.; Costes, M.; Capozza, G.; Cartechini, L.; Casavecchia, P.;
18 Volpi, G. G. Combined crossed-beam studies of $C(^3P_J)+C_2H_4 \rightarrow C_3H_3+H$ reaction dynamics
19 between 0.49 and 30.8 kJ mol⁻¹. *J. Chem. Phys.* **2003**, *119*, 10607-10617.
- 20
21
22 (36) Malik, M. A.; Hughes, D.; Malik, A.; Xiao, S.; Schoenbach, K. H. Study of the
23 production of hydrogen and light hydrocarbons by spark discharges in diesel, kerosene,
24 gasoline, and methane. *Plasma Chem. and Plasma Process.* **2013**, *33*, 271-279.
- 25
26
27 (37) Pascoli, G.; Polleux, A. Condensation and growth of hydrogenated carbon clusters in
28 carbon-rich stars. *Astron. Astrophys.* **2000**, *359*, 799-810.
- 29
30
31 (38) Lee, Y. T. Molecular-beam studies of elementary chemical processes. *Science* **1987**,
32 *236*, 793-798.
- 33
34
35 (39) Chin, C. H.; Chen, W. K.; Huang, W. J.; Lin, Y. C.; Lee, S. H. Exploring the dynamics
36 of reaction $C(^3P)+C_2H_4$ with crossed beam/photoionization experiments and quantum
37 chemical calculations. *J. Phys. Chem. A* **2012**, *116*, 7615-7622.
- 38
39
40 (40) Bergeat, A.; Loison, J. C. Reaction of carbon atoms, $C(2p^2, ^3P)$ with C_2H_2 , C_2H_4 and
41 C_6H_6 : Overall rate constant and relative atomic hydrogen production. *Phys. Chem. Chem.*
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 (41) Hickson, K. M.; Loison, J. C.; Wakelam, V. Temperature dependent product yields for
4 the spin forbidden singlet channel of the $C(^3P) + C_6H_2$ reaction. *Chem. Phys. Lett.* **2016**, *659*,
5 70-75.
6
7

8
9
10 (42) Bond, J. Q.; Alonso, D. M.; Wang, D.; West, R. M.; Dumesic, J. A. Integrated catalytic
11 conversion of gamma-valerolactone to liquid alkenes for transportation fuels. *Science* **2010**,
12 327, 1110-1114.
13
14

15 (43) Mehl, M.; Pitz, W. J.; Westbrook, C. K.; Yasunaga, K.; Conroy, C.; Curran, H. J.
16 Autoignition behavior of unsaturated hydrocarbons in the low and high temperature regions.
17
18
19
20
21 *Proc. Comb. Inst.* **2011**, *33*, 201-208.
22

23 (44) Zhao, P.; Yuan, W. H.; Sun, H. Y.; Li, Y. Y.; Kelley, A. P.; Zheng, X. L.; Law, C. K.
24 Laminar flame speeds, counterflow ignition, and kinetic modeling of the butene isomers.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

(45) Zhang, Y. J.; Cai, J. H.; Zhao, L.; Yang, J. Z.; Jin, H. F.; Cheng, Z. J.; Li, Y. Y.; Zhang,
L. D.; Qi, F. An experimental and kinetic modeling study of three butene isomers pyrolysis at
low pressure. *Combust. Flame* **2012**, *159*, 905-917.

(46) Zhang, H. L.; Wu, W. D.; Gong, C. S.; Wang, W.; He, Z. B.; Li, J.; Ju, X.; Tang, Y. J.;
Xie, E. Q. Structural and optical properties of Fe-doped hydrogenated amorphous carbon
films prepared from trans-2-butene by plasma enhanced metal organic chemical vapor
deposition. *App. Phys. A* **2010**, *98*, 895-900.

(47) Lavvas, P. P.; Coustenis, A.; Vardavas, I. M. Coupling photochemistry with haze
formation in Titan's atmosphere, part I: Model description. *Planet. Space Sci.* **2008**, *56*, 27-
66.

(48) Lavvas, P. P.; Coustenis, A.; Vardavas, I. M. Coupling photochemistry with haze
formation in Titan's atmosphere, Part II: Results and validation with Cassini/Huygens data.
Planet. Space Sci. **2008**, *56*, 67-99.

- 1
2
3 (49) Atkinson, R.; Aschmann, S. M. Rate constants for the reaction of the OH radical with
4 series of alkenes and dialkenes at 295 +/- 1 K. *Int. J. Chem. Kinet.* **1984**, *16*, 1175-1186.
5
6
7 (50) Loison, J.-C.; Daranlot, J.; Bergeat, A.; Caralp, F.; Mereau, R.; Hickson, K. M. Gas-
8
9 phase kinetics of hydroxyl radical reactions with C₃H₆ and C₄H₈: product branching ratios
10 and OH addition site-specificity. *J. Phys. Chem. A* **2010**, *114*, 13326-13336.
11
12 (51) Bouwman, J.; Fournier, M.; Sims, I. R.; Leone, S. R.; Wilson, K. R. Reaction rate and
13 isomer-specific product branching ratios of C₂H + C₄H₈: 1-butene, cis-2-butene, trans-2-
14 butene, and isobutene at 79 K. *J. Phys. Chem. A* **2013**, *117*, 5093-5105.
15
16
17 (52) Nizamov, B.; Leone, S. R. Kinetics of C₂H reactions with hydrocarbons and nitriles in
18 the 104-296 K temperature range. *J. Phys. Chem. A* **2004**, *108*, 1746-1752.
19
20
21 (53) Laufer, A. H.; Fahr, A. Reactions and kinetics of unsaturated C₂ hydrocarbon radicals.
22
23
24
25
26
27
28
29 (54) Li, Y.; Liu, H. L.; Huang, X. R.; Wang, D. Q.; Sun, C. C. Theoretical study of the C(³P)
30 + trans-C₄H₈ reaction. *J. Phys. Chem. A* **2009**, *113*, 6800-6811.
31
32
33 (55) Miller, J. A.; Pilling, M. J.; Troe, E. Unravelling combustion mechanisms through a
34 quantitative understanding of elementary reactions. *Proc. Comb. Inst.* **2005**, *30*, 43-88.
35
36
37 (56) McEnally, C. S.; Pfefferle, L. D.; Atakan, B.; Kohse-Hoeinghaus, K. Studies of
38 aromatic hydrocarbon formation mechanisms in flames: Progress towards closing the fuel
39 gap. *Progress. Ener. Comb. Sci.* **2006**, *32*, 247-294.
40
41
42 (57) Hansen, N.; Klippenstein, S. J.; Taatjes, C. A.; Miller, J. A.; Wang, J.; Cool, T. A.;
43 Yang, B.; Yang, R.; Wei, L. X.; Huang, C. Q. *et al.* Identification and chemistry of C₄H₃ and
44
45
46
47
48
49
50 C₄H₅ isomers in fuel-rich flames. *J. Phys. Chem. A* **2006**, *110*, 3670-3678.
51
52 (58) Miller, J. A.; Melius, C. F. Kinetic and thermodynamic issues in the formation of
53 aromatic-compounds in flames of aliphatic fuels. *Combust. Flame* **1992**, *91*, 21-39.
54
55
56
57
58
59
60

- 1
2
3 (59) Melius, C. F.; Colvin, M. E.; Marinov, N. M.; Pitz, W. J.; Senkan, S. M. *Reaction*
4
5 *mechanisms in aromatic hydrocarbon formation involving the C₅H₅ cyclopentadienyl moiety*;
6
7 Combustion Institute: Pittsburgh, 1996.
8
9
10 (60) Miller, J. A. *Theory and modeling in combustion chemistry*; Combustion Institute:
11
12 Pittsburgh, 1996.
13
14 (61) Osborn, D. L.; Zou, P.; Johnsen, H.; Hayden, C. C.; Taatjes, C. A.; Knyazev, V. D.;
15
16 North, S. W.; Peterka, D. S.; Ahmed, M.; Leone, S. R. The multiplexed chemical kinetic
17
18 photoionization mass spectrometer: A new approach to isomer-resolved chemical kinetics.
19
20 *Rev. Sci. Instrum.* **2008**, *79*, 104103: 1-10.
21
22 (62) Taatjes, C. A.; Hansen, N.; Osborn, D. L.; Kohse-Hoeinghaus, K.; Cool, T. A.;
23
24 Westmoreland, P. R. "Imaging" combustion chemistry via multiplexed synchrotron-
25
26 photoionization mass spectrometry. *Phys. Chem. Chem. Phys.* **2008**, *10*, 20-34.
27
28
29 (63) Shannon, R. J.; Cossou, C.; Loison, J. C.; Caubet, P.; Balucani, N.; Seakins, P. W.;
30
31 Wakelam, V.; Hickson, K. M. The fast C(³P) + CH₃OH reaction as an efficient loss process
32
33 for gas-phase interstellar methanol. *RSC Advances* **2014**, *4*, 26342-26353.
34
35 (64) Vaghjiani, G. L. Kinetics of CH radicals with O₂: Evidence for CO chemiluminescence
36
37 in the gas phase reaction. *J. Chem. Phys.* **2003**, *119*, 5388-5396.
38
39
40 (65) Hickson, K. M.; Loison, J.-C.; Lique, F.; Klos, J. An experimental and theoretical
41
42 investigation of the C(¹D) + N₂ → C(³P) + N₂ quenching reaction at low temperature. *J. Phys.*
43
44 *Chem. A* **2016**, DOI 10.1021/acs.jpca.6b00480.
45
46 (66) Le Picard, S. D.; Honvault, P.; Bussery-Honvault, B.; Canosa, A.; Laube, S.; Launay, J.
47
48 M.; Rowe, B.; Chastaing, D.; Sims, I. R. Experimental and theoretical study of intramultiplet
49
50 transitions in collisions of C(³P) and Si(³P) with He. *J. Chem. Phys.* **2002**, *117*, 10109-10120.
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (67) Es-sebbar, E. T.; Benilan, Y.; Farooq, A. Temperature-dependent absorption cross-
4 section measurements of 1-butene (1-C₄H₈) in VUV and IR. *J. Quant. Spectrosc. Radiat.*
5 *Transfer* **2013**, *115*, 1-12.
6
7
8
9
10 (68) Barone, V.; Bloino, J.; Biczysko, M.; Santoro, F. Fully integrated approach to compute
11 vibrationally resolved optical spectra: From small molecules to macrosystems. *J. Chem.*
12 *Theo. Comp.* **2009**, *5*, 540-554.
13
14 (69) Simmie, J. M.; Somers, K. P. Benchmarking compound methods (CBS-QB3, CBS-
15 APNO, G3, G4, W1BD) against the active thermochemical tables: A litmus test for cost-
16 effective molecular formation enthalpies. *J. Phys. Chem. A* **2015**, *119*, 7235-7246.
17
18 (70) Ruzsicska, B. P.; Jodhan, A.; Choi, H. K. J.; Strausz, O. P.; Bell, T. N. Chemistry of
19 carbynes - Reaction of CF, CCl, and CBr with alkenes. *J. Am. Chem. Soc.* **1983**, *105*, 2489-
20 2490.
21
22 (71) Savee, J. D.; Welz, O.; Taatjes, C. A.; Osborn, D. L. New mechanistic insights to the
23 O(³P) + propene reaction from multiplexed photoionization mass spectrometry. *Phys. Chem.*
24 *Chem. Phys.* **2012**, *14*, 10410-10423.
25
26 (72) Keyser, L. F. High-pressure flow kinetics. A study of the OH + HCl reaction from 2 to
27 100 torr. *J. Phys. Chem.* **1984**, *88*, 4750-4758.
28
29 (73) Bergeat, A.; Calvo, T.; Dorthe, G.; Loison, J. C. Fast-flow study of the CH plus CH
30 reaction products. *J. Phys. Chem. A* **1999**, *103*, 6360-6365.
31
32 (74) Schulenburg, A. M.; Alcaraz, C.; Grassi, G.; Merkt, F. Rovibrational photoionization
33 dynamics of methyl and its isotopomers studied by high-resolution photoionization and
34 photoelectron spectroscopy. *J. Chem. Phys.* **2006**, *125*, 104310 1-10.
35
36 (75) Fleming, I. *Frontier orbitals and organic chemical reactions*; Wiley-Interscience West
37 Sussex, Engalnd, 2006.
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (76) Lang, M.; Holzmeier, F.; Hemberger, P.; Fischer, I. Threshold photoelectron spectra of
4 combustion relevant C₄H₅ and C₄H₇ isomers. *J. Phys. Chem. A* **2015**, *119*, 3995-4000.
5
6
7 (77) Savee, J. D.; Soorkia, S.; Welz, O.; Selby, T. M.; Taatjes, C. A.; Osborn, D. L. Absolute
8 photoionization cross-section of the propargyl radical. *J. Chem. Phys.* **2012**, *136*, 134307 1-
9 10.
10
11 (78) Ju, Y. G.; Sun, W. T. Plasma assisted combustion: Dynamics and chemistry. *Progress.*
12 *Ener. Comb. Sci.* **2015**, *48*, 21-83.
13
14 (79) Yang, B.; Li, Y. Y.; Wei, L. X.; Huang, C. Q.; Wang, J.; Tian, Z. Y.; Yang, R.; Sheng,
15 L. S.; Zhang, Y. W.; Qi, F. An experimental study of the premixed benzene/oxygen/argon
16 flame with tunable synchrotron photoionization. *Proc. Comb. Inst.* **2007**, *31*, 555-563.
17
18 (80) Henning, T.; Salama, F. Carbon - Carbon in the universe. *Science* **1998**, *282*, 2204-
19 2210.
20
21 (81) Phillips, T. G.; Huggins, P. J. Abundance of atomic carbon (C) in dense interstellar
22 clouds. *Astrophys. J.* **1981**, *251*, 533-540.
23
24 (82) Schilke, P.; Benford, D. J.; Hunter, T. R.; Lis, D. C.; Phillips, T. G. A line survey of
25 Orion-KL from 607 to 725 GHz. *Astrophys. J. Supp. Series* **2001**, *132*, 281-364.
26
27 (83) Stark, R.; Wesselius, P. R.; vanDishoeck, E. F.; Laureijs, R. J. Neutral carbon in
28 translucent regions of the dark cloud L 183. *Astron. Astrophys.* **1996**, *311*, 282-290.
29
30 (84) Loison, J. C.; Wakelam, V.; Hickson, K. M.; Bergeat, A.; Mereau, R. The gas-phase
31 chemistry of carbon chains in dark cloud chemical models. *Mon. Not. R. Astron. Soc.* **2014**,
32 *437*, 930-945.
33
34 (85) Vuitton, V.; Yelle, R. V.; Lavvas, P.; Klippenstein, S. J. Rapid association reactions at
35 low pressure: impact on the formation of hydrocarbons in Titan. *Astrophys. J.* **2012**, *744*, 1-7.
36
37 (86) Krasnopolsky, V. A. Chemical composition of Titan's atmosphere and ionosphere:
38 Observations and the photochemical model. *Icarus* **2014**, *236*, 83-91.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (87) Dobrijevic, M.; Hebrard, E.; Loison, J. C.; Hickson, K. M. Coupling of oxygen,
4 nitrogen, and hydrocarbon species in the photochemistry of Titan's atmosphere. *Icarus* **2014**,
5 228, 324-346.
6
7
8
9
10 (88) Dobrijevic, M.; Loison, J. C.; Hickson, K. M.; Gronoff, G. 1D-coupled photochemical
11 model of neutrals, cations and anions in the atmosphere of Titan. *Icarus* **2016**, 268, 313-339.
12
13 (89) Woon, D. E.; Park, J. Y. Modeling chemical growth processes in Titan's atmosphere 2.
14 Theoretical study of reactions between C₂H and ethene, propene, 1-butene, 2-butene,
15 isobutene, trimethylethene, and tetramethylethene. *Icarus* **2009**, 202, 642-655.
16
17
18
19
20 (90) Haider, N.; Husain, D. The collisional behavior of ground-state atomic carbon,
21 C(2p²(³P_J)), with unsaturated cyclic-compounds studied by time-resolved atomic resonance-
22 absorption spectroscopy in the vacuum ultra-violet *Ber. Bunsen-Ges. Phys. Chem. Chem.*
23 *Phys.* **1993**, 97, 571-577.
24
25
26
27
28
29 (91) Chastaing, D.; Le Picard, S. D.; Sims, I. R.; Smith, I. W. M. Rate coefficients for the
30 reactions of C(³P_J) atoms with C₂H₂, C₂H₄, CH₃C=CH and H₂C=C=CH₂ at temperatures
31 down to 15 K. *Astron. Astrophys.* **2001**, 365, 241-247.
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

TOC Graphic

