Consumption and hydrocarbon growth processes in a 2-methyl-2-butene flame

Lena Ruwe¹, Kai Moshhammer^{2*}, Nils Hansen², Katharina Kohse-Höinghaus^{1*}

Abstract

This paper is concerned with the investigation of the chemical structure of a low-pressure, fuel-rich ($\phi=1.8$) premixed laminar flame fueled with 2-methyl-2-butene employing flame-sampling molecular-beam mass spectrometry with vacuum-ultraviolet single-photon ionization. Partially isomer-resolved mole fraction profiles can be explained by a decomposition scheme based on hydrogen abstraction and addition reactions. The presence of 9 allylic C—H bonds compared to only one vinylic C—H bond is the key feature that governs the fuel consumption and subsequent hydrocarbon growth reactions. Compared to other alkenes, including e.g., 1-butene, 2-butene, and *iso*-butene [Schenk *et al.*, Combust. Flame. 160 (2013) 487–503], 2-methyl-2-butene shows a remarkable tendency to form soot precursor molecules such as toluene. In particular, experimental evidence is provided here that toluene, *o*-xylene, and styrene can be a starting point for PAH formation, thus serving as *first aromatic rings* besides benzene. The formation of toluene, *o*-xylene, and styrene can be traced back to the reactions of the resonantly stabilized C_4H_5 [$\bullet CH_2-C\equiv C-CH_3$ and $CH_2=CH-\bullet C=CH_2$] radicals and the C_5H_7 [$CH_2=C(CH_3)-\bullet C=CH_2$] radicals that are readily formed

1 through fuel-specific decomposition channels. Our experimental data in form of mole fraction
2 profiles as a function of height above the burner for a mass range from 2 to 210 u can serve as
3 reliable validation targets for model development. A preliminary comparison to the model of
4 Westbrook *et al.* [Westbrook *et al.*, J. Phys. Chem. A 119 (2015) 7462–7480] that was optimized to
5 capture ignition delay times and the low-temperature oxidation regime, shows promising elements
6 already for the initial fuel consumption.
7
8
9
10
11
12

13 **Key words**

14 2-Methyl-2-butene; Alkene combustion; Allylic bond; Premixed laminar flame; Molecular-beam mass
15 spectrometry; Photoionization
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
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1. Introduction

2-Methyl-2-butene [(CH₃)₂C=CHCH₃, C₅H₁₀, 2M2B] is an unsaturated branched hydrocarbon that has not been studied extensively by the combustion community, although it is characterized by some interesting chemical features. It is a branched alkene with a C=C double-bond in the center and a total of one vinylic and 9 allylic C—H bonds. Only recently, Westbrook *et al.* [1] studied the low-temperature oxidation regime in a combined experimental and modeling paper by providing ignition delay times behind reflected shock waves, species concentration measurements in a jet-stirred reactor, and a detailed chemical kinetic reaction mechanism. With a research octane number (RON) of 97.3 and a motored octane number (MON) of 84.7, 2M2B is a promising fuel for engine applications with a strong octane sensitivity [1,2]. The present work complements the earlier study [1] by providing detailed chemical insights into fuel consumption and hydrocarbon growth pathways at high temperatures in premixed flames of 2M2B.

To understand the combustion chemistry of 2M2B, it is necessary to recognize the importance of allylic bonds. Generally speaking, the C—H or C—C bonds adjacent to a C=C double-bond are called allylic because breaking them results in a resonance-stabilized allylic (CH₂=CH—•CH₂ ↔ •CH₂—CH=CH₂) system. As a consequence, allylic bonds are systematically weaker than their alkylic and vinylic counterparts as summarized in Table 1. Note that bond dissociation energies differ for primary, secondary, tertiary, and quaternary central atoms and that these differences are not included in Table 1. For further details please refer to Ref. [3]. It can then be assumed that in flames, fuel consumption steps that are initiated by H-atom abstraction reactions starting from the allylic C—H bonds (if present), are more likely than the equivalent abstraction reactions from alkylic or vinylic sites.

Table 1: Typical bond dissociation energies (in kcal/mol) of alkylic, vinylic, and allylic C—H and C—C bonds of organic molecules. Energies are taken from Ref. [3].

	Alkylic	vinylic	allylic
C—H	96.5-104.9	110.7	88.8
C—C	78.6-90.1	97.8-116.0	62.7-87.3

The high-temperature oxidation of many fuels with allylic C—H and C—C bonds has been investigated before, and studies on large alkenes have attracted considerable interest [4–19]. In particular, experimental work has been provided, for example, in hydrocarbon flames fueled by propene (the smallest molecule possessing an allylic C-H bond) [20–23]; 1-, 2-, and *iso*-butene [24]; 1,3-butadiene [25,26]; 1,3-pentadiene [27]; 1-pentene [12]; hexenes [13–16]; hexadienes [17]; and cyclopentene [11,18–20]. Flame chemistry modeling of the C₃ and C₄ flames [20,23–25] confirmed that fuel consumption is indeed initiated by H-atom abstractions to form the resonantly stabilized, allylic fuel radicals. However, large linear molecules ($\geq C_4$) that possess an allylic C—H bond, always feature an allylic C—C bond, and it is conceivable that fuel consumption can be initiated also by unimolecular dissociation of this bond which is even weaker than the allylic C—H bond. This reaction, which gives immediate access to the C₃ chemistry of the allyl radical, was found to contribute in the 1-butene flame [24] and to dominate in the 1-hexene flames [14,15]. In Ref. [13] it was speculated that the dissociation of the allylic C—C bond contributes largely to the consumption of 3,3-dimethyl-1-butene, a fuel that is characterized by three vinylic C—H and three allylic C—C bonds. 2M2B does not contain any allylic C—C bond and is instead characterized by three vinylic C—C bonds that are considerably more stable than their allylic counterparts.

To contribute to the understanding of the reaction pathways resulting from the unique molecular structure of this interesting fuel, this paper concerns initial fuel consumption steps in premixed low-pressure flames of 2-methyl-2-butene. Based on the above discussion it seems likely that under the conditions investigated here, 2M2B is consumed largely by H-atom abstraction reactions to form the respective allylic C₅H₉ fuel radicals. Unimolecular breaking of an allylic C—H

1 bond has not yet been found to be an important pathway for fuel consumption. Molecules with
2 allylic C—H and/or C—C bonds also possess a C=C double-bond, and H-addition reactions can,
3 especially in the hydrogen-rich environment of a rich low-pressure flame, contribute towards fuel
4 consumption. A special emphasis in this paper is placed on the initial fuel consumption pathways,
5 and it will be discussed how the C_5H_{11} and the resonantly stabilized (allylic) C_5H_9 radical
6 intermediates impact the formation of the commonly considered precursors for aromatic species. As
7 pointed out by Hansen *et al.* [28], the first initial fuel consumption steps are critically important to
8 understand the influence of various benzene formation pathways. Our experimental results in form
9 of species identification and mole fraction profiles are then compared to modeling results performed
10 with the sole existing model of Westbrook *et al.* [1], that was constructed to explain data from jet-
11 stirred reactor and shock-tube experiments. An improvement of this combustion chemistry model
12 for 2M2B would provide a useful base-mechanism for the development of a kinetic model for
13 branched alkenes.

34 2. Experimental procedure and data evaluation

35 In this paper, new experimental data in form of isomer-resolved species mole fraction profiles and
36 photoionization efficiency curves (PIE) of a premixed, laminar low-pressure flame fueled by
37 2-methyl-2-butene are presented. The flame was stabilized on a 6 cm diameter McKenna burner at
38 40 mbar and had a composition of 2M2B/oxygen/argon (14.5%/60.5%/25%) resulting in a
39 stoichiometry of $\phi=1.8$ and a mass flow rate through the burner surface of $0.00312\text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}$. The
40 gas flows were controlled with calibrated mass flow controllers (MKS) with a precision of $\pm 0.5\%$. The
41 2-methyl-2-butene (with a purity of $\geq 99\%$) was purchased from Sigma-Aldrich and the gases (purity
42 of 99.999%) from Praxair. All chemicals were used without further purification. Regarding its vapor
43 pressure of 965.25 mbar at 37.8°C , it was not necessary to use an evaporation system for 2M2B and
44 instead, the gaseous phase in the container was used directly.

1 The experiments were carried out at the Chemical Dynamics Beamline at the Advanced Light
2 Source (ALS) at the Lawrence Berkeley National Laboratory (LBNL). The isomer-resolved chemical
3 compositions were determined by flame-sampling molecular-beam mass spectrometry employing
4 single-photon ionization (PI-MBMS) by tunable synchrotron-generated vacuum-ultraviolet (VUV)
5 radiation. The flame-sampling photoionization mass spectrometer used for this study has been
6 described in detail elsewhere [29–31]. The instrument consists of a low-pressure flame chamber, a
7 differentially pumped vacuum system for flame sampling, and a time-of-flight (TOF) mass
8 spectrometer with a ~ 1 ppm detection limit. The flame gases were sampled via a quartz sampling
9 cone featuring an orifice of 500 μm at the tip. A pressure reduction from 40 mbar in the flame
10 chamber to $\sim 10^{-4}$ mbar in the first pumping stage interrupted further reactions and led to the
11 formation of a molecular beam which was guided through a nickel skimmer, located 23 mm
12 downstream, into the ionization region (10^{-6} mbar). Here it was crossed with tunable VUV light that
13 is characterized by an energy resolution of $\Delta E = 0.05$ eV. The different ions were mass-selected by
14 TOF mass spectrometry and detected using a multi-channel plate. The MBMS system provides a high
15 mass resolution of $m/\Delta m \approx 4000$ allowing the separation of the C/H/O elemental composition in the
16 investigated mass range from 2 to 210 u.
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36

37 The instrument is configured to collect data in two modes: First, the photon energy is fixed
38 and the position of the burner that is mounted on a translational stage is moved. By varying the
39 distance between the burner and the quartz sampling cone, mole fraction profiles as a function of
40 height above the burner (h) were obtained along the centerline of the flame. Different fixed soft
41 ionization energies of 8.7 eV, 9.0 eV, 9.2 eV, 9.5 eV, 9.7 eV, 9.9 eV, 10.0 eV, 10.5 eV, 10.6 eV,
42 11.0 eV, 11.5 eV, 12.3 eV, 13.2 eV, 14.35 eV, 15.4 eV, and 16.65 eV were used for the analysis of the
43 flame. The second mode is a key feature of the instrument and enables the recording of
44 photoionization efficiency (PIE) curves by scanning the photon energy while holding the position of
45 the burner fixed. It allows the detection of isomer-specific ionization thresholds for a given mass-to-
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

charge (m/z) ratio and thus enables the identification of isomeric components. In this study, the PIE curves were recorded tuning the energy over a range between 8.5 eV and 11.0 eV at $h = 4.75$ mm.

2.1 Data analysis

The data analysis procedure for MBMS flame data is widely described in Refs. [24,32–34]. Thus, only the key aspects of the data evaluation are reported here.

The integrated ion signal S_i of a species i is linked to its mole fraction x_i with the following relationship:

$$S_i = x_i \cdot \sigma_i(E) \cdot D(M_i) \cdot \varphi \cdot c \cdot FKT \quad (1)$$

Here, $\sigma_i(E)$ is the tabulated photoionization cross section at the photon energy E , $D(M_i)$ the mass discrimination factor for species i , φ the photon current, c an instrument parameter and FKT a temperature- and thus position-dependent sampling function. The photoionization cross sections for quantified species as well as the respective literature references are provided in Table S1 in the Supplemental Material. Except from the photoionization cross section $\sigma_i(E)$, all variables are individually determined by the PI-MBMS experiment. The photon current φ was recorded during the measurements by a calibrated photodiode. Mass discrimination factors were determined using the method described in Ref. [29] (see Fig. S1 in the Supplemental Material). The product $c \cdot FKT$ was obtained from Eq. (1):

$$c \cdot FKT = \frac{S_i}{x_i \cdot \sigma_i(E) \cdot D(M_i) \cdot \varphi} \quad (2)$$

Assuming that the instrument parameter c was constant for all scans, the product $c \cdot FKT$ was obtained for each position in the flame using the argon signal (measured at 16.65 eV) and its respective mole fraction adapted from the major species calculation (see below) using Eq. (2). Under identical experimental conditions, Eq. (1) can be simplified using a reference species R :

$$\frac{S_i}{S_R} = \frac{x_i \cdot \sigma_i(E) \cdot D(M_i) \cdot \varphi \cdot c \cdot FKT}{x_R \cdot \sigma_R(E) \cdot D(M_R) \cdot \varphi \cdot c \cdot FKT} = \frac{x_i}{x_R} \cdot k_{i/R}(E) \quad (3)$$

Here, $k_{i/R}(E)$ is a calibration factor that combines all species-dependent parameters and that is related to the ionization energy.

The major species, namely 2M2B, H_2 , H_2O , CO, O_2 , Ar, and CO_2 , were calculated from Eq. (3). To avoid fragmentation, signals were taken from a scan close to the ionization energy (IE) of the respective species, i.e., 10.0 eV for 2M2B, 12.3 eV for O_2 , 15.4 eV for H_2 , 13.2 eV for H_2O , 14.35 eV for CO and CO_2 , and 16.65 eV for Ar. Based on the elemental C, H and O balances and on a single cold-gas calibration measurement, the required calibration factors $k_{i/Ar}$ were determined using an internal calibration strategy [24,33]. To provide the local argon mole fraction for each flame position, the balance between the sum of all major species and unity was calculated. With known argon mole fraction, intermediate species concentrations were accessible via Eq. (1) in all situations where a photoionization cross section was available. Whenever necessary, a correction for the contribution of ^{13}C isotopes to the ion signal was performed.

A detailed discussion of the associated errors can be found in Ref. [35]. Briefly, the uncertainties for the major species are as low as 10-20%. For the intermediate species mole fraction profiles, the uncertainties depend mainly on the quality of the measured or estimated photoionization cross sections [36] used for the evaluation. The uncertainties were determined to be 30-40% for species using measured cross sections in the data evaluation, and they can be as large as a factor of 2-4 if estimated cross sections were used. For species with concentrations near the detection limit (~ 1 ppm), quantitative values must be regarded with caution, because the signal-to-noise ratio is low and thus errors can be significantly larger.

3. Results

In this section experimental mole fraction profiles of selected species are presented to demonstrate the combustion chemistry of 2-methyl-2-butene that is in particular governed by the presence of vinylic and allylic C—H bonds resulting in specific hydrocarbon growth reactions.

To provide an overview of the combustion process of 2-methyl-2-butene, we begin the discussion by presenting a mass spectrum that was recorded in the reaction zone of the flame at $h = 4.5$ mm and a photon energy of 10.5 eV. This spectrum, presented in Fig. 1, gives a general overview of signals at a variety of mass-to-charge ratios detected during the experiment. As can be seen from the spectrum, besides signals with lower mass-to-charge ratios than the fuel ($m/z = 70.078$ u), a significant number of signals with higher masses were observed (see enlarged section of Fig. 1), indicating a remarkable tendency of the fuel to form polycyclic aromatic hydrocarbons (PAHs).

Figure 1: Overview mass spectrum in the mass range of $m/z = 2-210$ u recorded in the reaction zone of a 2-methyl-2-butene flame at $h = 4.5$ mm and PE = 10.5 eV. The figure section enlarges the mass range of $m/z = 120-210$ u.

With the aim to further clarify this PAH formation tendency of 2M2B, the following discussion focuses on the role of the chemical fuel structure and how it impacts the formation of soot precursors.

3.1 Fuel consumption via H-atom abstraction

It is well understood that under low-pressure flame conditions, fuel destruction is initiated mainly by radical-initiated H-atom abstraction reactions and followed by subsequent β -scissions. This reaction pattern has been demonstrated in many other flame studies of different fuels [24,30,34,37–41].

Possible reaction pathways for the consumption of 2M2B are shown in Fig. 2. For clarification of the nomenclature that is introduced in Fig. 2 and further below in Fig. 4, Table S2 in the Supplemental Material provides the chemical formula, abbreviation, species name, and the chemical structure of all species discussed in this paper.

For 2M2B, H-atom abstraction reactions can take place at one of the allylic (1, 4, and 5) carbon atoms or at the vinylic (3) position (see Fig. 2). As already mentioned before, the allylic C—H bond has an energy of ~ 88.8 kcal/mol which is about 22 kcal/mol weaker than the vinylic C—H bond (110.7 kcal/mol), and thus the main consumption of the fuel should occur by H-atom abstraction from the carbon positions 1, 4 or 5.

The H-atom abstraction from the carbon position 4 leads to the formation of the allylic radical C_5H_9-2 . Note that the two related structures in Fig. 2 are not in equilibrium, but they are resonance structures of the allylic radical. The “true” structure of this allylic radical is a hybrid of the two resonance structures and its charge is delocalized. However, visualization of the two resonance structures makes it easier to discuss the subsequent possible β -scissions.

Figure 2: Possible reaction pathways for the consumption of 2-methyl-2-butene initiated by H-atom abstraction in a low-pressure, fuel-rich flame ($\phi = 1.8$).

In this context, the radical C_5H_9-2 is special because the two resonance structures only allow β -scissions that include another C—H bond breakage. As can be seen from Fig. 2, two different C_5H_8 isomers, namely 3-methyl-1,2-butadiene (C_5H_8-1) and 2-methyl-1,3-butadiene (C_5H_8-2), can be formed through further H-atom loss in β -position. C_5H_8-2 is also a decomposition product from the two alternative fuel radicals C_5H_9-3 and C_5H_9-4 which are results from H-atom abstraction reactions at the fuel's carbon positions 1 and 5. These two radicals also possess allylic properties and are resonantly stabilized. In contrast to the C_5H_9-2 radical, they can undergo subsequent β -scissions by both C—H and C—C bond breakage resulting in the loss of an H-atom or a CH_3 -group and the formation of 2-methyl-1,3-butadiene (C_5H_8-2), as mentioned above, or 1,2-butadiene (C_4H_6-2), respectively.

Figure 3: Flame-sampled PIE curve of (a) $m/z = 54.047$ u (C_4H_6) and (b) $m/z = 68.063$ u (C_5H_8). Closed symbols (connected to guide the eye) represent the measured signal and open symbols show the scaled photoionization cross section of the respective species. The obtained sum signal is shown as a dotted red line. Isomer-resolved mole fraction profiles of (c) C_4H_6 (C_4H_6 -1: 2-butyne, C_4H_6 -3: 1,3-butadiene and C_4H_6 -4: 1-butyne) and (d) C_5H_8 (C_5H_8 -1: 3-methyl-1,2-butadiene, C_5H_8 -2: 2-methyl-1,3-butadiene and C_5H_8 -3: 1,3-pentadiene). Note, that for C_4H_6 -1, C_4H_6 -3, C_4H_6 -4, C_5H_8 -1, and C_5H_8 -3, mole fractions were multiplied by factors of 15, 3, 15, 5, and 10 and the experimental data are fitted by dotted lines (B-spline) for better visualization.

Figure 3 (a) contains the flame-sampled photoionization efficiency (PIE) curve for $m/z = 54.047$ u which can be assigned to C_4H_6 . As can be seen from the PIE curve that was measured at $h = 4.50$ mm, 1,3-butadiene (C_4H_6 -3, IE = 9.072 eV), 1-butyne (C_4H_6 -4, IE = 10.18 eV), and 2-butyne (C_4H_6 -1, IE = 9.58 eV) contribute to the measured signal at $m/z = 54.047$ u and were identified clearly in the experiment by the respective trends in their photoionization cross sections. The experimental findings appear somewhat surprising because 1,2-butadiene (C_4H_6 -2, IE = 9.23 eV [42]) is expected to be one of the major intermediates in the fuel consumption (see Fig. 2), but the attempts to include the energy-dependent ionization cross section curve of 1,2-butadiene [43] have unexpectedly resulted in representations of the flame-sampled PIE signal with poorer agreement. This observation is supported by evaluating the 1,3-butadiene mole fraction profile from two independent scans at 9.2 eV that excludes contributions from 1,2-butadiene due to its ionization threshold above this energy, and at 9.5 eV where both species would contribute to the measured signal. The evaluation from the two scans results in the same peak mole fractions of about 2.8×10^{-3} and confirms the absence of 1,2-butadiene. This observation is consistent with the results from the analysis of the PIE curve.

One possible explanation might be a fast isomerization from 1,2-butadiene to 1,3-butadiene. Kern *et al.* [44] investigated the thermal decomposition of 1,2-butadiene behind reflected shock waves by time-of-flight mass spectrometry. In order to successfully model the obtained species profiles they had to include the isomerization from 1,2-butadiene to 1,3-butadiene and determined the energy barrier to be 67.7 kcal/mol. Similar values were found by Hidaka *et al.* [45] who analyzed the decomposition of 1,2-butadiene behind reflected shock waves with gas chromatography. They proposed that the isomerization of 1,2-butadiene to the thermodynamically more stable 1,3-butadiene includes two transition states (TS) with energy barriers of 63.3 kcal/mol (TS1) and 61.7 kcal/mol (TS2), respectively. These energy barriers are lower than the provided energy of 1,2-butadiene molecule in the flame, which can be roughly estimated – based on the equipartition theorem – to be about 90 kcal/mol (at 1500 K); the proposed isomerization reaction is thus a

conceivable step in the flame chemistry of 2M2B. Additionally, it is well known that radical-catalyzed reactions have significantly lower energy barriers. Several mechanisms (for example Ref. [1,46]) include an H-atom-catalyzed isomerization reaction from 1,2-butadiene (C_4H_6-2 in the reaction scheme, Fig. 2) to 1,3-butadiene (C_4H_6-3) [R(1)], and its energy barrier is estimated to be around 4 kcal/mol:

The H-atom-catalyzed isomerization reaction of 1,2-butadiene to 1,3-butadiene is, however, not yet well understood and its potential contribution remains unclear. Further plausible reasons for the observed absence of 1,2-butadiene could result from its molecular structure with three C—H bonds and one C—C bond which have partial allylic properties. Although adjacent to a double-bond, the respective radicals resulting from their cleavage are resonantly stabilized by the second double-bond in the molecule. For allene ($CH_2=C=CH_2$) which has a similar chemical structure to 1,2-butadiene ($CH_2=C=CH-CH_3$), the dissociation energy of the C—H bond was determined to be 88.7 kcal/mol [47], in the range of a classical allylic bond. Assuming that the bond dissociation energies of the respective single bonds in 1,2-butadiene are similar to that of allene, it might be possible that fast reactions to the resonance-stabilized C_4H_5 and C_3H_3 radicals occur, leading to a short lifetime that may preclude the experimental detection of 1,2-butadiene. However, given the hydrogen-atom-rich environment in the low-pressure flame, we consider the isomerization reaction to 1,3-butadiene (R1) more probable.

The mole fraction profile of 1,3-butadiene (C_4H_6-3), depicted in Fig. 3 (c), peaks at 4.25 mm with a value of 2.8×10^{-3} which is one order of magnitude larger than the peak mole fraction of 2-butyne (C_4H_6-1 , 2.8×10^{-4}) at the same height. Both intermediates are thus formed in the flame at a similar reaction time. Under the assumption that the C_5H_8 isomers are early fuel consumption products, the identical peak position of the C_5H_8 and C_4H_6 isomers [see Fig. 3 (d)] suggests that the profiles of C_4H_6-1 and C_4H_6-3 might be dominated by similar early reaction steps, consistent with the reaction scheme in Fig. 2. The large difference in their maximum mole fraction values can then be

easily explained by the respective importance of their precursor radicals (assuming that an isomerization reaction from 1,2-butadiene to 1,3-butadiene takes place): While the formation of C_4H_6-3 results from one of the allylic fuel radicals C_5H_9-3 or C_5H_9-4 , C_4H_6-1 is formed via the vinylic fuel radical C_5H_9-1 which should be present in significantly lower amounts due to the higher stability of the vinylic C—H bond in the fuel molecule (compare Table 1). According to Fig. 2, 1-butyne [C_4H_6-4 in Fig. 3 (c)] is not a fuel consumption product, thus its small concentration is likely a consequence of molecular growth reactions.

Figure 3 (b) provides the flame-sampled photoionization efficiency curve of $m/z = 68.063$ u (C_5H_8), which reveals contributions of 1,3-pentadiene, 3-methyl-1,2-butadiene (C_5H_8-1 in Fig. 2), and 2-methyl-1,3-butadiene (C_5H_8-2). The latter isomer is a major product of the fuel consumption because it can be formed by β -scissions from the three resonantly stabilized fuel radicals C_5H_9-2 , C_5H_9-3 , and C_5H_9-4 . In analogy to the H-atom-catalyzed transformation of 1,2-butadiene into 1,3-butadiene, 2-methyl-1,3-butadiene (C_5H_8-2) can be also formed by an H-atom-catalyzed isomerization from 3-methyl-1,2-butadiene (C_5H_8-1). The mole fraction profile of 2-methyl-1,3-butadiene (C_5H_8-2) is depicted in Fig. 3 (d) together with those of 3-methyl-1,2-butadiene (C_5H_8-1) as well as 1,3-pentadiene. The mole fraction profiles of those species were calculated using the respective percentages that were determined by weighted contributions from photoionization cross sections of each isomer (see Fig. 3 (b)). Indeed, the peak mole fraction of C_5H_8-2 (9.2×10^{-3}) is about a factor of 9 larger than that of C_5H_8-1 (1.3×10^{-3}) which is only formed through H-atom loss in β -position from the fuel radical C_5H_9-2 or by β -scission of the energetically unfavorable vinylic fuel radical C_5H_9-1 . Please note that in the absence of accurate values in the literature, an estimated photoionization cross section for 2-methyl-1,3-butadiene, originating from Ref. [48], was used for its identification in Fig. 3 (b) and in the determination of its mole fraction, thus the error can be up to a factor of 4. However, this uncertainty will not change our statements above. According to the proposed reaction scheme, 1,3-pentadiene [C_5H_8-3 in Fig. 3 (d)]

is not a fuel consumption product and therefore builds up only to small concentrations and shall not be further discussed here.

In summary, the observed mole fraction profiles are consistent with the consumption of 2M2B initiated by H-atom abstraction and subsequent β -scission reactions. This simple reaction sequence favorably leads to the formation of the observed cleavage products including the radical species CH_3 and H as well as the stable intermediates 2-butyne (C_4H_6 -1), 1,3-butadiene (C_4H_6 -2), 3-methyl-1,2-butadiene (C_5H_8 -1), and 2-methyl-1,3-butadiene (C_5H_8 -2).

These stable intermediates can decompose further via another H-atom abstraction reaction to the radicals C_4H_5 -1, C_4H_5 -2, C_5H_7 -1, and C_5H_7 -2, all depicted in Fig. 2. With the exception of C_5H_7 -1, these radicals have a chemical structure that enables them to serve as a PAH and soot precursor. The radical C_5H_7 -2 can decompose further via the breakage of its C—C single-bond in β -position forming allene ($\text{CH}_2=\text{C}=\text{CH}_2$) and the vinyl radical (C_2H_3), opening another pathway for the formation of soot precursors. In view of their contribution to the PAH formation, these species as well as the mentioned radicals C_4H_5 -1, C_4H_5 -2, and C_5H_7 -1 will be discussed in more detail in Section 3.3.

3.2 Fuel consumption via H-atom addition reactions

When a C=C double-bond is present in the fuel molecule, H-atom addition reactions should also be considered [40]. The energy barrier for the H-atom addition to ethylene was reported to be 8 kcal/mol [49], which is below the energy barrier for the initial H-atom abstraction reaction induced by O_2 [50] and can thus happen already at lower temperatures. Therefore, H-atom addition is expected to proceed at lower heights above the burner where flame temperatures are relatively low and H-atoms are present through back-diffusion. However, the overall net production of these addition products is predicted to be small because of the backwards reaction at higher temperature [40].

Assuming that the respective energy barrier of the H-atom addition reaction for 2M2B is similar to that of ethylene, this type of reaction should also be considered as possible fuel

consumption pathway for 2M2B. Figure 4 shows conceivable reaction pathways containing initial H-atom addition reactions leading to the isomeric radicals C_5H_{11-1} and C_5H_{11-2} . Due to the branched molecular structure of 2M2B, the resulting C_5H_{11-1} radical is a tertiary stabilized radical and should thus be more stable than the alternatively formed C_5H_{11-2} radical, which only includes two stabilizing alkyl groups. Addition reactions are thus to be expected to proceed mostly via the C_5H_{11-1} radical.

Figure 4: Possible reaction pathways for the consumption of 2-methyl-2-butene initiated by H-atom addition reactions in a low-pressure, fuel-rich flame ($\phi = 1.8$).

Figure 5 (a) presents the measured relative species profiles of C_5H_{10} (recorded at 8.7 eV), C_5H_{11} (9.0 eV) corrected for contributions from the ^{13}C isotope of C_5H_{10} , and of C_5H_9 (8.7 eV). The C_5H_{10} and C_5H_9 signal can easily be assigned to the fuel and the fuel radical, respectively. The peak position of the C_5H_{11} profile ($h = 0.75$ mm) which is close to the burner surface and detected at lower height than the peak position of C_5H_9 ($h = 3.5$ mm), adds confidence to the assignment of the $m/z = 71.086$ u signal to the H-adduct intermediate C_5H_{11} , confirming that H-atom addition reactions to the fuel plays a role in the combustion of 2M2B. Unfortunately, photoionization cross sections are absent for the proposed C_5H_{11} radicals and thus their identification and quantification would not be reliable.

Both C_5H_{11} isomers can undergo several further β -scission reactions. By H-atom loss from C_5H_{11-1} , two possible C_5H_{10} species can be formed of which one is the fuel and the other 2-methyl-1-butene (C_5H_{10-1} , IE = 9.12 eV). Additionally, the breakage of the C—C single bond in

1 β -position leads to the formation of *iso*-butene (C_4H_8 -1, IE = 9.22 eV). β -Scissions of the other C_5H_{11}
2 radical (C_5H_{11} -2) forms 3-methyl-1-butene (C_5H_{10} -2, IE = 9.52 eV) and also 2M2B through breakage of
3 the respective C—H bonds, or the C_4H_8 conformers *trans*- (C_4H_8 -2, IE = 9.10 eV) and *cis*-2-butene
4 (C_4H_8 -3, IE = 9.11 eV) through CH_3 cleavage. Note that the latter conformers are not distinguishable
5 in the mass spectra due to their close ionization thresholds and were therefore treated in the data
6 evaluation as *trans*-2-butene. The different resulting C_5H_{10} intermediates cannot be reliably
7 separated in the experiment because their ionization thresholds are all above the fuel's IE, and thus
8 the signal at $m/z = 70.078$ u is always overwhelmed by contributions from the fuel. It is thus not
9 possible to identify contributions from C_5H_{10} as an intermediate. However, the breakage of the
10 alkylic C—C bond in the precursor C_5H_{11} radicals is expected to be more prominent than the scission
11 of their alkylic C—H bond due to their different dissociation energies (see Table 1) and thus C_4H_8 -1
12 and C_4H_8 -2 should be preferably formed compared to the C_5H_{10} isomers. The ratio between the
13 decomposition products C_4H_8 -2 and C_4H_8 -1 can provide an idea of the branching fraction of the C_5H_{11}
14 radicals.
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
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure 5: (a) Species profiles of C_5H_{10} , C_5H_{11} and C_5H_9 . (b) Mole fraction profiles of the C_4H_8 isomers 1-butene, *trans*-2-butene and *iso*-butene. For better visualization, the experimental data are fitted by dotted lines (B-spline). Note that the 1-butene mole fraction is multiplied by a factor of 5 for better visualization.

Figure 5 (b) shows the mole fraction profiles of the detected C_4H_8 isomers, namely 1-butene, 2-butene (C_4H_8 -2, analyzed as *trans*-2-butene) and *iso*-butene (C_4H_8 -1). The ratio between the maximum mole fractions of C_4H_8 -2 (2.3×10^{-3}) and C_4H_8 -1 (3.2×10^{-3}) was determined to be 0.7 confirming our statement that the C_5H_{11} -1 radical is thermodynamically more stable than C_5H_{11} -2 and that the H-atom addition to the fuel mostly proceeds via the more stable radical. The noticeably lower concentration of 1-butene (3.2×10^{-4}), which is about one order of magnitude lower than for 2-butene and *iso*-butene, shows that this isomer probably results from reactions that are different from the anticipated fuel consumption pathways.

1 In summary, the high concentrations of 2-butene and *iso*-butene illustrate that H-atom
2 addition reactions play an important role in the fuel's flame chemistry under our conditions. As will
3
4 be discussed in the next section, 2-butene as well as *iso*-butene can further decompose forming
5
6 important PAH and soot precursors.
7
8
9

10 11 12 3.3 Formation of PAH and soot precursors 13

14 In view of the remarkable tendency of 2M2B to form PAHs, the role of the fuel-specific consumption
15 reactions in hydrocarbon growth processes will be discussed in this section. In general, soot
16 formation is assumed to start with the formation of small aromatic rings. Species that are commonly
17
18 accepted to be involved in aromatics formation [25,51] are C_2H_2 (acetylene) and the radical species
19
20 CH_3 (methyl), C_3H_3 (propargyl), C_3H_5 (allyl), C_4H_5 (but-2-yn-1-yl and *iso*- C_4H_5), and C_5H_5
21
22 (cyclopentadienyl). Their mole fraction profiles in the present flame are depicted in Fig. 6. As shown
23
24 in Fig. 2, methyl, but-2-yn-1-yl, and *iso*- C_4H_5 radicals are readily formed through the H-atom-
25
26 abstraction-initiated fuel consumption. It has been argued [28] that these initial steps are critically
27
28 important aromatics formation pathways.
29
30
31
32
33
34

35 Specifically, the addition of *iso*- C_4H_5 ($CH_2=CH-C=CH_2$, C_4H_5 -2 in Fig. 2) to C_2H_2 forms
36
37 benzene, the simplest aromatic species and an important soot precursor. Fulvene ($cyC_5H_4=CH_2$) is a
38
39 main product of this reaction and thus represents a key intermediate in the overall benzene
40
41 formation chemistry [52,53]. It should be pointed out that the importance of *iso*- C_4H_5 towards
42
43 benzene formation is limited by hydrogen-assisted decomposition into methyl (CH_3) and propargyl
44
45 (C_3H_3) [25]. Typically, the reaction of $C_3H_3 + C_3H_3$ is considered to dominate the benzene formation.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure 6: Experimental mole fraction profiles of (a) CH_3 (methyl), (b) C_2H_2 (acetylene), (c) C_3H_3 (propargyl), (d) C_3H_5 (allyl), (e) C_4H_5 (but-2-yn-1-yl and *i*- C_4H_5), and (f) C_5H_5 (cyclopentadienyl). For better visualization, the experimental data are fitted by dotted lines (B-spline) and for CH_3 and C_3H_5 , mole fractions are multiplied by factors of 5 and 2, respectively.

An upper limit for the benzene concentration that can be formed through $\text{C}_3 + \text{C}_3$ reactions was estimated by Hansen *et al.* [13]. They correlated the maximum mole fraction of benzene to that of the propargyl radical. For a given C_3H_3 mole fraction, they observed a higher benzene formation for fuels containing a ring structure and reasoned that direct routes via dehydrogenation and ring-enlargement reactions are also responsible for the production of benzene. However, non-cyclic fuels showed an upper limit of benzene formation that correlated linearly with the observed maximum

1 mole fraction of C_3H_3 . For the 2M2B flame we notice that under our conditions the experimentally
2 derived value of the C_6H_6 -to- C_3H_3 ratio (0.57) is about a factor of 4 larger than the proposed limit
3
4 (C_6H_6/C_3H_3 -ratio: 0.15) observed in other typical flames fueled by C_2 - C_6 hydrocarbons. This large
5
6 value indicates that other precursors might play a role in the benzene formation chemistry in 2M2B
7
8 flames.
9

10
11 To experimentally establish the contributions of C_4H_5 radicals towards benzene formation in
12 the 2M2B flame, it must be considered that the two radicals but-2-yn-1-yl (C_4H_5 -1) and *iso*- C_4H_5
13 (C_4H_5 -2) are directly formed in the fuel consumption (see Fig. 2). However, C_4H_5 -1 is only a product of
14 the consumption pathway via the vinylic fuel radical (C_5H_9 -1, see Fig. 2) and is thus expected to be of
15
16 lesser importance. As a consequence, the mole fraction profile of C_4H_5 , depicted in Fig. 6 (e), can be
17
18 attributed mainly to that of the resonantly stabilized radical *iso*- C_4H_5 . Considering the position of the
19
20 *iso*- C_4H_5 peak mole fraction in the sequence 1,3-butadiene ($h = 4.25$ mm) $\rightarrow$ *iso*- C_4H_5 (4.50 mm) $\rightarrow$
21
22 fulvene (4.50 mm) $\rightarrow$ benzene (4.75 mm), it becomes evident that it coincides with that of fulvene,
23
24 revealing their formation at similar reaction times. The isomer-separated mole fraction profiles of
25
26 benzene and fulvene are presented in Fig. 7 (a). Note that the reaction of the allyl radical (C_3H_5) with
27
28 propargyl (C_3H_3) can also form fulvene and that the concentration and peak position of C_3H_5
29
30 ($h = 4.50$ mm) might indicate its contribution to the fulvene formation as well.
31
32

33
34 It should be pointed out that under our conditions the mentioned recombination of two
35
36 propargyl radicals (C_3H_3) is probably still the most important channel in the benzene formation.
37
38 Both, the initiated decompositions of 2M2B by H-atom abstraction and by H-atom addition, can
39
40 serve as sources for C_3H_3 radicals. The radical C_5H_7 -2 (see Fig. 2), which is the main consumption
41
42 product from the H-atom-abstraction-initiated decomposition of 2M2B, as well as *iso*-butene
43
44 (C_4H_8 -1, see Fig. 4) can both decompose to allene ($CH_2=C=CH_2$, peak mole fraction: 1.8×10^{-3}), that can
45
46 easily equilibrate with propyne ($CH_3-C\equiv CH$, 2.8×10^{-3}) [54]. Their high peak mole fractions
47
48 substantiate the important role of propargyl, which can be obtained through H-atom abstraction
49
50 from both allene and propyne, in the formation process of benzene.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure 7: Experimental mole fraction profiles of (a) C_6H_6 (benzene, fulvene) and (b) C_7H_8 (toluene). For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fraction of fulvene is multiplied by a factor of 10. (c) Flame-sampled PIE curve of $m/z = 92.063$ u (C_7H_8). Closed symbols (connected to guide the eye) represent the measured signal and open symbols show the scaled photoionization cross section of toluene. The measured signal is shown enlarged by a factor of 10 in the region between 8.0 and 8.75 eV for a better illustration of the photoionization thresholds (grey, closed symbols).

Concerning larger aromatics, Table 2 gives an overview of the maximum mole fraction values of benzene and toluene that were experimentally determined with molecular-beam mass spectrometry for different fuels [24,46,55,56]. According to (R2), methyl addition to benzene is a direct pathways leading to toluene. In a semi-empirical approach similar to that of Hansen *et al.* [13] who correlated the maximum mole fractions of benzene and that of the propargyl radical, we now consider the ratio of the maximum concentrations of toluene to benzene. These ratios (also listed in Table 2) indicate a maximum toluene concentration for a given benzene mole fraction when reaction

(R2) dominates the formation of toluene. Please note that for the comparison in Table 2 only experimental studies with similar boundary conditions were used.

Table 2: Peak mole fraction values of benzene (C_6H_6) and toluene (C_7H_8) as well as their ratios (C_7H_8/C_6H_6) for different fuels. 2-Methyl furan is abbreviated as 2-MF and 2-methyl-2-butene as 2M2B.

Fuel	1-butene	2-butene	<i>iso</i> -butene	<i>n</i> -butane	<i>iso</i> -butane	<i>n</i> -heptane	2-MF	2M2B
Ref.	[24]	[24]	[24]	[55]	[55]	[46]	[56]	this study
C_6H_6	1.6×10^{-4}	1.2×10^{-4}	2.7×10^{-4}	5.2×10^{-5}	1.1×10^{-4}	7.9×10^{-5}	4.5×10^{-4}	4.3×10^{-4}
C_7H_8	2.1×10^{-5}	1.7×10^{-5}	5.4×10^{-5}	5.7×10^{-6}	1.4×10^{-5}	8.6×10^{-6}	1.0×10^{-4}	1.8×10^{-4}
C_7H_8/C_6H_6	0.13	0.14	0.20	0.11	0.13	0.11	0.23	0.43

For most of the chosen fuels, the ratio ranges between 0.11 and 0.20, while it becomes clear that 2M2B represents an outlier with a toluene-to-benzene ratio of 0.43 that is at least a factor of 2 up to almost a factor of 4 larger than for the other fuels. A comparison with C_5 and C_6 fuels under similar premixed flame conditions is not obvious because reliable toluene or benzene mole fractions are often not reported. Unpublished data for premixed flames fueled by 1-hexene and 3,3-dimethyl-1-butene show toluene-to-benzene ratios of 0.13 and 0.23, respectively [57], again confirming the present 2M2B value as unusually large. Further reactions in addition to R2 must thus contribute to toluene formation in the combustion of 2M2B. Figure 7 (b) shows the measured mole fraction profile of toluene. It is noteworthy that its maximum value is reached at a lower height ($h = 4.5$ mm) than that for benzene (4.75 mm), revealing contributions from earlier-formed species to the toluene formation. As discussed in Section 3.1, the radical C_5H_7-1 is a main product of the H-atom-abstraction-initiated fuel consumption (see Fig. 2), and is thus formed in an early step. Its molecular structure contains the structural motif of an *iso*- C_4H_5 radical extended with a methyl substituent. Assuming that the C_5H_7-1 radical undergoes similar types of reactions as the *iso*- C_4H_5

radical, its reaction with C₂H₂ would lead to a methyl-substituted fulvene that can then react further to toluene via an H-atom-catalyzed reaction (see R3):

Figure 7 (c) shows the flame-sampled PIE curve of $m/z = 92.063$ u that can be assigned to the elemental composition of C₇H₈. The curve has a strong similarity to the shape of the photoionization cross section of toluene indicating that toluene is the main contributor to the signal of $m/z = 92.063$ u. A slight increase in the PIE signal is already observable below its ionization threshold (IE = 8.83 eV) showing that other species with the same mass-to-charge ratio as toluene can participate in the combustion process. Several known ionization thresholds [11] of some potential C₇H₈ isomers are marked in Fig. 7 (c) but none matches the onset of the signal around 8.05 eV. Unfortunately, with the exception of 6-methylfulvene (IE = 8.10 eV [58], cyC₅H₄=CH—CH₃), neither ionization thresholds nor photoionization cross sections are reported in the literature for methyl-substituted fulvenes and thus an unambiguous identification of the proposed structure (see R3) is not feasible in this case. However, reaction R3 provides a possible pathway that would certainly explain the high toluene-to-benzene ratio and would lead to an early toluene formation. This reaction yields toluene without benzene as a precursor and thus makes toluene another possible *first aromatic ring*. This conclusion is also consistent with the different peak positions of toluene and benzene as already mentioned above.

Even if the radical C₄H₅-1 (CH₂—C≡C—CH₃) results only from the consumption pathway via the vinylic fuel radical, its potential role in soot precursor formation shall be discussed next. Similar to *iso*-C₄H₅, the C₄H₅-1 radical is also resonantly stabilized and should therefore have a longer lifetime than non-stabilized radicals. As a consequence, it can accumulate to high enough concentrations to play a possible role in aromatics formation. Its molecular structure can be considered as a methyl-substituted propargyl radical, and it is thus expected to undergo similar

reactions as the propargyl radical (C_3H_3). The reaction with C_3H_3 , as shown in R4, contributes to the formation of toluene in addition to R3 and would also bridge benzene as the *first aromatic ring*.

Another interesting reaction is the recombination of two C_4H_5-1 radicals. It opens a pathway to form *ortho*-xylene (C_8H_{10} , see R5), another aromatic intermediate species and even another *first aromatic ring* in the soot precursor formation.

Figure 8 (a) presents the flame sampled PIE curve of $m/z = 106.078$ u which can be assigned to the elemental composition of C_8H_{10} . Several photoionization cross sections have been considered to obtain good agreement between the simulated (closed symbols) and measured signal (connected closed symbols). The best agreement was achieved considering 59.1% *o*-xylene, 21.1% ethylbenzene, 14.1% *p*-xylene, and 5.6% *m*-xylene. It should be noted that the respective photoionization cross sections have a similar shape, and the absolute percentages should therefore be treated with caution. However, our finding that *o*-xylene is dominantly formed is consistent with the fact that its formation can result from the recombination of two radicals which are directly formed during the decomposition of the fuel. In addition, its peak mole fraction at $h = 4.25$ mm (see Table S1) relates to an early formation in the flame and indicates that *o*-xylene is not formed through growth reactions starting from benzene or toluene. The latter is consistent with recent findings from Shukla *et al.* [59] who reported that abstraction of hydrogen from a side chain with further addition of methyl radical is preferred over H-atom abstraction by methyl radical from the aromatic ring of alkyl-aromatic compounds. Their statement also explains the observed predominant formation of ethylbenzene over *p*- and *m*-xylene. It should be pointed out again that *iso*- C_4H_5 is of higher importance in the fuel consumption than the C_4H_5-1 radical and that the discussed reactions involving C_4H_5-1 might contribute just little to the soot precursor formation in 2M2B flames.

Nevertheless, reactions of C_4H_5 -1 provide more possibilities to bypass benzene as the *first aromatic ring*.

As already stated in Section 3.2, due to its double bond, 2M2B is predestined to undergo addition reactions. Regarding that the different resonantly stabilized C_5H_9 isomers can accumulate in the system because of their relative long lifetime, another conceivable reaction is the addition of the C_5H_9 fuel radicals to the fuel itself. This type of reaction would lead to the formation of intermediates that are prone to form cyclic molecules and in turn aromatic species, and would thus also bridge benzene as the *first aromatic ring*. However, these ring closure reactions, leading to multiple methyl-substituted 6-membered ring species, require first an intramolecular rearrangement of a substituent (H-atom shift, CH_3 -group shift). To assess the significance of this type of reaction under the present flame conditions, the recorded mass spectra were carefully evaluated for species at $m/z = 138.141$ u and $m/z = 134.110$ u, assuming a ring closure and successive dehydrogenation leading to cyclic isomers with the elemental composition of $C_{10}H_{18}$ and $C_{10}H_{14}$, respectively. For $C_{10}H_{18}$, indeed a slight signal can be observed with its maximum at $h = 2.75$ mm, indicating an early formation pathway that would be consistent with the assumed type of reaction. However, the observed signal is close to the detection limit of the instrument, implying an only small importance of the described reaction under our conditions. Only an insignificant signal for $m/z = 134.110$ u correlated with the respective aromatic isomers is observable. Note, that the low signal-to-noise ratio and, in particular, the strong overlaps of the numerous respective isomers' photoionization cross section curves prevent a clear identification of the isomeric contributions to $m/z = 138.141$ u. A similar issue occurs for a significant number of further signals observed in the mass range of 80-90 u (see Fig. 1), corresponding, for example, to different cyclohexadiene (C_6H_8), hexadiene (C_6H_{10}), and hexene (C_6H_{12}) isomers. Mole fractions of the contributing isomers for this mass range could thus not be evaluated and presented.

Figure 8: (a) Flame-sampled PIE curve of $m/z = 106.078 \text{ u (C}_8\text{H}_{10}\text{)}$. Closed symbols (connected to guide the eye) represent the measured signal and open symbols show the scaled photoionization cross section of the respective species. The obtained sum signal is shown as a dotted line. Experimental mole fraction profiles of (b) C_8H_8 (styrene), (c) C_9H_8 (indene), (d) C_{10}H_8 (naphthalene) and (e) $\text{C}_{16}\text{H}_{10}$ (pyrene). For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fraction of pyrene is multiplied by a factor of 20. Note that the naphthalene mole fraction was calculated using an estimated photoionization cross section [48] and the pyrene mole fraction profile was smoothed because of the low signal-to-noise ratio (moving average with 5 data points).

In Fig. 8 (b-e) experimental mole fraction profiles of C_8H_8 (styrene), C_9H_8 (indene), C_{10}H_8 (naphthalene) and $\text{C}_{16}\text{H}_{10}$ (pyrene) are shown, species that are known to be important for the

formation of soot. While styrene is an important precursor for the formation of polycyclic aromatic hydrocarbons, the latter three are PAHs. Styrene is often suggested to be formed starting from benzene but its mole fraction (2.8×10^{-4} , $h = 4.25$ mm) peaks already at lower heights above the burner than benzene (4.75 mm) indicating that earlier reaction steps are responsible for its formation. For example, reaction R6 provides one possible pathway for the early formation of styrene.

Analogous to the reaction of the *iso*-C₄H₅ radical with C₂H₂ forming benzene via fulvene and reaction R3, the reaction of *iso*-C₄H₅ (C₄H₅-2) with 1-buten-3-yne (C₄H₄, HC≡C—CH=CH₂) would lead directly to styrene, again by passing benzene as the *first aromatic ring*. Several possible reaction channels exist in the combustion of 2M2B that can provide C₄H₄. Besides the *iso*-C₄H₅ radical itself (through H-atom loss), further C₄ species like *trans*- and *cis*-2-butene, which mainly result from the fuel consumption initiated by H-atom addition (see Fig. 4), can form C₄H₄ through successive dehydrogenation steps.

The formation of PAHs is typically described as a sequence of molecular growth reactions starting from the *first aromatic ring*, normally identified as benzene [60,61]. As described above, in the 2M2B flame studied here, benzene, toluene, *o*-xylene, and styrene can be considered as the *first aromatic ring*. In addition, naphthalene was suggested to be formed through recombination of cyclopentadienyl radicals (C₅H₅) without passing through benzene [51,60,62]. It is obvious that starting from the *various first aromatic rings*, multiple reaction routes are available to form polycyclic aromatic hydrocarbons, such as indene, naphthalene, and pyrene. The importance of these individual pathways can currently not be determined based on our experimental data and shall therefore not be discussed here. However, the respective mole fraction profiles, depicted in Fig. 8 (c-e), give an impression about the high concentrations of these PAHs compared to other fuel-rich premixed flames, for example fueled by 1-pentene [12] or acetylene [63]. Especially the

1 detection of pyrene, whose dimerization is often considered as a crucial connection between mass
2 growth of PAHs and inception of soot particles [64,65], reflects the tendency of 2M2B to form
3 polycyclic aromatic species.
4
5
6
7
8

9 **4. Supplementary modeling**

10
11 The presented experimental results obtained for the 2M2B flame provide useful targets to further
12 develop the kinetic mechanism of Westbrook *et al.* [1] for 2-methyl-2-butene combustion. As a first
13 test, the existing model that was assembled to determine the oxidation of 2M2B in jet-stirred
14 reactor and ignition delay times in shock-tube experiments, is now examined against the
15 experimental data of the premixed flame. This comparison is performed to evaluate the accuracy of
16 the existing model for flame data prediction. It should be clearly pointed out that no improvements
17 to the model have been made in this study. In contrast, the focus of our work was the experimental
18 analysis of the initial fuel consumption pathways and understanding how they impact the formation
19 of PAH and soot precursors. However, aspects for potential improvements of the model are
20 identified to eventually enhance its performance.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37

38 *4.1 Modeling details*

39
40 The chemical structure of the low-pressure premixed flame was simulated using Chemkin-Pro [66]
41 considering thermal diffusion and multi-component transport properties. For the simulation, a
42 “disturbed” temperature profile was used as input parameter, it was calculated from the Ar signal
43 following a procedure described in Refs. [46,67], assuming an exhaust gas temperature of 1900 K.
44
45 The required parameter as well as the thermodynamic and transport data were taken from Ref. [1]
46 and Ref. [68], respectively. The adaptive grid control values for solution gradient and curvature were
47 set to 0.1 and 0.5, respectively. The maximum number of grid point was set to 250. These settings
48 were found to be an appropriate compromise between required CPU time and accuracy of the
49 calculations.
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

4.2 Comparison of experiment and modeling

For the presented 2M2B flame, mole fractions of 54 species were quantified. An overview of all intermediate species that were quantified by the PI-MBMS experiment as well as the modeling results are presented in Tab. S1 in the Supplemental Material, where peak mole fractions of the respective species are reported together with their positions. Corresponding cross section values used for the data evaluation are also provided. All experimental mole fraction profiles can also be found in the Supplemental Material.

Mole fraction profiles of the major species (H_2 , H_2O , O_2 , CO , CO_2 , Ar, 2M2B) from experiment and model are shown in Fig. 9. Experimental and simulated mole fraction profiles show good agreement, providing confidence that the developed mechanism gives a reasonable description of the global 2M2B combustion chemistry. Minor discrepancies between modeling and experiment might be explained by the fact that an estimated exhaust gas temperature was used to calibrate the experimental temperature profile that was used as an input parameter for the simulations.

Figure 9: Major species mole fractions and calculated temperature profile. Symbols represent the experimental data, lines the modeling results. The dashed line corresponds to the temperature profile that was used as input parameter for the modeling. Note that the H_2 mole fraction profile was smoothed because of the low signal-to-noise ratio (moving average with 5 data points).

1 A more powerful test for the quality of the model and the experimental data is provided by
2 comparing modeled and experimental mole fraction profiles of intermediate species. Considering
3 that the model of Westbrook *et al.* [1] was validated against mole fractions obtained with JSR
4 experiments, we first want to compare some intermediate species of the premixed flame that also
5 served as validation target in Ref. [1] and were considered to play an important role in the
6 combustion of 2M2B.
7
8
9
10
11
12

13 Figure 10 exemplarily presents the mole fraction profiles of the oxygenated intermediate
14 species (a) acetaldehyde (C_2H_4O) and (b) acetone (C_3H_6O) as well as the non-oxygenated species (c)
15 propene (C_3H_6), and (d) *iso*-butene (C_4H_8). Regarding the peak mole fractions as well as the profile
16 shapes, reasonably good agreement between experiment and model can be observed for all of these
17 species, only a shift of about 1 mm between modeled and measured profiles is visible. While a slight
18 under-prediction is stated for C_3H_6O and a close match can be observed for C_3H_6 , the intermediates
19 C_2H_4O and C_4H_8 are slightly over-predicted by the model. However, all species predictions are within
20 the stated error limit of the experiment. The good capability of the model to reasonably predict
21 these species is in agreement with the results from Ref. [1], while even better agreement is
22 observable for C_3H_6O . In contrast to our data, both C_2H_4O and C_3H_6 are, however, slightly under-
23 predicted in their study.
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
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Figure 10: Mole fraction profiles for (a) acetaldehyde, (b) acetone, (c) propene, and (d) *iso*-butene. Symbols represent experimental results, thick lines the corresponding simulations with the only existing mechanism of Westbrook *et al.* [1]. For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fractions of C_3H_6O and C_3H_6 are multiplied by a factor of 2.

From this comparison it is evident that the model can quite reasonably predict the formation of *iso*-butene which is, as mentioned earlier, a product from the H-addition-initiated fuel consumption. The fuel flux and rate of production analyses in Fig. S2 and Fig. S3 (Supplemental Material) show indeed that *iso*-butene is mainly produced from the C_5H_{11-1} radical. Additionally, the model can confirm the substantial temperature dependence of the initial H-atom addition mentioned before in Section 3.2. A rate of production analysis at two different heights above the burner ($h = 2$ mm, $T = 900$ K and $h = 3.5$ mm, $T = 1380$ K; shown in Fig. S4 in the Supplemental Material) reveals a change of the dominant initial fuel reactions: In particular, a change from the H-atom addition reactions (at $h = 2$ mm) to the H-atom abstraction reactions (at $h = 3.5$ mm) is observed.

Regarding the H-atom-abstraction-initiated fuel consumption, some discrepancies are seen between our experimentally derived pathways and those predicted by the model. In the simulations, the fuel decomposition proceeds via the two allylic radicals C_5H_9-2 and C_5H_9-4 , consistent with our experimental findings. Note, however, that *cis-trans* isomerism of the resonance structures of the C_5H_9-4 radical leading to the C_5H_9-3 radical structure in Fig. 2 was not considered in the Westbrook *et al.* [1] mechanism. This simplification in the model should be only of minor influence because the isomeric forms lead to the same stable reaction products. The flux analysis in Fig. S5 is only in partial agreement with our experimental findings, however. It reveals further decomposition pathways of the fuel radicals C_5H_9-3 and C_5H_9-4 to isoprene (C_5H_8-2) and directly to 1,3-butadiene (C_4H_6-3). As already discussed in Section 3.1, 1,2-butadiene (C_4H_6-2) is supposed to be a main product of the fuel decomposition and has been assumed to isomerize fast to 1,3-butadiene (C_4H_6-1). According to Ref. [1], 1,2- and 1,3-butadiene have been lumped in the mechanism, and the corresponding isomerization step is thus missing in the model, resulting in a direct formation of C_4H_6-1 from C_5H_9-4 .

In addition, 3-methyl-1,2-butadiene (C_5H_8-1) was also found experimentally to be part of the fuel decomposition. This species is, however, not included in the mechanism [1] and reactions from C_5H_9-2 forming C_5H_8-1 are thus omitted in the model. Without these important species, discussed already in Section 3.1, building blocks for the formation of PAHs are lacking, especially regarding also C_5H_7-1 (a directly formed radical from C_5H_8-1) as precursor for toluene. The absence of the vinylic fuel radical (C_5H_9-1) in the mechanism [1] prevents the fuel decomposition channel to C_4H_5-1 to be entered from C_5H_9-1 via C_4H_6-1 (see Fig. 2 and Section 3.3) even though it may be of lesser importance under the present conditions, it should be systematically included.

Figure 11 shows the experimentally obtained mole fraction profiles of (a) the propargyl radical (C_3H_3) and (b) benzene (C_6H_6) together with the respective modeling results. The model over-predicts the maximum C_3H_3 concentration by a factor of about 3, while C_6H_6 is under-predicted by a factor of 12 (outside the error limits of the experiment). The flux analysis reveals that most of the C_3H_3 is consumed by reaction with OH and that only a minor part recombines to benzene (see

Supplemental Material Fig. S6). Furthermore, the formation of benzene via fulvene starting from the *iso*-C₄H₅ radical, which was discussed in the first part of this paper and which was found to play a dominant role in the combustion of 2M2B, is not considered in the mechanism, providing a potential explanation for the strong deviation between model and experimental data. However, it is not surprising that the model is not capable to accurately predict the benzene formation because it was developed to predict experiments that do not usually lead to soot formation. This limited validation regime might explain that further reactions to soot precursors like those discussed in this study, are currently not included in the mechanism. In view of the discussed differences it is therefore suggested that our experimental results may serve as validation targets and provide guidance towards the development of a next-generation 2M2B combustion chemistry model.

Figure 11: Mole fraction profiles for (a) propargyl and (b) benzene. Symbols represent experimental results, thick lines the corresponding simulations. For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fraction of benzene is multiplied by a factor of 5.

5. Conclusion

In the present work, a premixed fuel-rich flame was studied in detail to obtain new insights into the combustion chemistry of 2-methyl-2-butene which is expected to be dominated by the formation of allylic-type resonantly stabilized fuel radicals. Flame-sampling high-resolution molecular-beam mass

1 spectrometry with single-photon ionization via synchrotron-generated vacuum-ultraviolet radiation
2 was used to provide experimental data in the form of isomer-resolved species mole fraction profiles
3
4 as a function of height above the burner. The flame revealed a tendency to form PAH and soot
5 precursors that was traced back in this study to the fuel structure. The experimental data imply that
6
7 initial fuel consumption pathways mainly proceeds via H-atom abstraction reactions mostly at one of
8
9 the allylic carbon atoms as well as H-atom addition reactions to the double-bond.
10
11
12

13
14 It is shown that both fuel consumption pathways subsequently form the resonantly-
15 stabilized propargyl (C_3H_3) and *iso*- C_4H_5 radicals, which are assumed in this study to contribute to the
16 formation of benzene via propargyl + propargyl reaction or the reaction of *iso*- C_4H_5 with C_2H_2 .
17
18 Attributed to the branched structure of 2M2B and the position of the double-bond, further
19 resonantly-stabilized radicals, *i.e.*, C_4H_5-1 ($\bullet CH_2-C\equiv C-CH_3$) and C_5H_7-1 [$CH_2=C(CH_3)-\bullet C=CH_2$], are
20
21 part of the fuel consumption. Their chemical structures can be considered as methyl-substituted
22
23 C_3H_3 and *iso*- C_4H_5 radicals and are therefore expected to undergo analogous reactions. It is argued
24
25 here that reactions of these derivatives can directly form toluene and *o*-xylene which can serve as an
26
27 alternative *first aromatic ring* bridging the formation of benzene. Together with styrene (formed by
28
29 *iso*- $C_4H_5+C_4H_4$) and naphthalene (formed by $C_5H_5+C_5H_5$) our results reveal a multiple-based, intense
30
31 formation of soot precursors and PAHs that should be considered in perspective to the applicability
32
33 of 2M2B as a promising fuel in engines as indicated by its strong octane sensitivity.
34
35
36
37
38
39
40
41
42

43 The obtained mole fraction profiles were used for an initial examination of the recently
44 published model of Westbrook *et al.* [1] that was only validated against jet-stirred reactor and
45 shock tube data. While the model is sufficient to predict the global combustion chemistry of 2M2B
46
47 and some main intermediate species, it appears that the PAH and soot precursor formation
48
49 processes are not yet sufficiently considered. It is suggested that our experimental data should
50
51 provide guidance towards the development of a next-generation 2M2B combustion chemistry
52
53 model.
54
55
56
57
58
59
60
61
62
63
64
65

Acknowledgements

The authors are grateful to Paul Fugazzi for expert technical assistance. The measurements were performed within the “Flame Team” collaboration at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, Berkeley, USA, and the authors thank the students and postdocs for the help with the data acquisition. NH and KM are supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000. The Advanced Light Source is supported by the Director, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We thank Dr. C.K. Westbrook for providing the mechanism and transport data. LR thanks Bielefeld University for a scholarship.

References

- [1] C.K. Westbrook, W.J. Pitz, M. Mehl, P.-A. Glaude, O. Herbinet, S. Bax, F. Battin-Leclerc, O. Mathieu, E.L. Petersen, J. Bugler, H.J. Curran, Experimental and kinetic modeling study of 2-methyl-2-butene: Allylic hydrocarbon kinetics, *J. Phys. Chem. A* 119 (2015) 7462–7480.
- [2] W.G. Lovell, Knocking characteristics of hydrocarbons, *Ind. Eng. Chem.* 40 (1948) 2388–2438.
- [3] S.J. Blanksby, G.B. Ellison, Bond dissociation energies of organic molecules, *Acc. Chem. Res.* 36 (2003) 255–263.
- [4] F. Yang, F. Deng, P. Zhang, Z. Tian, C. Tang, Z. Huang, Experimental and kinetic modeling study on *trans*-3-hexene ignition behind reflected shock waves, *Energy Fuels* 30 (2016) 706–716.
- [5] S.W. Wagnon, C.L. Barraza-Botet, M.S. Wooldridge, Effects of bond location on the ignition and reaction pathways of *trans*-hexene Isomers, *J. Phys. Chem. A* 119 (2015) 7695–7703.
- [6] W. Tsang, C.M. Rosado-Reyes, Unimolecular rate expression for cyclohexene decomposition and its Use in chemical thermometry under shock tube conditions, *J. Phys. Chem. A* 119 (2015) 7155–7162.
- [7] F. Battin-Leclerc, A. Rodriguez, B. Husson, O. Herbinet, P.-A. Glaude, Z. Wang, Z. Cheng, F. Qi, Products from the oxidation of linear isomers of hexene, *J. Phys. Chem. A* 118 (2014) 673–683.
- [8] M. Mehl, G. Vanhove, W.J. Pitz, E. Ranzi, Oxidation and combustion of the *n*-hexene isomers: A wide range kinetic modeling study, *Combust. Flame* 155 (2008) 756–772.
- [9] O. Herbinet, A. Rodriguez, B. Husson, F. Battin-Leclerc, Z. Wang, Z. Cheng, F. Qi, Study of the formation of the first aromatic rings in the pyrolysis of cyclopentene, *J. Phys. Chem. A* 120 (2016) 668–682.
- [10] Y. Cheng, E. Hu, F. Deng, F. Yang, Y. Zhang, C. Tang, Z. Huang, Experimental and kinetic

- comparative study on ignition characteristics of 1-pentene and *n*-pentane, Fuel 172 (2016) 263–272.
- [11] N. Hansen, T. Kasper, S.J. Klippenstein, P.R. Westmoreland, M.E. Law, C.A. Taatjes, K. Kohse-Höinghaus, J. Wang, T.A. Cool, Initial steps of aromatic ring formation in a laminar premixed fuel-rich cyclopentene flame, J. Phys. Chem. A 111 (2007) 4081–4092.
- [12] G. González Alatorre, H. Böhm, B. Atakan, K. Kohse-Höinghaus, Experimental and modelling study of 1-pentene combustion at fuel-rich conditions, Z. Phys. Chem. 215 (2001) 981–995.
- [13] N. Hansen, T. Kasper, B. Yang, T.A. Cool, W. Li, P.R. Westmoreland, P. Oßwald, K. Kohse-Höinghaus, Fuel-structure dependence of benzene formation processes in premixed flames fueled by C₆H₁₂ isomers, Proc. Combust. Inst. 33 (2011) 585–592.
- [14] N. Hansen, W. Li, M.E. Law, T. Kasper, P.R. Westmoreland, B. Yang, T.A. Cool, A. Lucassen, The importance of fuel dissociation and propargyl + allyl association for the formation of benzene in a fuel-rich 1-hexene flame, Phys. Chem. Chem. Phys. 12 (2010) 12112–12122.
- [15] A. Nawdiyal, N. Hansen, T. Zeuch, L. Seidel, F. Mauß, Experimental and modelling study of speciation and benzene formation pathways in premixed 1-hexene flames, Proc. Combust. Inst. 35 (2015) 325–332.
- [16] C.S. McEnally, L.D. Pfefferle, Decomposition and hydrocarbon growth processes for hexenes in nonpremixed flames, Combust. Flame 143 (2005) 246–263.
- [17] C.S. McEnally, L.D. Pfefferle, Decomposition and hydrocarbon growth processes for hexadienes in nonpremixed flames, Combust. Flame 152 (2008) 469–481.
- [18] A. Lamprecht, B. Atakan, K. Kohse-Höinghaus, Fuel-rich flame chemistry in low-pressure cyclopentene flames, Proc. Combust. Inst. 28 (2000) 1817–1824.
- [19] M. Köhler, A. Brockhinke, M. Braun-Unkhoff, K. Kohse-Höinghaus, Quantitative laser

- diagnostic and modeling study of C₂ and CH chemistry in combustion, J. Phys. Chem. A 114 (2010) 4719–4734.
- [20] M. Kamphus, M. Braun-Unkhoff, K. Kohse-Höinghaus, Formation of small PAHs in laminar premixed low-pressure propene and cyclopentene flames: Experiment and modeling, Combust. Flame 152 (2008) 28–59.
- [21] K. Kohse-Höinghaus, B. Atakan, A. Lamprecht, G. González Alatorre, M. Kamphus, T. Kasper, N.-N. Liu, Contributions to the investigation of reaction pathways in fuel-rich flames, Phys. Chem. Chem. Phys. 4 (2002) 2056–2062.
- [22] J. Wang, U. Struckmeier, B. Yang, T.A. Cool, P. Oßwald, K. Kohse-Höinghaus, T. Kasper, N. Hansen, P.R. Westmoreland, Isomer-specific influences on the composition of reaction intermediates in dimethyl ether/propene and ethanol/propene flame, J. Phys. Chem. A 112 (2008) 9255–9265.
- [23] S.D. Thomas, A. Bhargava, P.R. Westmoreland, R.P. Lindstedt, G. Skevis, Propene oxidation chemistry in laminar premixed flames, Bull. Soc. Chim. Belg. 105 (1996) 501–512.
- [24] M. Schenk, L. Leon, K. Moshhammer, P. Oßwald, T. Zeuch, L. Seidel, F. Mauss, K. Kohse-Höinghaus, Detailed mass spectrometric and modeling study of isomeric butene flames, Combust. Flame 160 (2013) 487–503.
- [25] N. Hansen, J.A. Miller, T. Kasper, K. Kohse-Höinghaus, P.R. Westmoreland, J. Wang, T.A. Cool, Benzene formation in premixed fuel-rich 1,3-butadiene flames, Proc. Combust. Inst. 32 (2009) 623–630.
- [26] J.A. Cole, J.D. Bittner, J.P. Longwell, J.B. Howard, Formation mechanisms of aromatic compounds in aliphatic flames, Combust. Flame 56 (1984) 51–70.
- [27] B. Atakan, A. Lamprecht, K. Kohse-Höinghaus, An experimental study of fuel-rich 1,3-

- pentadiene and acetylene/propene flames, *Combust. Flame* 133 (2003) 431–440.
- [28] N. Hansen, J.A. Miller, S.J. Klippenstein, P.R. Westmoreland, K. Kohse-Höinghaus, Exploring formation pathways of aromatic compounds in laboratory-based model flames of aliphatic fuels, *Combust. Expl. Shock Waves* 48 (2012) 508–515.
- [29] T.A. Cool, A. McIlroy, F. Qi, P.R. Westmoreland, L. Poisson, D.S. Peterka, M. Ahmed, Photoionization mass spectrometer for studies of flame chemistry with a synchrotron light source, *Rev. Sci. Instrum.* 76 (2005) 094102.
- [30] A. Lucassen, S. Park, N. Hansen, S.M. Sarathy, Combustion chemistry of alcohols: Experimental and modeled structure of a premixed 2-methylbutanol flame, *Proc. Combust. Inst.* 35 (2015) 813–820.
- [31] N. Hansen, T.A. Cool, P.R. Westmoreland, K. Kohse-Höinghaus, Recent contributions of flame-sampling molecular-beam mass spectrometry to a fundamental understanding of combustion chemistry, *Prog. Energy Combust. Sci.* 35 (2009) 168–191.
- [32] P. Osswald, U. Struckmeier, T. Kasper, K. Kohse-Höinghaus, J. Wang, T.A. Cool, N. Hansen, P.R. Westmoreland, Isomer-specific fuel destruction pathways in rich flames of methyl acetate and ethyl formate and consequences for the combustion chemistry of esters, *J. Phys. Chem. A* 111 (2007) 4093–4101.
- [33] T.A. Cool, K. Nakajima, C.A. Taatjes, A. McIlroy, P.R. Westmoreland, M.E. Law, A. Morel, Studies of a fuel-rich propane flame with photoionization mass spectrometry, *Proc. Combust. Inst.* 30 (2005) 1681–1688.
- [34] K. Moshhammer, S. Vranckx, H.K. Chakravarty, P. Parab, R.X. Fernandes, K. Kohse-Höinghaus, An experimental and kinetic modeling study of 2-methyltetrahydrofuran flames, *Combust. Flame* 160 (2013) 2729–2743.

- [35] F.N. Egolfopoulos, N. Hansen, Y. Ju, K. Kohse-Höinghaus, C.K. Law, F. Qi, Advances and challenges in laminar flame experiments and implications for combustion chemistry, Prog. Energy Combust. Sci. 43 (2014) 36–67.
- [36] D. Felsmann, K. Moshhammer, J. Krüger, A. Lackner, A. Brockhinke, T. Kasper, T. Bierkandt, E. Akyildiz, N. Hansen, A. Lucassen, P. Oßwald, M. Köhler, G.A. Garcia, L. Nahon, P. Hemberger, A. Bodi, T. Gerber, K. Kohse-Höinghaus, Electron ionization, photoionization and photoelectron/photoion coincidence spectroscopy in mass-spectrometric investigations of a low-pressure ethylene/oxygen flame, Proc. Combust. Inst. 35 (2015) 779–786.
- [37] T. Kasper, P. Oßwald, U. Struckmeier, K. Kohse-Höinghaus, C.A. Taatjes, J. Wang, T.A. Cool, M.E. Law, A. Morel, P.R. Westmoreland, Combustion chemistry of the propanol isomers - investigated by electron ionization and VUV-photoionization molecular-beam mass spectrometry, Combust. Flame 156 (2009) 1181–1201.
- [38] P. Oßwald, H. Güldenbergl, K. Kohse-Höinghaus, B. Yang, T. Yuan, F. Qi, Combustion of butanol isomers - A detailed molecular beam mass spectrometry investigation of their flame chemistry, Combust. Flame 158 (2011) 2–15.
- [39] M.E. Law, T. Carrière, P.R. Westmoreland, Allene addition to a fuel-lean ethylene flat flame, Proc. Combust. Inst. 30 (2005) 1353–1361.
- [40] A. Bhargava, P.R. Westmoreland, MBMS analysis of a fuel-lean ethylene flame, Combust. Flame 115 (1998) 456–467.
- [41] Z. Wang, Y. Li, F. Zhang, L. Zhang, W. Yuan, Y. Wang, F. Qi, An experimental and kinetic modeling investigation on a rich premixed *n*-propylbenzene flame at low pressure, Proc. Combust. Inst. 34 (2013) 1785–1793.
- [42] A.C. Parr, F.A. Elder, Photoionization of 1,3-butadiene, 1,2-butadiene, allene, and propyne, J.

- Chem. Phys. 49 (1968) 2659–2664.
- [43] C.A. Taatjes, Personal Communication, (2016).
- [44] R.D. Kern, H.J. Singh, C.H. Wu, Thermal decomposition of 1,2 butadiene, Int. J. Chem. Kinet. 20 (1988) 731–747.
- [45] Y. Hidaka, T. Higashihara, N. Ninomiya, T. Oki, H. Kawano, Thermal isomerization and decomposition of 1,2-butadiene in shock waves, Int. J. Chem. Kinet. 27 (1995) 331–341.
- [46] L. Seidel, K. Moshhammer, X. Wang, T. Zeuch, K. Kohse-Höinghaus, F. Mauss, Comprehensive kinetic modeling and experimental study of a fuel-rich, premixed *n*-heptane flame, Combust. Flame 162 (2015) 2045–2058.
- [47] M.S. Robinson, M.L. Polak, V.M. Bierbaum, C.H. DePuy, W.C. Lineberger, Experimental studies of allene, methylacetylene, and the propargyl radical: Bond dissociation energies, gas-phase acidities, and ion-molecule chemistry, J. Am. Chem. Soc. 117 (1995) 6766–6778.
- [48] Photonionization Cross Section Database (Version 1.0), National Synchrotron Radiation Laboratory, Hefei, China, (2011) <http://flame.nsrl.ustc.edu.cn/en/database.htm>.
- [49] C. Sosa, H.B. Schlegel, Ab initio calculations on the barrier height for the hydrogen addition to ethylene and formaldehyde. The importance of spin projection, Int. J. Quantum Chem. 29 (1986) 1001–1015.
- [50] H. Wang, A new mechanism for initiation of free-radical chain reactions during high-temperature, homogeneous oxidation of unsaturated hydrocarbons: Ethylene, propyne, and allene, Int. J. Chem. Kinet. 33 (2001) 698–706.
- [51] C.S. McEnally, L.D. Pfefferle, B. Atakan, K. Kohse-Höinghaus, Studies of aromatic hydrocarbon formation mechanisms in flames: Progress towards closing the fuel gap, Prog. Energy Combust. Sci. 32 (2006) 247–294.

- [52] J.P. Senosiain, J.A. Miller, The reaction of *n*- and *i*-C₄H₅ radicals with acetylene, J. Phys. Chem. A 111 (2007) 3740–3747.
- [53] A.W. Jasper, N. Hansen, Hydrogen-assisted isomerizations of fulvene to benzene and of larger cyclic aromatic hydrocarbons, Proc. Combust. Inst. 34 (2013) 279–287.
- [54] N. Hansen, J.A. Miller, P.R. Westmoreland, T. Kasper, K. Kohse-Höinghaus, J. Wang, T.A. Cool, Isomer-specific combustion chemistry in allene and propyne flames, Combust. Flame 156 (2009) 2153–2164.
- [55] P. Oßwald, K. Kohse-Höinghaus, U. Struckmeier, T. Zeuch, L. Seidel, L. Leon, F. Mauss, Combustion chemistry of the butane isomers in premixed low-pressure flames, Z. Phys. Chem. 225 (2011) 1029–1054.
- [56] K. Moshhammer, A. Lucassen, C. Togbé, K. Kohse-Höinghaus, N. Hansen, Formation of oxygenated and hydrocarbon intermediates in premixed combustion of 2-methylfuran, Z. Phys. Chem. 229 (2015) 507–528.
- [57] N. Hansen, extended analysis of the experimental data from Ref. [13], (2016).
- [58] S. Rayne, K. Forest, Estimated adiabatic ionization energies for organic compounds using the Gaussian-4 (G4) and W1BD theoretical methods, J. Chem. Eng. Data. 56 (2011) 350–355.
- [59] B. Shukla, A. Miyoshi, M. Koshi, Role of methyl radicals in the growth of PAHs, J. Am. Soc. Mass Spectrom. 21 (2010) 534–544.
- [60] H. Richter, J.B. Howard, Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways, Prog. Energy Combust. Sci. 26 (2000) 565–608.
- [61] H. Wang, Formation of nascent soot and other condensed-phase materials in flames, Proc. Combust. Inst. 33 (2011) 41–67.

- 1
2
3
4
5
6
7
8
9
10
11
12
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
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
- [62] N.M. Marinov, M.J. Castaldi, C.F. Melius, W. Tsang, Aromatic and polycyclic aromatic hydrocarbon formation in a premixed propane flame, *Combust. Sci. Technol.* 128 (1997) 295–342.
- [63] Y. Li, L. Zhang, Z. Tian, T. Yuan, K. Zhang, B. Yang, F. Qi, Investigation of the rich premixed laminar acetylene/oxygen/argon flame: Comprehensive flame structure and special concerns of polyynes, *Proc. Combust. Inst.* 32 (2009) 1293–1300.
- [64] C.A. Schuetz, M. Frenklach, Nucleation of soot: Molecular dynamics simulations of pyrene dimerization, *Proc. Combust. Inst.* 29 (2002) 2307–2314.
- [65] H. Sabbah, L. Biennier, S.J. Klippenstein, I.R. Sims, B.R. Rowe, Exploring the role of PAHs in the formation of soot: Pyrene dimerization, *J. Phys. Chem. Lett.* 1 (2010) 2962–2967.
- [66] Chemkin PRO, Reaction Design. Inc., San Diego, California, (2015).
- [67] S.M. Sarathy, S. Vranckx, K. Yasunaga, M. Mehl, P. Oßwald, W.K. Metcalfe, C.K. Westbrook, W.J. Pitz, K. Kohse-Höinghaus, R.X. Fernandes, H.J. Curran, A comprehensive chemical kinetic combustion model for the four butanol isomers, *Combust. Flame* 159 (2012) 2028–2055.
- [68] C.K. Westbrook, Personal Communication, (2016).

Figure Captions

Figure 1: Overview mass spectrum in the mass range of $m/z = 2-210$ u recorded in the reaction zone of a 2-methyl-2-butene flame at $h = 4.5$ mm and PE = 10.5 eV. The figure section enlarges the mass range of $m/z = 120-210$ u.

Figure 2: Possible reaction pathways for the consumption of 2-methyl-2-butene initiated by H-atom abstraction in a low-pressure, fuel-rich flame ($\phi = 1.8$).

Figure 3: Flame-sampled PIE curve of (a) $m/z = 54.047$ u (C_4H_6) and (b) $m/z = 68.063$ u (C_5H_8). Closed symbols (connected to guide the eye) represent the measured signal and open symbols show the scaled photoionization cross section of the respective species. The obtained sum signal is shown as a dotted red line. Isomer-resolved mole fraction profiles of (c) C_4H_6 (C_4H_6 -1: 2-butyne, C_4H_6 -3: 1,3-butadiene and C_4H_6 -4: 1-butyne) and (d) C_5H_8 (C_5H_8 -1: 3-methyl-1,2-butadiene, C_5H_8 -2: 2-methyl-1,3-butadiene and C_5H_8 -3: 1,3-pentadiene). Note, that for C_4H_6 -1, C_4H_6 -3, C_4H_6 -4, C_5H_8 -1, and C_5H_8 -3, mole fractions were multiplied by factors of 15, 3, 15, 5, and 10 and the experimental data are fitted by dotted lines (B-spline) for better visualization.

Figure 4: Possible reaction pathways for the consumption of 2-methyl-2-butene initiated by H-atom addition reactions in a low-pressure, fuel-rich flame ($\phi = 1.8$).

Figure 5: (a) Species profiles of C_5H_{10} , C_5H_{11} and C_5H_9 . (b) Mole fraction profiles of the C_4H_8 isomers 1-butene, *trans*-2-butene and *iso*-butene. For better visualization, the experimental data are fitted by dotted lines (B-spline). Note that the 1-butene mole fraction is multiplied by a factor of 5 for better visualization.

Figure 6: Experimental mole fraction profiles of (a) CH_3 (methyl), (b) C_2H_2 (acetylene), (c) C_3H_3 (propargyl), (d) C_3H_5 (allyl), (e) C_4H_5 (but-2-yn-1-yl and *i*- C_4H_5), and (f) C_5H_5 (cyclopentadienyl). For better visualization, the experimental data are fitted by dotted lines (B-spline) and for CH_3 and C_3H_5 , mole fractions are multiplied by factors of 5 and 2, respectively.

Figure 7: Experimental mole fraction profiles of (a) C_6H_6 (benzene, fulvene) and (b) C_7H_8 (toluene). For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fraction of fulvene is multiplied by a factor of 10. (c) Flame-sampled PIE curve of $m/z = 92.063$ u (C_7H_8). Closed symbols (connected to guide the eye) represent the measured signal and open symbols show the scaled photoionization cross section of toluene. The measured signal is shown enlarged by a factor of 10 in the region between 8.0 and 8.75 eV for a better illustration of the photoionization thresholds (grey, closed symbols).

Figure 8: (a) Flame-sampled PIE curve of $m/z = 106.078$ u (C_8H_{10}). Closed symbols (connected to guide the eye) represent the measured signal and open symbols show the scaled photoionization cross section of the respective species. The obtained sum signal is shown as a dotted line. Experimental mole fraction profiles of (b) C_8H_8 (styrene), (c) C_9H_8 (indene), (d) $C_{10}H_8$ (naphthalene) and (e) $C_{16}H_{10}$ (pyrene). For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fraction of pyrene is multiplied by a factor of 20. Note that the naphthalene mole fraction was calculated using an estimated photoionization cross section [48] and the pyrene mole fraction profile was smoothed because of the low signal-to-noise ratio (moving average with 5 data points).

Figure 9: Major species mole fractions and calculated temperature profile. Symbols represent the experimental data, lines the modeling results. The dashed line corresponds to the temperature profile that was used as input parameter for the modeling. Note that the H_2 mole fraction profile was smoothed because of the low signal-to-noise ratio (moving average with 5 data points).

Figure 10: Mole fraction profiles for (a) acetaldehyde, (b) acetone, (c) propene, and (d) *iso*-butene. Symbols represent experimental results, thick lines the corresponding simulations with the only existing mechanism of Westbrook *et al.* [1]. For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fractions of C_3H_6O and C_3H_6 are multiplied by a factor of 2.

Figure 11: Mole fraction profiles for (a) propargyl and (b) benzene. Symbols represent experimental results, thick lines the corresponding simulations. For better visualization, the experimental data are fitted by dotted lines (B-spline) and the mole fraction of benzene is multiplied by a factor of 5.