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1 Refining the chain-branching process in the low-
2 temperature oxidation of 1-hexene with synchrotron-
3 based PEPICO spectroscopy

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28 ABSTRACT

29 Understanding the chemical reactions that occur during the low-temperature
30 oxidation of alkenes is crucial for developing advanced energy conversion devices, as alkenes
31 are significant components of realistic fuels. Despite extensive experimental and theoretical
32 studies, the oxidation chemistry of alkenes remains less understood compared to that of
33 alkanes. The present study investigates the low-temperature oxidation of 1-hexene in a jet-
34 stirred reactor, using synchrotron-based PEPICO spectroscopy at a fixed temperature ($T =$
35 625 K) and an equivalence ratio ($\phi = 0.5$). Previous studies in the literature have suggested
36 that the discrepancy between experiments and predictions from kinetic models might be
37 due to the kinetics considered for the chain branching process. The sensitivity of the PEPICO
38 technique to molecular structure allowed for a comprehensive examination of the
39 conformational landscape, facilitating the differentiation of isomers among the main
40 intermediates: hydroperoxides, cyclic ethers, and ketohydroperoxides. Other intermediates
41 and primary products were also quantified and compared to the predictions of a kinetic
42 model from the literature. The results confirm that kinetic models overpredict the formation
43 of hydroxyl ketohydroperoxides and that alkenyl hydroperoxides are the primary chain-
44 branching agents during 1-hexene oxidation. This work underscores the need for a
45 reassessment of the branching ratio between O_2 -addition and the isomerization of hydroxy
46 alkyl radicals.

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48 KEYWORDS:

49 Alkene oxidation | Jet-stirred reactor | synchrotron radiation | photoelectron spectroscopy
50 | kinetic modeling

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52 ABBREVIATIONS:

53 low temperature oxidation, LTO; ketohydroperoxides, KHPs; hydroxyl cyclic ethers, HyCE;
54 alkenyl cyclic ethers, AnCE; alkenyl ketohydroperoxides, AnKHP; hydroxyl
55 ketohydroperoxides, HyKHP; jet-stirred reactor, JSR; gas chromatography, GC; mass
56 spectrometry, MS; synchrotron vacuum ultraviolet photoionization, SVUV-PIMS; total ion
57 yield, TIY; adiabatic ionization energy, AIE; photoionization cross sections, PICS; synchrotron-
58 based photoelectron photoion coincidence, SVUV-PEPICO; threshold photoelectron

59 spectrum, TPES; velocity map imaging, VMI; density functional theory, DFT; time-
60 independent adiabatic Hessian Franck-Condon, TI-AH|FC.

61

62 NOVELTY AND SIGNIFICANCE STATEMENT

63 In the context of the development of detailed chemical kinetic model for the design of
64 advanced energy conversion devices, this work involves utilizing synchrotron-based
65 photoelectron spectroscopy to identify and quantify intermediates during the low-
66 temperature oxidation of 1-hexene in a jet-stirred reactor. By thoroughly examining the
67 conformational landscape and effectively distinguishing between isomers, comparisons with
68 current kinetic models from the literature indicate the need for a reevaluation of the chain-
69 branching process.

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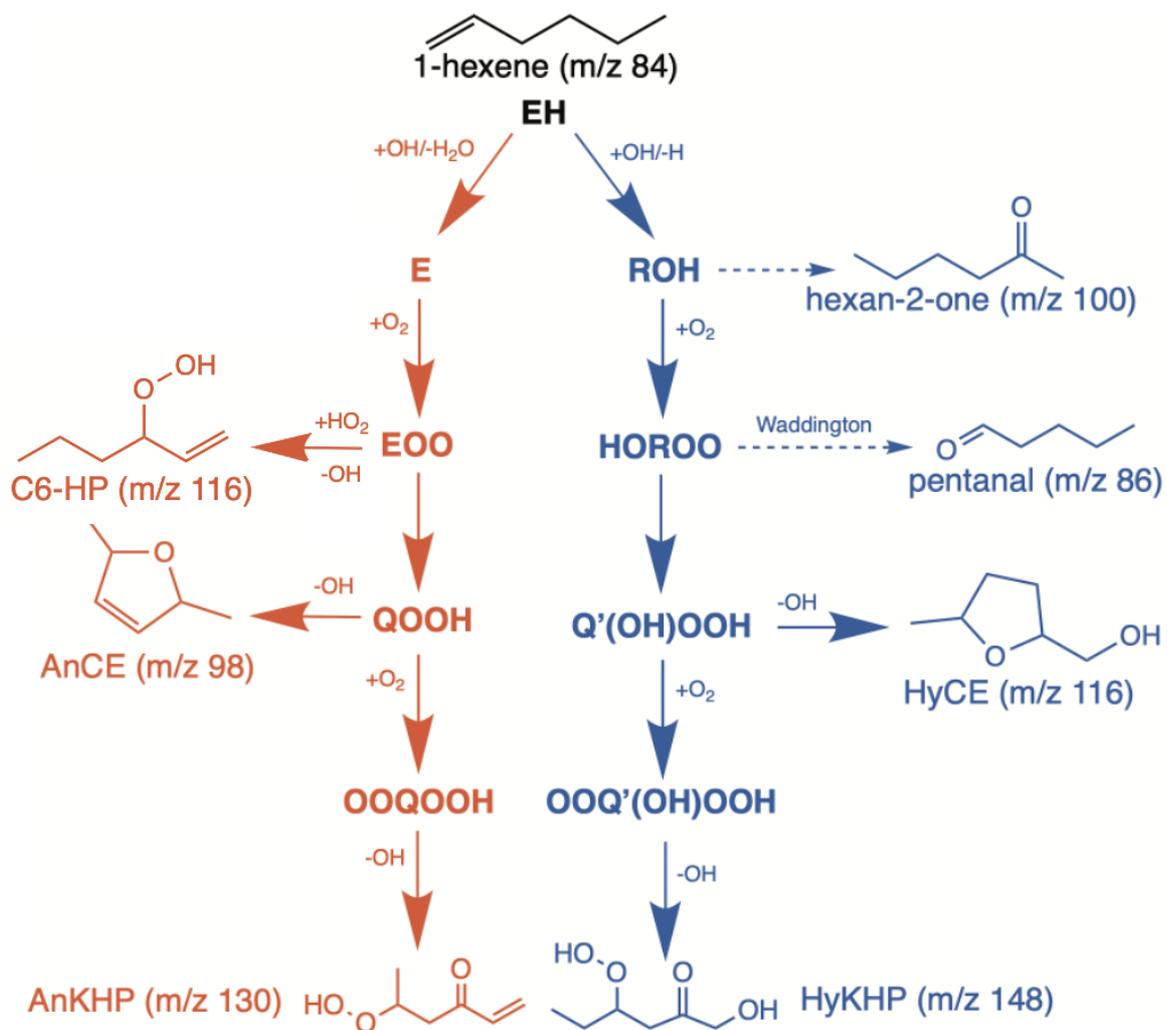
71 AUTHOR CONTRIBUTIONS

72 JB, OH, CSL, PA, LST, GV, and FBL collected the experimental data. GAG and LN
73 provided support for the analysis. JB performed the theoretical calculations, analyzed the
74 data, and wrote the original draft. All the authors contributed to review the final manuscript.

75 I. INTRODUCTION

76 Alkenes constitute a significant portion of practical fuels, making up to 20% of the
77 total volume in gasoline blends, depending on the composition and source of crude oil [1]. In
78 the pursuit of developing cost-effective and environmentally friendly combustion processes,
79 it is crucial to comprehend the chemical reactions occurring during the low-temperature
80 oxidation (LTO) of alkenes. Moreover, the unsaturated nature of alkenes causes their
81 chemistry to differ from that of alkanes, necessitating an understanding of the impact of this
82 unsaturation on auto-ignition. Despite extensive experimental and theoretical studies, the
83 LTO chemistry of long-chain alkenes with at least five carbon atoms is less well-understood
84 compared to alkanes [2–10]. Consequently, the comprehension of the chain branching
85 mechanism triggered by the decomposition of intermediates, such as ketohydroperoxides
86 (KHPs), and its influence on the ignition delay during alkene LTO remains limited.

87 1-hexene is commonly employed as a representative alkene in surrogate fuels
88 designed for gasoline [11]. Numerous studies have extensively explored its oxidation
89 chemistry across a broad spectrum of temperatures and pressures, utilizing various
90 laboratory facilities such as shock tubes, rapid compression machines, and jet-stirred
91 reactors [3,4,6,8,12–16]. The LTO of 1-hexene (EH) primarily follows two pathways: H-
92 abstraction and OH-addition onto the double bond of the carbon chain. These pathways lead
93 to the formation of alkenyl radicals, mainly allylic (E) and hydroxy alkyl radicals (ROH),
94 respectively (see Figure 1). Analogous to alkane LTO, these radicals undergo a sequence of
95 reactions, including O₂-addition, H-shift, and decomposition. These reactions culminate in
96 the formation of hydroxyl cyclic ethers (HyCE, m/z 116), alkenyl cyclic ethers (AnCE, m/z =
97 98), alkenyl ketohydroperoxides (AnKHP, m/z 130), and hydroxyl ketohydroperoxides
98 (HyKHP, m/z 148). The reactivity of 1-hexene at low temperatures is controlled by the
99 delicate balance between the formation of KHPs, which act as chain branching agents, the
100 Waddington mechanism [17] (a crucial chain propagation channel that promotes aldehyde
101 formation), and the formation of CEs.



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Figure 1. Simplified scheme of the two main reaction pathways in the LTO of 1-hexene showing a non-exhaustive list of the isomers detected in this work. Only the products of interest in this work are represented. The dotted arrows refer to more than one reaction step and co-products are not displayed for the sake of clarity.

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Battin-Leclerc et al. [3] were the first to use a near-atmospheric jet-stirred reactor (JSR) coupled to a time-of-flight mass spectrometer with synchrotron vacuum ultraviolet photoionization (SVUV-PIMS) to detect elusive intermediates in the LTO of 1-hexene [3]. They compared the ionization threshold of the total ion yield (TIY) curve of m/z 116 to the calculated adiabatic ionization energy (AIE) of the most expected CE isomers and 3-hydroperoxyhex-1-ene (C6-HP). The AIE analysis suggested that C6-HP formation, by combination of E and HO₂ radicals, would be favored over HyCEs, formed by O₂ addition to the radical obtained by OH-addition to the fuel. Battin-Leclerc et al. [3] suggested that the non-observation of HyCEs might be due to dissociative ionization, a view now contradicted by the understanding that only hydroperoxides are prone to strong fragmentation upon

117 photoionization [18,19]. However, Battin-Leclerc et al. [3] noted that the shape of the
118 temperature evolution of the signal at m/z 116 supported the possible presence of HyCEs
119 above 700 K; in the same work, they also quantified a HyCE (5-methyltetrahydrofuran-2-
120 yl)methanol) by gas chromatography (GC) with mass spectrometry (MS) identification.

121 In subsequent work by the same team, Meng et al. [4] compared experimental
122 measurements of mole fractions of products to predictions from their detailed kinetic
123 model. They found that HyCEs were relatively well predicted, while C6-HP was overpredicted
124 by a factor of 6, with a predicted C6-HP/HyCE mole fraction ratio of ~ 0.1 at 625 K.

125 Dong et al. [6] conducted a more recent study with a new kinetic model,
126 demonstrating that CEs are key species in the LTO of 1-hexene. Their kinetic model also
127 predicts that chain branching mainly occurs via the formation of HyKHP over AnKHP, with a
128 AnKHP/HyKHP ratio < 1 , in agreement with Meng et al.'s kinetic model [4]. However, no
129 experimental evidence of HyKHP formation was provided in Meng et al. [4].

130 Recently, Xie et al. [8] detected a signal at m/z 148 using a similar JSR-SVUV-PIMS
131 setup as Battin-Leclerc et al. [3], but with a more sensitive mass spectrometer than in the
132 2014 study. They estimated an AnKHP/HyKHP ratio by adding the signals at the masses
133 corresponding to those of KHPs (M) as well as their main fragments (M-33 amu). They
134 assumed that the photoionization cross sections (PICS) were similar for both types of KHPs
135 and that the loss of OOH was the main fragmentation pathway [20,21]. They found an
136 experimental AnKHP/HyKHP ratio ~ 4 , showing that the kinetic models from the literature
137 significantly underpredict the formation of AnKHP. By comparing the ionization threshold of
138 the TIY curves of m/z 130 and m/z 148 with the calculated AIE of the isomers predicted by
139 the kinetic models, they differentiated between KHP isomers. However, the ionization
140 thresholds did not match the most anticipated KHPs according to the predictions of the
141 kinetic models, suggesting an incomplete understanding of the chain branching mechanisms.

142 Accurately distinguishing between KHP isomers in SVUV-PIMS requires precise
143 ionization energy calculations. However, none of the aforementioned studies included a
144 comprehensive conformational analysis, essential for floppy molecular systems such as
145 KHPs, whose population might be distributed over several thermally accessible conformers.
146 The conformational landscape of the molecule can have a significant impact on the
147 ionization energy (IE), with IEs spanning a range of over more than 1.5 eV [19] in a typical

148 KHP such as 3-hydroperoxybutal. This contradicts the 100 meV uncertainty assumed in Xie et
149 al. [8].

150 The present study aims, for the first time, to utilize synchrotron-based photoelectron
151 photoion coincidence (SVUV-PEPICO) spectroscopy in conjunction with high-level theoretical
152 quantum calculations to investigate the low-temperature branching mechanism involved in
153 the oxidation of 1-hexene. The SVUV-PEPICO technique offers enhanced structural
154 sensitivity for analyzing complex mixtures by employing mass-selected photoelectron
155 spectroscopy [22]. This approach provides an electronic isomer-sensitive footprint that
156 supplements mass spectrometry, adding a new dimension to the analysis. A comprehensive
157 review of this method's application in combustion studies has been presented by Hemberger
158 et al. [23].

159 The experiments conducted in this study were carried out using a JSR, with specific
160 conditions optimized for detecting KHPs. These conditions were closely aligned with the
161 operating parameters utilized by Xie et al. [8]. To record the threshold mass-selected
162 photoelectron spectra (TPES) of the intermediates and products, the JSR was coupled to the
163 DELICIOUS III spectrometer of the VUV DESIRS beamline, located at the SOLEIL synchrotron
164 in Saint-Aubin, France. Subsequently, the TPES were analyzed through conformer-dependent
165 electronic structure and energy calculations. This analytical process enabled the
166 identification and quantification of the main intermediates present under specific
167 experimental conditions ($\phi = 0.5$ and $T = 625$ K), facilitating a comparison with predictions
168 from a detailed kinetic model.

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170 II. EXPERIMENTAL AND THEORETICAL METHODS

171 *Experimental procedure*

172 The experimental setup employed in this study closely follows the description
173 provided in Bourgalais et al. [24–26], with only pertinent details presented herein. A lean
174 reactive gas mixture of 1-hexene, O_2 , and He was continuously fed into a JSR operating at
175 near-atmospheric pressure. The liquid fuel was uniformly mixed with the gas flow and
176 evaporated, using He as the carrier gas, through a controlled evaporator mixer upstream of
177 the JSR. The inlet flow rates were adjusted to maintain a constant temperature of 625 K (1-
178 hexene: 1.44 g/h, O_2 : 115 Nml/min, and He: 0.516 Nl/min), a specific equivalence ratio ($\phi =$

179 0.5), and a residence time ($\tau = 2.5$ s), parameters similar to those used in previous studies.
180 The inlet mole fraction of the fuel was set to 0.01.

181 The heated JSR was located within the permanent end-station of the SAPHIRS
182 chamber [27], situated at one of the monochromatized branches of the DESIRS VUV
183 beamline at the SOLEIL synchrotron [28]. The gas mixture within the JSR was sampled via a
184 micrometer pinhole, creating a molecular-beam expansion in the vacuum chamber ($\sim 10^{-4}$
185 mbar), connected through two consecutive skimmers to the ionization chamber. This
186 expansion created cooled molecular beam where reactive collisions were minimized due to
187 low number density and dilution with a carrier gas (He). Consequently, reactive
188 intermediates were preserved during the expansion and traveled collision-free to the
189 ionization chamber.

190 In the ionization chamber, the VUV synchrotron light was focused on the gas mixture,
191 leading to the production of photoelectrons and photoions detected in coincidence using
192 the double-imaging photoelectron/photoion (i^2 PEPICO) spectrometer DELICIOUS III [29].
193 These particles traveled in opposite directions, dispersing based on their respective kinetic
194 energies before reaching the velocity map imaging (VMI) spectrometer and forming
195 concentric rings. The arrival times of the dispersed particles were recorded, and by selecting
196 the electron arrival time as the reference time for time-of-flight detection of the photoion,
197 mass spectra could be plotted. With photoion-mass selection, the VMI system allowed the
198 construction of a two-dimensional matrix of mass-selected photoelectron spectra (PES) as a
199 function of photon energy [30] using an Abel inversion technique. By selecting a specific
200 kinetic energy range (100 meV in this work) the corresponding TPES could be obtained, here
201 within a photon energy range from 8.5 to 10.5 eV, with a step size of 10 meV and an
202 acquisition time of 60 s per step. The error bars in TPES were obtained by assuming a
203 Poisson distribution of the photoelectron image pixel counts, which is propagated through
204 the image Abel inversion transformation using standard error propagation formulae. In TPES,
205 the signal-to-noise ratio is influenced by the number of false coincidences, when more two
206 or more ionization events arrive too close in time. This false coincidence background leads to
207 a uniform background in the mass spectrum but can hinder the detection of minor species
208 when the true coincidence signal becomes commensurate with the Poisson noise of the
209 background.

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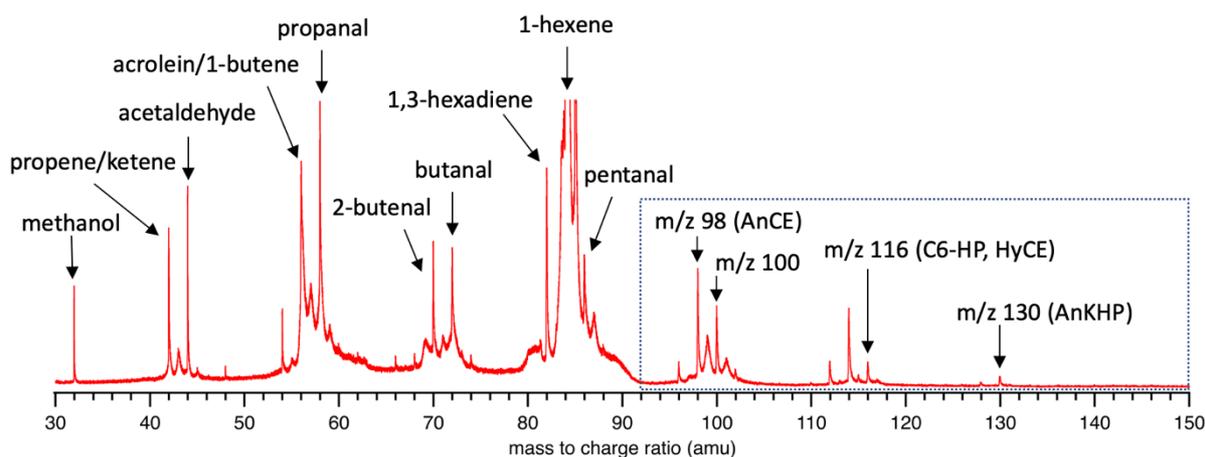
211 *Theoretical calculations*

212 In this study, the Merck molecular force field MMFF94 approach was employed to
213 generate the initial structures of the conformers [31], which were then optimized at a higher
214 level of theory using density functional theory (DFT) with the M06-2X-D3 functional [32]. The
215 DFT functional was combined with the aug-cc-pVTZ Dunning's correlation consistent basis
216 set [33], augmented with diffuse functions, and the zero-damped D3 dispersion correction
217 by Grimme et al. [34] was applied to M06-2X. The optimized structures of the neutral
218 species were used as the initial structures for the cationic forms. Two-electron integrals with
219 tight optimization criteria were utilized to ensure the reliability of the conformer energies
220 and vibrational frequencies, computed within the harmonic approximation at the same level
221 of theory.

222 The optimized individual structures were subjected to conformational averaging
223 using Boltzmann weighting based on electronic energies and the JSR temperature of 625 K.
224 In this work, all reactants and products are assumed to reach equilibrium at 625 K, and the
225 distribution of conformers remains unchanged after the expansion through the pinhole. To
226 simulate transitions between vibrational levels of the lowest-energy neutral conformers and
227 their cations, the time-independent adiabatic Hessian Franck-Condon (TI-AH|FC) model was
228 used at 625 K [35]. The resulting stick spectrum was convolved with a Gaussian profile with a
229 200 cm^{-1} bandwidth to match the experimental resolution. The calculation of the AIEs was
230 performed at the CBS-QB3 level of theory from the ground state of both neutral and cationic
231 species, using optimized DFT structures [36,37]. The 0-0 transition of the computed stick
232 spectra was adjusted to match the experimental spectra within the uncertainty of the
233 energy calculation.

234 It should be noted that when dealing with flexible molecular structures like
235 hydroperoxides, the analysis of TPES presents challenges arising from the presence of
236 vibrational modes characterized by low frequencies, which often lead to limited overlaps
237 between vibrational wavefunctions washing out the vibrational information which,
238 combined with a low signal-to-noise ratio with possibly some spurious peaks and a notable
239 number of potential isomers, make individual assignments challenging. Therefore, while
240 simulated spectra can assist in extracting critical features from experimental spectra, they
241 might not encompass all potential molecular structures.

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Figure 2. Typical time-of-flight mass spectrum obtained by integration over the photon energy range from 8.5 to 10.5 eV with a step size of 10 meV and an acquisition time of 60 s per step during the LTO of 1-hexene at $\phi = 0.5$ and $T = 625$ K. The dashed box shows the region of interest in this work. The vertical scale is reduced to zoom out the low intensity peaks so that 1-hexene (m/z 84) and its ^{13}C isotopomer (m/z 85) are cut off. In contrast to the indicated m/z values, the given chemical names related to an unambiguous identification of the isomers.

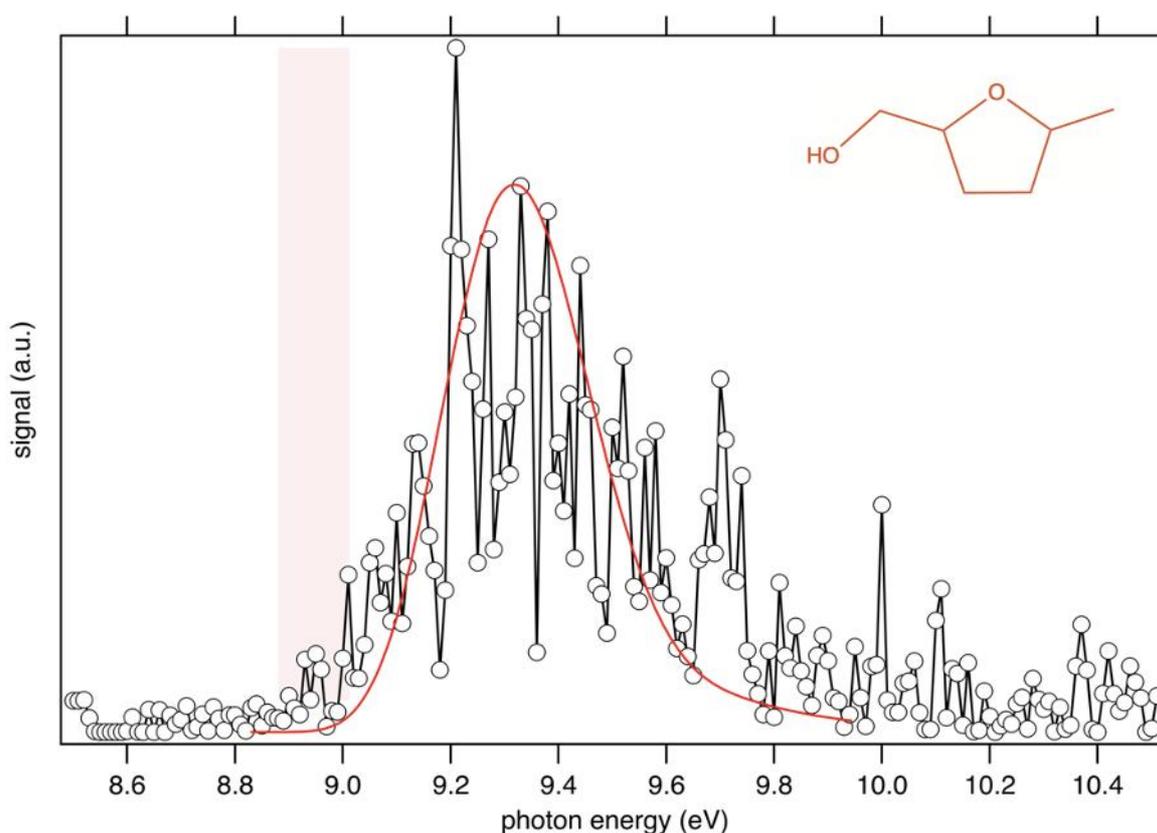
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The mass spectrum obtained during the LTO of 1-hexene at $\phi = 0.5$ and $T = 625$ K is displayed in Figure 2. The spectrum identifies some of the primary intermediates reported in the literature, with $m/z = 130$ being the highest mass detected and $m/z = 32$ the lowest. The predominant signal at $m/z = 84$ corresponds to 1-hexene, while decomposition products (with fewer than 6 carbons) and oxidized products (6 carbon atoms with one or more oxygen atoms) are present in the spectrum with a good signal-to-noise ratio. Although the highest oxidized product at $m/z = 130$ (AnKHP, $\text{C}_6\text{H}_{10}\text{O}_3$) has a weak signal, it is still visible. However, no signal could be observed at $m/z = 148$ (HyKHP, $\text{C}_6\text{H}_{12}\text{O}_4$). The dashed box in Figure 2 highlights the area of interest in this study.

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In Figure 3, the TPES of $m/z = 116$ is compared with a simulated spectrum of the trans configuration of (5-methyltetrahydrofuran-2-yl)methanol (HyCE). The experimental TPES displays a noticeable ionization threshold around 9 eV. The previous study by Battin-Leclerc et al. [3] reported an ionization threshold of $m/z = 116$ around 9.2 eV based on the TIY curve. However, upon closer inspection, a signal is already present at 9.0 eV in their reported TIY of $m/z = 116$. Table S1 presents the calculated AIEs of the expected isomers of $m/z = 116$ for the lowest-energy conformer compared to previous calculations from Battin-Leclerc et al. [3]. The two sets of calculations are in good agreement. The AIE of HyCE is the only one compatible with the measured ionization threshold of $m/z = 116$. All other isomers have AIEs above a reasonable value for the accuracy of the present calculations, 9.1 eV, including 3-hydroperoxyhex-1-ene (C6-HP) for which 70 conformers have been considered in this work,

271 having AIEs within a 318 meV range (9.06 – 9.38 eV). The simulated spectrum of HyCE,
272 agrees well with the experimental spectrum, indicating that it is the dominant isomer at m/z
273 = 116. Although the prevailing isomer at m/z = 116 is seemingly HyCE, the existence of other
274 isomers cannot be ruled out in this work.
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277 *Figure 3. TPES of m/z 116 (open dots) compared to a simulated spectrum of the lowest energy neutral conformer of*
278 *5-methyltetrahydrofuran-2-yl)methanol (red line). The red shaded region shows the conformer-dependent AIE of the HyCE.*

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280 In this work, to convert the normalized ion signal of a given species i to its mole fraction at a
281 specific temperature, the fuel was used as an internal standard [25]. The fuel mole fraction
282 value under the current conditions ($\phi = 0.5$ and $T = 625$ K) was taken from Meng et al. [4],
283 and its PICS at 10.6 eV from Yang et al. [38]. When a molecule is ionized, the total charge on
284 the produced ions equals the charge of the parent molecule. Therefore, the sum of the
285 signals from all fragments and that of the parent must equal the total signal intensity. This
286 relationship allows the use of a fragment signal to determine the concentration of a given
287 species, as the signal of a fragment is proportional to the concentration of the parent

288 molecule. When one of the fragments has a distinct m/z and a relatively good signal-to-noise
289 ratio, the mole fraction of the species of interest can be calculated using the following
290 equation [39]:

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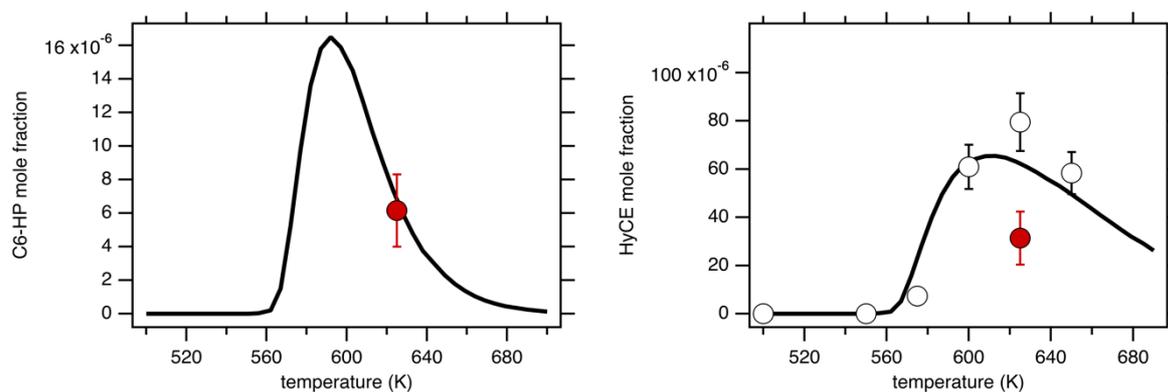
$$x_i(T) = x_{fuel}(T) \cdot \frac{S_i(T, E)}{S_{fuel}(T, E)} \cdot \frac{\sigma_{fuel}(E)}{\sigma_i(E)} \cdot \frac{D_{fuel}}{D_p} \cdot \frac{\rho_{fuel}}{\rho_i}$$

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293 Here, $x_i(T)$, $S_i(T, E)$, $\sigma_i(E)$, and $\rho_i(E)$ represent the mole fraction, signal, PICS, and
294 transmission factor of species i or one of its fragments at photon energy E and temperature
295 T , respectively. For compounds where the PICS is not available in the literature, an estimate
296 was made using the group additivity method proposed by Bobeldijk et al. [40], in which
297 groups are defined as atom pairs in the considered molecules. The value of each group was
298 estimated from published data of known species at the given photon energy. Note this
299 method only provides an estimate of the total PICS. In this work, the values of each group at
300 10.6 eV were summed to constitute the related molecule, thereby estimating the PICS. Table
301 S2 provides the list of the estimated PICS at 10.6 eV used for quantifying species in this
302 study. D_p is the mass discrimination factor of the neutral parent p of ion i until it reaches the
303 ionization region. The transmission factor ρ_i in coincidence experiments, refers to the
304 combined efficiency of electrons and ions passing through the VMI and time-of-flight mass
305 analyzer, respectively. With the 88 V/cm extraction field applied in this work, the electrons
306 are fully transmitted up to 3.5 eV kinetic energy and ion transmission is independent of mass
307 [41]. Additionally, it is important to note that with an ion impact energy of 3.8 kV and within
308 the mass range investigated in this study, any mass effects on ion detection efficiency are
309 anticipated to be minimal.

310 A weak signal is detected at m/z 83, which could be attributed to a fragment $C_6H_{11}^+$ ion
311 resulting from the dissociative ionization of C6-HP. Hydroperoxides are known to undergo
312 fragmentation upon photoionization, mainly by losing an OOH group [21]. Assuming no
313 other contribution to m/z 83, C6-HP can be quantified under the specific conditions of
314 $\phi = 0.5$ and $T = 625$ K using the peak area at m/z 83 in the registered mass spectra and its
315 partial PICS, estimated to be 13.5 Mb at a photon energy of 10.6 eV using Bobeldijk's
316 method [40]. Figure 4 compares the mole fraction of C6-HP from this work with the
317 prediction of a detailed kinetic model from Nancy [4]. The results in this work were also

318 compared to the experimental data of Meng et al. [4]. It is worth noting that simulation
319 results for the kinetic model from Galway [6] are not reported, due to its poor agreement
320 with experiments for the equivalence ratio of 0.5 used in this work. The mole fraction of
321 7×10^{-6} for C6-HP obtained in this work at 625 K is in excellent agreement with the
322 predictions of the kinetic model from Nancy, especially considering the discrepancy factor of
323 6 previously reported in the literature between experiments and simulations [4].
324 Considering that the signal at m/z 116 is mainly due to HyCE, its mole fraction was calculated
325 using the peak area of m/z 116, and by taking 16.7 Mb as its partial PICS using Bobeldijk's
326 method [40]. The mole fraction agrees within a factor of 2 with the previous mole fraction
327 from Meng et al. [4] (see Figure 4). The C6-HP/HyCE mole fraction ratio of 0.2 ± 0.1
328 obtained in this work is in line with the predicted mole fraction ratio of 0.1 using the kinetic
329 model from Nancy [4].
330



331
332 *Figure 4. Comparison of the calculated mole fraction of C6-HP (left) and HyCE (right) from the kinetic model from Nancy*
333 *[4] (black line), the GC experimental measurements of Meng et al. [4] (open dots), and the experimental measurements from*
334 *this work (red dots).*

335
336 Figure 5 illustrates the comparison between the TPES of m/z 130 obtained and the simulated
337 spectra of AnKHP isomers. The ionization threshold is around 8.9 eV, slightly lower than the
338 value reported by Xie et al. [8]. However, there is a small signal below 9.0 eV visible in the
339 TIY curve of m/z 130. Despite a low signal-to-noise ratio, the experimental TPES of m/z 130 is
340 relatively well-fitted by a convolution of the simulated PES of the lowest-energy conformers
341 of 5-hydroperoxyhexen-3-one and 3-hydroperoxyhexen-5-one. The fit yields a
342 5-hydroperoxyhexen-3-one:3-hydroperoxyhexen-5-one signal ratio of 1.0 ± 0.2 :
343 1.0 ± 0.2 within a 2σ confidence interval (see Figure 5), after moderately shifting the

344 simulated spectra by ~ 30 and ~ 70 meV from their respective calculated AIE at the CBS-QB3
345 level of theory.

346 By assuming a similar PICS for both isomers, the ratio derived from experimentation is
347 higher than the predicted mole fraction ratios of 1:0.5 and 1:0.2 from the kinetic models of
348 Nancy [4] and Galway [6], respectively. It is worth noting that this comparison assumes equal
349 transition strength between the isomers and neglects the effects that autoionization might
350 have on the different isomers . As mentioned in the theoretical methods, weak FC
351 overlap integrals between the vibrational ground states of the initial and final states
352 introduce a level of uncertainty that affects the reliability of the results. Nevertheless, the
353 underprediction of 5-hydroperoxyhexen-3-one's presence aligns with the experimental
354 observations made by Xie et al. [8].

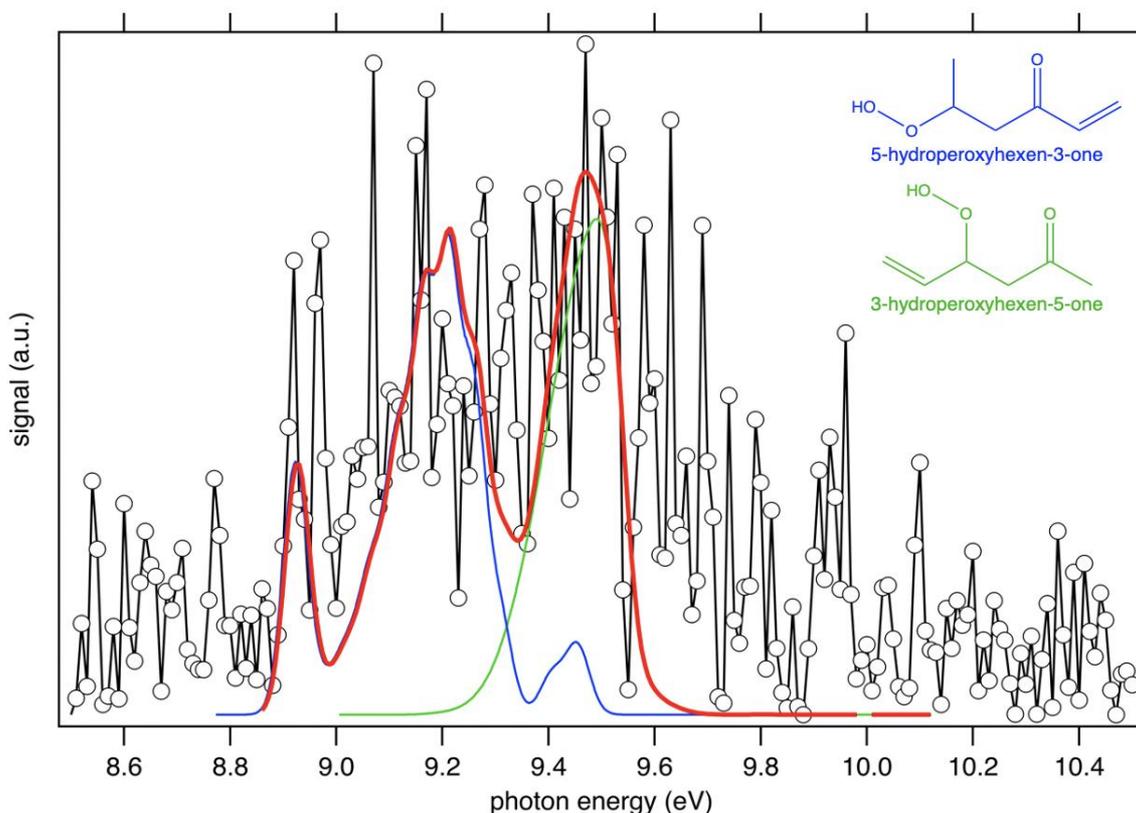
355 Furthermore, because of the flexible structure of AnKHP isomers, a rigorous conformer
356 analysis was performed using electronic structure calculations at the M06-2X-D3/aug-cc-
357 pVTZ level of theory. Figure S1 shows a conformational analysis performed for the AnKHP
358 isomer, 3-hydroperoxyhexen-5-one, revealing that its lowest-energy conformer has a
359 calculated AIE lower by 350 meV than the value reported by Xie et al. [8]. Using this level of
360 theory, 45 conformers were analyzed, and the maximum AIE difference among them was
361 found to be 1.35 eV (8.26 – 9.61 eV).

362 The structure analysis identified 33 neutral 5-hydroperoxyhexen-3-one conformers, and
363 their AIE, electronic energy, and expected Boltzmann fractions at $T = 625$ K are summarized
364 in Figure S2. The analysis revealed that the maximum AIE difference among the conformers
365 is 0.9 eV (8.83 – 9.73 eV). Out of the 33 conformers, three have small energy difference (less
366 than 50 meV), and the two lowest-energy conformers have almost the same energy but
367 distinct structures and AIE (see Figure S2). The lowest-energy conformer has an AIE that
368 agrees well with the value reported by Xie et al. [8]. However, when performing FCF
369 simulations, it was observed that the simulated spectrum of the second lowest-energy
370 conformer of 5-hydroperoxyhexen-3-one overlaps with the simulated spectrum of the
371 lowest-energy conformer of 3-hydroperoxyhexen-5-one. By substituting the simulating
372 spectrum of 3-hydroperoxyhexen-5-one with that of the second lowest-energy conformer of
373 5-hydroperoxyhexen-3-one, a similar fit with a ratio of $1.0 \pm 0.2 : 1.0 \pm 0.1$ as shown in
374 Figure 5 can be achieved (see Figure S3). This indicates that providing an accurate ratio of
375 5-hydroperoxyhexen-3-one to 3-hydroperoxyhexen-5-one is challenging due to potential

376 contributions from different conformers of 5-hydroperoxyhexen-3-one and a low signal-to-
377 noise ratio.

378 A comparison between the integral of the simulated spectra shown in Figure 5 and the TIY of
379 m/z 130 is provided in the SM (see Figure S4). The weighted fit using the integral of the
380 simulated spectra of 5-hydroperoxyhexen-3-one and 3-hydroperoxyhexen-5-one leads to a
381 signal ratio of 1.0 : 1.0, similar to the one found in the TPES analysis of Figure 5. Thus, it can
382 be confidently stated that the predictions of the kinetic models in the literature
383 underestimate the presence of 5-hydroperoxyhexen-3-one.

384 In the kinetic model from Nancy [4], the rate constants for the reaction 1-hexene + OH are
385 set equal to the values suggested by Zádor et al. [42] for propene. When it comes to 1-
386 hexene, this reaction forms allylic radicals (E) which eventually produce AnKHP (see Figure
387 1). The rate constant of H-abstraction from the CH_2 group closest to the unsaturated bond
388 forms hex-1-en-3-yl which leads to 5-hydroperoxyhexen-3-one. However, this H-abstraction
389 reaction is slower than the formation of hex-1-en-5-yl leading to 3-hydroperoxyhexen-5-one.
390 However, our calculations at the CBS-QB3 level of theory indicate that the energy required
391 to break the bond is about 20% less when abstracting hydrogen from the CH_2 group closest
392 to the unsaturation than from the secondary C-H bond site. It could be valuable to
393 individually assess the rate constants of the hexene and OH reaction to determine if this
394 could account for the observed underestimation of 5-hydroperoxyhexen-3-one. This should
395 be done in combination with an inspection of the kinetics of hex-1-en-3-yl + HO_2 , which is
396 the main sink of this allylic radical. An important overprediction of the decomposition
397 products from hex-1-en-3-yl + HO_2 (unsaturated aldehydes such as hexenal and acrolein)
398 has been shown in Meng et al. [4].



400

401

402 *Figure 5. TPES of m/z 130 (open dots) compared to simulated spectra of the lowest-energy conformer of 5-*
 403 *hydroperoxyhexen-3-one (blue line) and 3-hydroperoxyhexen-5-one (green line). The thick red line is the result of a weighted*
fit (see text for details).

404

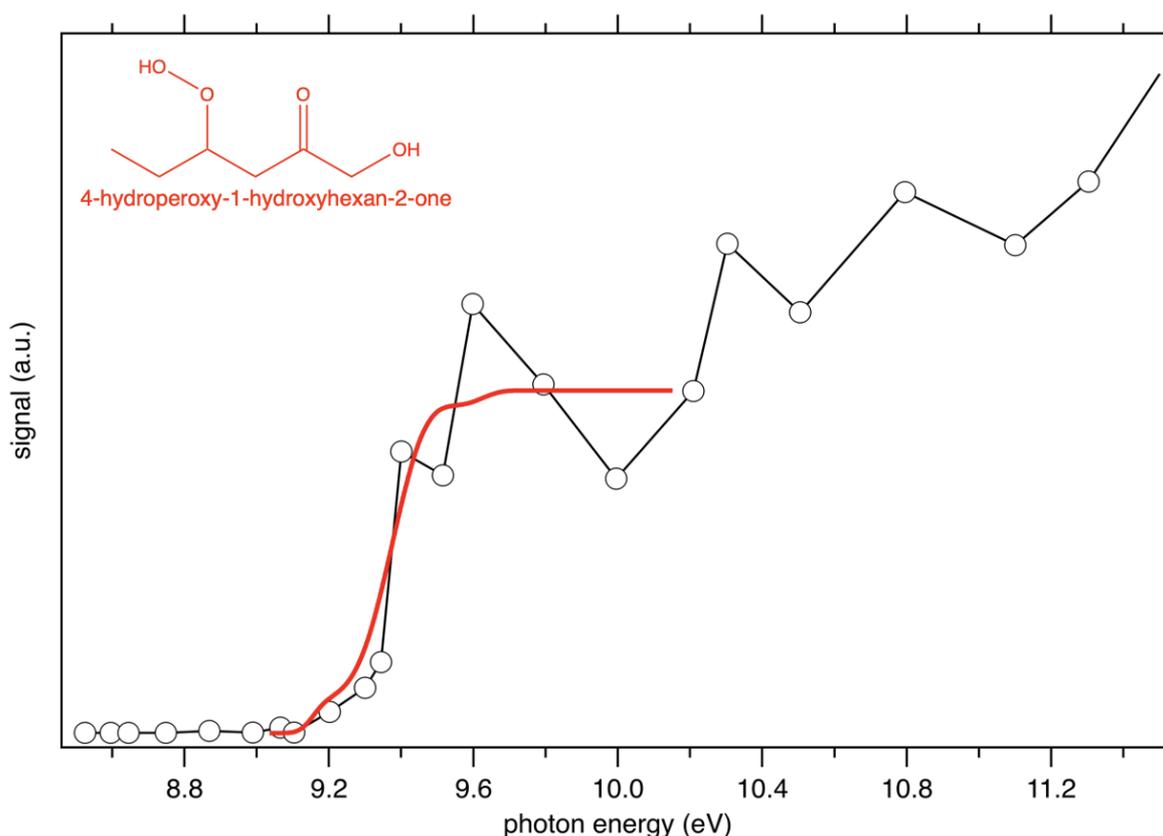
405 In the current work, no signal was detected at m/z 148 for HyKHP ($C_6H_{12}O_4$). This lack of
 406 detection can be attributed to a lower sensitivity compared to the study by Xie et al. [8]. In
 407 their study, the signal ratio between m/z 130 and m/z 148 indicated that m/z 148 was 15
 408 times lower than m/z 130, causing the signal to be overshadowed by noise in the registered
 409 mass spectra of the current work. Additionally, the temperature used in the current
 410 experiment (625 K) was slightly higher than the temperature used in Xie et al.'s study [8]
 411 (600 K). According to the kinetic model found in the literature, this lower working
 412 temperature in the study by Xie et al. [8] favors the formation of HyKHP over AnKHP.

413 Therefore, the theoretical calculations on HyKHP isomers performed in this work are used to
 414 analyze the TIY curve of m/z 148 presented in Xie et al. [8]. The addition of a hydroxyl group
 415 made the analysis of HyKHP isomers more challenging, resulting in the calculation of over
 416 100 conformers for each of the four isomers considered in Xie et al. [8]. Table S3 compares
 417 the AIE calculated by Xie et al. [8] with those calculated in this study, and strong

418 disagreements were found between the two sets of calculations for all isomers, except for 4-
419 hydroperoxy-2-hydroxyhexan-1-one.

420 According to our analysis, 4-hydroperoxy-1-hydroxyhexan-2-one, the most abundant isomer
421 predicted by kinetic models in the literature, is the only one whose AIE matches the TIY
422 ionization threshold of m/z 148 estimated at 9.20 eV in Xie et al. [8]. Additionally, the
423 simulated TIY obtained by integration of the calculated FCF of 4-hydroperoxy-1-
424 hydroxyhexan-2-one matches the beginning of the TIY curve well (see Figure 6). Therefore, it
425 is possible to conclude, based on available data, that 4-hydroperoxy-1-hydroxyhexan-2-one
426 is the dominant HyKHP isomer, this conclusion is in agreement with the predictions of the
427 kinetic model.

428



429

430 *Figure 6. TIY curve of m/z 148 (open dots) from Xie et al. compared to a simulated spectrum of 4-hydroperoxy-1-*
431 *hydroxyhexan-2-one (red line).*

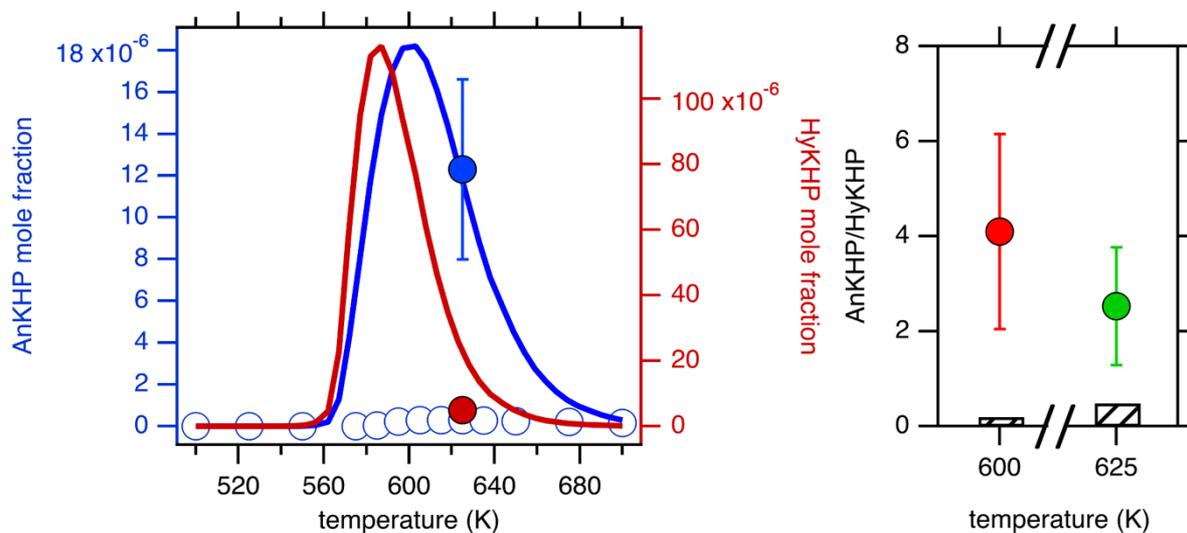
432

433 In this study, AnKHP and HyKHP were quantified at 625 K using the same quantification
434 method previously applied to C6-HP and HyCE. The quantification of AnKHP was performed
435 using the peak area of m/z 130, with the assumption of no significant fragmentation upon
436 photoionization. The lack of a peak at m/z 97, which would have matched a $C_6H_9O^+$ fragment

437 resulting from AnKHP fragmentation with HO₂-loss, supports this assumption. The total PICS
438 of C₆H₁₀O₃ was estimated to be 25.2 Mb at a photon energy of 10.6 eV, and this value was
439 used in the quantification of AnKHP.

440 As for HyKHP, no peak was detected at m/z 148, but a signal was observed at m/z 115,
441 corresponding to the loss of an HO₂ group from HyKHP. It is worth noting that the higher
442 temperature used in this study might have caused increased fragmentation of the m/z 148
443 ion, contributing to its non-detection in the current mass spectra. This phenomenon could
444 also explain why m/z 148 was not identified. The signal of m/z 115 was utilized to quantify
445 HyKHP, assuming a partial PICS of a C₆H₁₁O₂⁺ fragment, estimated to be 12.3 Mb at 10.6 eV.
446 Experimental results revealed an AnKHP/HyKHP ratio of 2.5 ± 1.2 at 625 K, aligning well with
447 the ratio of 4.1 by Xie et al. [43] at 600 K. When compared with the predictions from the
448 kinetic model provided by Nancy [4], it was confirmed that the AnKHP/HyKHP ratio is
449 underpredicted. The discrepancy can be visualized in Figure 7 (right), illustrating the
450 comparison between experimental findings and model predictions.

451



452
453 *Figure 7. (left) Simulated mole fraction profile (lines) of AnKHP (blue) and HyKHP (red) from the kinetic model of Nancy*
454 *[4] compared to the experimental mole fraction measured in this work (full dots) and by MS in Meng et al. [4] (open dots);*
455 *(right) Experimental AnKHP/HyKHP ratio at 600 K from Xie et al.[8] (red dots) and at 625 K from this work (green dots)*
456 *compared to the predictions of the kinetic model from Nancy (bars) [4].*

457
458 Figure 7 (left) displays the experimental mole fraction of AnKHP at 625 K. This result aligns
459 well with the predictions from the kinetic model by Nancy [4], yielding a value of 12 ppm.
460 However, the same model falls short according to the findings of Meng et al. [4], who
461 reported an underestimation by a factor of 25.

462 Interestingly, Figure 7 (left) also highlights an overprediction by the model for HyKHP,
463 overestimating it by a factor of 5. This discrepancy contributes to the higher observed
464 experimental between AnKHP and HyKHP, as depicted in Figure 7 (right).

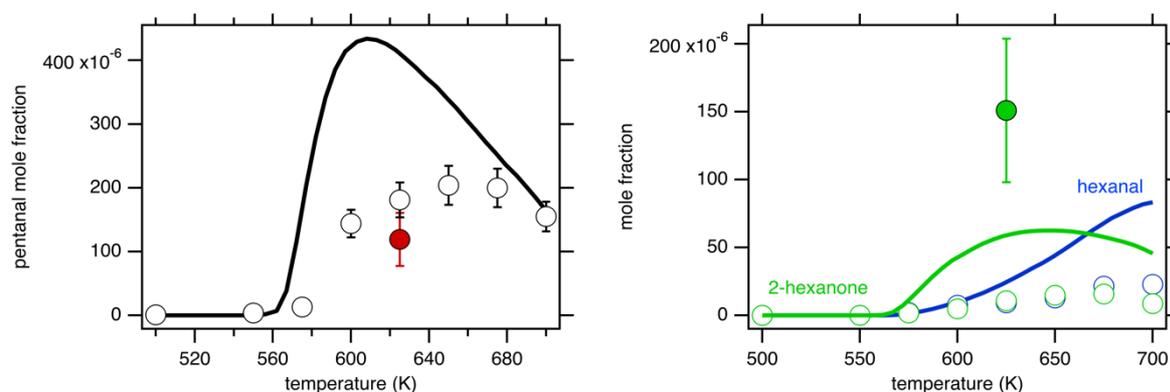
465 These findings reinforce the observations made by Xie et al. [8], the chain branching
466 pathway through the formation of AnKHP dominates the low-temperature chemistry,
467 contrary to the predictions from the kinetic models in the literature.

468 Xie et al. [8] speculated that the discrepancy might be linked to the competition between
469 two chemical mechanisms: the Waddington reaction and the chain branching process
470 through HyKHP. Stark and Waddington [17] previously suggested a reaction pathways
471 involving hydroxyperoxyradicals that leads to the formation of radicals and aldehydes, like
472 pentanal (m/z 86).

473 The experimental mole fraction of pentanal at 625 K, depicted in Figure 8 (left), is 119 ppm.
474 While this is overpredicted by a factor of 3.5 by the kinetic model, it aligns with previous
475 experimental data from Meng et al. [4]. This overprediction applies to both pentanal and
476 HyKHP.

477 However, it's important to recognize that simply reevaluating the branching ratio of the
478 Waddington channel and the HyKHP chain branching channel may not resolve the
479 inconsistency between the simulations and experimental results concerning the
480 AnKHP/HyKHP ratio. This realization suggests that more detailed and nuanced
481 understanding may be required to bridge the gap between theory and experimental
482 observation.

483



484

485 *Figure 8. (left) Simulated mole fraction profile (black line) of pentanal from the kinetic model of Nancy [4] compared to the*
486 *experimental mole fraction calculated in this work (red dot) and from Meng et al. [4] (open dots) ; (right) Simulated mole*
487 *fraction profile (line) of hexanal (blue) and 2-hexanone (green) from the kinetic model of Nancy [4] compared to the*
488 *experimental mole fraction measured in this work (green dot) and GC ones from Meng et al. [4] (open dots).*

489
490 Hydroxy alkyl radicals (ROH) produced by the OH-addition to 1-hexene have two main
491 pathways: they can react with molecular oxygen or undergo a two-step isomerization
492 process, as shown in Figure 1. The isomerization has an inhibiting effect because it can lead
493 to the creation of unreactive HO₂ radicals, hexanal, and 2-hexanone (m/z 100).

494 When comparing the predicted mole fraction of hexanal and 2-hexanone with experimental
495 data, the kinetic model seems to overpredict these values (see Figure 8 (right)). In this
496 particular study, the experimental mole fraction of 2-hexanone was measured at 151 ppm at
497 625 K, which not only contrasts with previous experimental values but is also underpredicted
498 by nearly a factor of 3 (see Figure 8).

499 Unfortunately, the formation of hexanal couldn't be thoroughly analyzed in this study
500 because it overlaps structurally with 2-hexanone (as referenced in Figure S5). However,
501 previous experimental mole fractions of hexanal have also been found to be slightly
502 overpredicted by the kinetic model.

503 These inconsistencies suggest that a reevaluation of the branching ratio between the
504 isomerization and O₂-addition of ROH radicals might be necessary. According to a reaction
505 flux analysis using the kinetic model from Nancy, the O₂-addition reaction currently seems to
506 be ten times faster than the isomerization towards hexan-2-one. This discrepancy might be
507 an underlying reason for the overprediction of HyKHP and warrants further investigation to
508 align the kinetic model with experimental observations.

509

510 CONCLUSION

511 In this study, the SVUV-PEPICO technique was employed for the first time to investigate
512 1-hexene LTO in a near-atmospheric JSR at a fixed temperature of 625 K and an equivalence
513 ratio of 0.5. The isomeric structures of the primary hydroperoxides, cyclic ethers, and
514 ketohydroperoxides were refined, with a thorough study of the conformational landscape,
515 and their experimental mole fractions were compared to predictions from a kinetic model
516 found in the literature.

517 The results indicate that existing kinetic models inaccurately predict the formation of HyKHP.
518 However, the current work demonstrates that the formation of AnKHP, along with the ratio
519 of unsaturated C6 hydroperoxides to HyCE, aligns closely with model predictions. It can,
520 therefore, be concluded that the overprediction of HyKHP is not due to the branching ratio

521 between H-atom abstraction and OH radical addition reactions on 1-hexene or the
522 competition between the Waddington mechanism and the chain branching process through
523 HyKHP. Conversely, the model appears to underestimate the formation of 2-hexanone, a
524 product of the isomerization of ROH radicals. This finding suggests that reevaluating the
525 branching ratio of these radicals might resolve the discrepancy between the model's
526 predictions and the experimental data concerning the AnKHP/HyKHP ratio.

527

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534

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