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# 1-Hexene Ozonolysis across Atmospheric and Combustion Temperatures via Synchrotron-Based Photoelectron Spectroscopy and Chemical Ionization Mass Spectrometry

Caroline Smith Lewin, Avinash Kumar, Olivier Herbinet, Philippe Arnoux, Rabbia Asgher, Shawon Barua, Frédérique Battin-Leclerc, Sana Farhoudian, Gustavo Garcia, Luc-Sy Tran, et al.

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1 **1-Hexene Ozonolysis Across Atmospheric and Combustion Temperatures via Synchrotron-**  
2 **Based Photoelectron Spectroscopy and Chemical Ionization Mass Spectrometry**

3  
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### **Abstract**

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### **Keywords**

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This study investigates the complex interaction between ozone and the autoxidation of 1-hexene over a wide temperature range (300 – 800 K), overlapping atmospheric and combustion regimes. It is found that atmospheric molecular mechanisms initiate the oxidation of 1-hexene from room temperature up to combustion temperatures, leading to the formation of highly oxygenated organic molecules. As temperature rises, the highly oxygenated organic molecules contribute to radical-branching decomposition pathways inducing a high reactivity in the low temperature combustion region, i.e. from 550 K. Above 650 K, the thermal decomposition of ozone into oxygen atoms becomes the dominant process, and a remarkable enhancement of the conversion is observed due to their diradical nature, counteracting the significant negative temperature coefficient behavior usually observed for 1-hexene. In order to better characterize the formation heavy oxygenated organic molecules at the lowest temperatures, two analytical performant methods have been combined for the first time: synchrotron-based mass-selected photoelectron spectroscopy and orbitrap chemical ionization mass spectrometry. At the lowest studied temperatures (below 400 K), this analytical work has demonstrated the formation of the ketohydroperoxides usually found during the LTC oxidation 1-hexene, as well as of molecules containing up to 9 O-atoms.

Autoxidation, Highly Oxygenated Organic Molecules, Synchrotron Radiation, Photoelectron Spectroscopy, Quantum Chemistry, Chemical Ionization Mass Spectrometry

## 56 Introduction

57 The intricacies of the combustion of organic compounds at low-temperature, i.e.  
58 from 550 K, so called Low-Temperature Combustion (LTC), are fundamental in  
59 comprehending environmental dynamics and promoting energy efficiency. A key aspect of  
60 this is the autoxidation of fuel components and of volatile organic compounds (VOCs). This  
61 process has repercussions on both atmospheric pollution and combustion pathways <sup>1-7</sup>.  
62 Central to VOC oxidation are repeated radical-chain reactions, initiated by the formation of  
63 carbon-centered radicals (R) from organic species (RH) <sup>8-10</sup>.

64 The rate at which VOCs oxidize is notably temperature dependent. Above 500 K, the  
65 oxidation accelerates via sequences of intramolecular H-shift/O<sub>2</sub>-addition reactions  
66 producing, via successive isomerization of peroxy (ROO) radicals into hydroperoxyalkyl  
67 (QOOH) radicals, oxygenated intermediates whose exothermic decomposition enriches the  
68 radical pool <sup>11</sup>. However, for most of the aliphatic hydrocarbons, there is a twist: beyond a  
69 certain temperature threshold  $\sim 650$  K, the negative temperature-coefficient (NTC)  
70 emerges <sup>12</sup>, causing an unexpected dip in rates of branching reactions responsible for  
71 propagation (QOOH oxidation, cyclic ether decomposition) as temperatures soar further  
72 <sup>13,14</sup>. The implications of this NTC behavior are substantial, shaping both the efficiency and  
73 reliability of combustion, and consequently guiding the evolution of energy devices.

74 At ambient temperature, it was historically posited that VOC autoxidation had  
75 minimal impact at ambient temperatures, stemming from the belief that peroxy ROO radical  
76 reactions were primarily terminated by chain-ending events and that high C-H bond  
77 strengths prevent fast ROO H-migrations under standard conditions <sup>15</sup>. A more detailed  
78 analysis, however, reveals that the series of ROO  $\rightarrow$  QOOH reactions lead to much higher  
79 oxygen contents with the formation of highly oxygenated organic molecules (HOMs) usually  
80 defined as containing six or more oxygen atoms <sup>16</sup>. This transformation is influenced by  
81 temperature and the presence of substituents, such as -OH, C=C, and C=O, in ROO radical  
82 structures <sup>17,18</sup>. Although there exists other oxidation mechanisms in the troposphere, ozone  
83 (O<sub>3</sub>) initiated oxidation of VOC via ozonolysis has been shown to have the highest HOM  
84 yields <sup>16</sup>.

85 In contrast to its relevance in atmospheric sciences, O<sub>3</sub> has only recently been  
86 identified as a species of interest in combustion chemistry <sup>19</sup>. In the case of saturated  
87 reactants, O<sub>3</sub> acts as a promoter for oxidation reactions at combustion-relevant

88 temperatures due to the production of O-atoms from O<sub>3</sub>-thermal decomposition. O-atoms  
89 readily assist in H-abstraction to initiate VOC oxidation at temperatures lower than in LTC  
90 chemistry<sup>20–23</sup>. For fuels presenting a NTC behavior, this can be significantly reduced by the  
91 presence of O-atoms, as it has been shown in the case of dimethylether<sup>24</sup>,  
92 methylhexanoate<sup>25</sup>, and propane<sup>23</sup>. In the case of unsaturated reactants, the interest of  
93 ozonolysis mechanism for combustion has received much less attention<sup>26–28</sup>. While in this  
94 case the impact of O<sub>3</sub> is not limited to merely hastening reactions as ozonolysis profoundly  
95 alters kinetic networks by modifying molecular structures, the influence of O<sub>3</sub> on fuel  
96 reactivity has only been investigated for ethylene<sup>29</sup> and methylcrotoate<sup>30</sup>, two fuels which do  
97 not present a NTC behavior.

98         The chemistry of autoxidation systems, particularly those initiated by O<sub>3</sub>, is highly  
99 complex. This complexity arises from the formation of numerous reactive intermediates that  
100 can be present in only trace amounts and that result from various radical reaction pathways  
101 influenced by temperature. This work presents an investigation over a wide temperature  
102 range (300–800 K) of the influence of O<sub>3</sub> addition on the autoxidation chemistry of 1-  
103 hexene (C<sub>6</sub>H<sub>12</sub>), a representative aliphatic compound in surrogate gasoline fuels<sup>31–33</sup>,  
104 presenting a notable NTC behavior<sup>34</sup>. The accuracy of chemical kinetic models depends on  
105 experimental data used for both identifying and structurally characterizing these species;  
106 however, obtaining reliable data is difficult using only a single analytical tool. As this work  
107 especially focuses on product identification, an orbitrap mass spectrometer equipped with a  
108 multi-scheme chemical ionization inlet (O-MION-CIMS) has been used to detect trace species  
109 such as HOMs while a spectrometer using a photoelectron photoionization coincidence  
110 scheme coupled to synchrotron radiation (SVUV-PEPICO) has been used to detect lower  
111 oxygenated species.

112

### 113         **Experimental and theoretical methods**

114         This part describes the three experimental setups, a Jet-Stirred Reactor (JSR)<sup>35</sup> with  
115 analysis using gas chromatographs (GCs), a JSR coupled to mass spectrometry with i<sup>2</sup>PEPICO  
116 spectroscopy, and a Tubular Flow Reactor (TFR) with orbitrap Chemical Ionization Mass  
117 Spectrometry (O-CIMS), as well as the related theoretical calculations needed to analyze the  
118 obtain data.

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### *JSR + GCs*

This spherical JSR, used by LRGP to study the oxidation of 1-hexene is made from fused silica, has a volume of roughly 81.2 cm<sup>3</sup>, and is maintained at isothermal and isobaric conditions.<sup>35</sup> Gas blends of fuel and O<sub>2</sub> with and without O<sub>3</sub> continuously flows in, with a significant inert gas dilution to counteract the temperature variations from the exothermic oxidation. The reactants are introduced into the JSR using helium as a transport gas, via four central cross-shaped nozzles. These nozzles are designed to enhance turbulence and ensure a homogeneous mixture. There is a preheating section before the reactor's entrance to diminish internal temperature variations. Both the JSR and this preheating section are heated by thermocoax resistances. A K-type thermocouple, located near the center of the JSR in a glass sleeve, monitors the temperature, boasting an accuracy of about 1%. Gases resulting from oxidation in the JSR are conveyed through heated tubes to a pair of GCs for examination. These tubes are made of stainless steel, with an external diameter of 1/8 inch and a length of approximately 5 meters.

At LRGP, the gas leaving the reactor are analyzed thanks to two GCs. The first GC has a carbosphere-packed column and utilizes a thermal conductivity detector (TCD) to measure lightweight and permanent gas species. The second GC comes with a Q-Bond capillary column and a flame ionization detector (FID) which is preceded by a methanizer. This GC specializes in measuring organic compounds. The methanizer contains a hydrogenation Ni bed catalyst. A mix of buffer gas and H<sub>2</sub> (also utilized for the FID) passes through this catalyst, turning species with carbonyl groups into their respective alkanes and converting CO and CO<sub>2</sub> into methane. To identify different species, the GC with the Q-Bond capillary column was paired with a quadrupole mass spectrometer. Ion generation was achieved using electron impact ionization at 70 eV.

Calibrations for FID and TCD were carried out with gaseous standards supplied by Air Liquide for O<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub>. Any other species that the FID detected were calibrated using the effective carbon number (ECN) approach.<sup>36</sup> Calibration factors for these species were derived from those of the calibrated ones, factoring in their effective carbon number. The estimated relative uncertainties for species calibrated with gaseous standards stood at

151 ±5%. For species calibrated via the ECN approach, the uncertainties were estimated to be  
152 around ±10%.

### 153 *JSR + i<sup>2</sup>PEPICO spectroscopy*

154 The same heated JSR was positioned within the SAPHIRS chamber's permanent end-  
155 station,<sup>37</sup> found at one of the DESIRS VUV beamline's monochromatized branches at the  
156 SOLEIL synchrotron.<sup>38</sup> There, the JSR's internal gas mixture was extracted through a  
157 micrometer-sized hole, facilitating a molecular-beam expansion in the vacuum chamber with  
158 a pressure of approximately  $10^{-4}$  mbar. This chamber was linked through two sequential  
159 skimmers to the ionization chamber. This process produced a cooled molecular beam where  
160 the likelihood of reactive collisions was significantly reduced due to its low number density  
161 and dilution with helium. As a result, reactive intermediates were maintained throughout  
162 the expansion and made their way to the ionization chamber without any collisions.

163 Within the ionization chamber, the VUV synchrotron light targeted the gas mix,  
164 leading to the formation of photoelectrons and photoions. These were detected  
165 simultaneously by the double-imaging photoelectron/photoion (*i<sup>2</sup>PEPICO*) spectrometer  
166 known as DELICIOUS III.<sup>39</sup> These particles moved in opposite directions, diverging based on  
167 their kinetic energies before arriving at the velocity map imaging (VMI) spectrometer,  
168 forming circular patterns. The particles' times of arrival were documented. Using the  
169 electron's time of arrival as a benchmark, mass spectra were plotted. With the help of the  
170 VMI system and photoion-mass selection, a two-dimensional matrix of mass-selected  
171 photoelectron spectra (PES) could be created based on photon energy,<sup>40</sup> using the Abel  
172 inversion method. By choosing a specific kinetic energy range (100 meV in this study), the  
173 corresponding threshold photoelectron spectra (TPES) could be deduced, specifically within  
174 a photon energy span from 9.0 to 10.4 eV, advancing in 10 meV increments with each step  
175 taking 60 seconds. The error margins in TPES were calculated using a Poisson distribution of  
176 the photoelectron image pixel counts. This was carried through the image's Abel inversion  
177 transformation using standard error propagation equations. In TPES, the clarity of the signal  
178 can be affected by the occurrence of false coincidences when two or more ionization  
179 incidents happen nearly simultaneously. This can obscure the identification of lesser species  
180 when the actual coincidence signal aligns with the background's Poisson noise. In scenarios  
181 where the signal-to-background ratio is insufficient for an electron kinetic energy analysis,  
182 the total ion yield (TIY) for each mass is determined by integrating over all electron energies.

183 TPES provides a glimpse into the isomers' electronic structures. These isomers can be  
184 pinpointed by comparing them to the reference spectra of individual entities. If reference  
185 spectra are not present in existing studies, the PES of specific entities can be modeled using  
186 advanced theoretical computations.

187

#### 188 *TFR + O-CIMS*

189 Gas-phase ozonolysis initiated 1-hexene oxidation was studied in a borosilicate glass  
190 flow tube reactor (5 cm o.d. and 100 cm length) coupled with the multi-scheme chemical  
191 ionization inlet (MION, Karsa Inc.)<sup>41,42</sup> and an orbitrap MS (ThermoScientific Exploris 240).  
192 The MION inlet was operated with nitrate ( $\text{NO}_3^-$ ) ionization scheme. The 1-hexene (Sigma  
193 Aldrich >99% purity) was used from a premixed gas cylinder with a concentration of 100.6  
194 ppm diluted in scientific grade  $\text{N}_2$ . The  $\text{O}_3$  in the experiments was produced by an ozone  
195 generator (UVP Ozone Generator, Analytik Jena US), from a 2 SLPM flow of purified air  
196 (AADCO 737-15), which was also utilized as the bath gas in the experiments. A total flow rate  
197 of around 15 SLPM was applied, with the reaction time controlled by a moveable injector for  
198 reagent gas introduction and resulted in 1.5 to 9.2 seconds residence times. All flows were  
199 regulated by calibrated mass flow controllers (Alicat Scientific). In a set of experiments  $\text{D}_2\text{O}$   
200 was added to the gas stream to provide further verification on the detected product  
201 identities. The  $\text{C}_5\text{H}_9\text{O}_7$  radical and its OH loss product  $\text{C}_5\text{H}_8\text{O}_6$  both exchanged 2 H to D, and  
202 the preceding  $\text{C}_5\text{H}_9\text{O}_5$  radical 1 H to D, in accordance with their proposed production  
203 pathway (see Figure 3 in the main text). Importantly, the conversion of the reagent ion  
204 adduct  $\text{HNO}_3 \cdot \text{NO}_3^-$  to  $\text{DNO}_3 \cdot \text{NO}_3^-$  was complete, indicating that the H to D exchange of the  
205 reaction products also run to competition (i.e., every labile H-atom was quantitatively  
206 converted to D-atoms).

207

#### 208 *Theoretical calculations*

209 In this work, we utilized the Merck molecular force field MMFF94 methodology to  
210 create initial conformer structures for each isomer considered.<sup>43</sup> These were further refined  
211 using a superior theoretical approach, namely density functional theory (DFT) with the M06-  
212 2X-D3 functional.<sup>44</sup> This DFT functional was paired with the aug-cc-pVTZ Dunning's  
213 correlation consistent basis set,<sup>45</sup> enhanced with diffuse functions. Additionally, the zero-  
214 damped D3 dispersion correction developed by Grimme and colleagues<sup>46</sup> was integrated



215 into M06-2X. The refined neutral species structures then served as starting points for the  
216 ionic forms. We employed two-electron integrals with strict optimization criteria to  
217 guarantee the dependability of conformer energies and vibrational frequencies. These were  
218 computed within the harmonic approximation at the consistent theoretical level.

219 The refined individual structures underwent conformational averaging through  
220 Boltzmann weighting, considering electronic energies and a JSR temperature of 400 K. For  
221 this study, it's assumed that all reactants and products stabilize at 400 K. Additionally, the  
222 conformer distribution remains constant after expansion via the pinhole. To model  
223 transitions between the vibrational stages of the most stable neutral conformers and their  
224 ions, we used the time-independent adiabatic Hessian Franck-Condon (TI-AH|FC) model at  
225 400 K.<sup>47</sup> The derived stick spectrum was then combined with a Gaussian profile featuring a  
226 200 cm<sup>-1</sup> bandwidth, aligning with the experimental resolution. The adiabatic ionization  
227 energy (AIE) calculations were conducted at the CBS-QB3 theoretical level, originating from  
228 the foundational state of both neutral and ionic forms, and using the refined DFT structures.  
229<sup>48,49</sup> We aligned the 0-0 transition of the computed stick spectra to correspond with the  
230 experimental spectra, keeping within the energy calculation's uncertainty.

231 It's crucial to highlight that when examining flexible molecular constructs, such as  
232 hydroperoxides, the TPES analysis faces complications. These stem from the existence of  
233 vibrational modes with low frequencies. Often, these lead to minimal overlaps between  
234 vibrational wave functions, which dilutes the vibrational information. Combined with a  
235 diminished signal-to-noise ratio, potential erroneous peaks, and a considerable count of  
236 potential isomers, individual assignments become complex. Thus, while simulated spectra  
237 are helpful in deducing key elements from experimental spectra, they might not capture all  
238 conceivable molecular formations.

239

## 240 **Experimental Results and Theoretical Analysis**

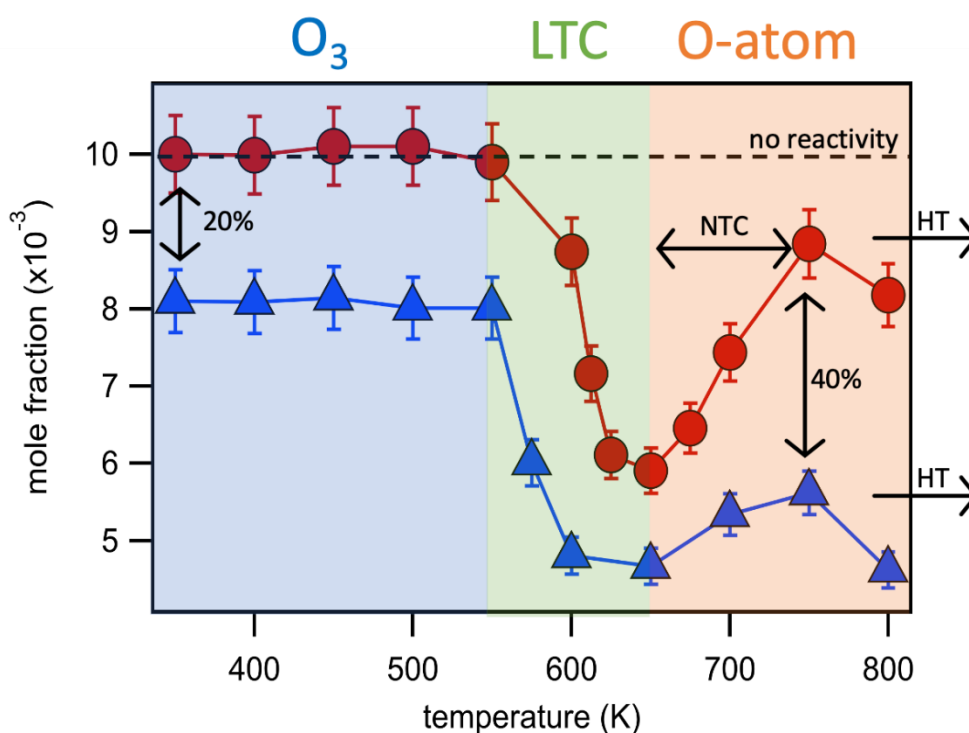
241 This part describes the results obtained for the temperature evolution of 1-hexene  
242 mole fraction in JSR and then focuses on the ozonolysis products measured both in TFR and  
243 JSR with discussing only a few products measured by GC; the full details of product  
244 formation will be given in a future paper.

245

246 *JSR 1-hexene reactivity*

247 This research first examined the reactivity of 1-hexene during its JSR oxidation with  
 248 and without O<sub>3</sub> in JSR using GCs. Experiments were conducted over a temperature range of  
 249 350-800 K with constant parameters: pressure at 800 torr, equivalence ratio of 0.5, and a  
 250 0.01 initial mole fraction of 1-hexene diluted in He. Residence times were 2.0 s (without O<sub>3</sub>)  
 251 and 2.5 s (with O<sub>3</sub>). An O<sub>3</sub> mole fraction of 1,000 ppm was introduced through an O<sub>3</sub>  
 252 generator using an O<sub>2</sub>/He mixture, and its mole fraction quantified by an O<sub>3</sub> analyzer (a  
 253 scheme of the experimental setup can be found in Smith Lewin et al. <sup>27</sup>). The overall mole  
 254 fraction of O<sub>2</sub> is less than 10%.

255 Reactants and products from 350 to 800 K were identified and using two GCs.  
 256 1-hexene mole fraction profiles are depicted in Figure 1. The O<sub>3</sub>-profile is not shown because  
 257 it is almost consumed at 350 K in its reaction with 1-hexene via ozonolysis, despite having a  
 258 low rate coefficient ( $\sim 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ ).



259  
 260 **Figure 1.** Temperature evolution of the 1-hexene mole fraction as measured by GC during the oxidation  
 261 of a reactive gas mixture composed of 1-hexene/O<sub>2</sub>/He, with (blue triangles) and without (red dots) O<sub>3</sub> with  
 262 figures indicating the conversion yield due to O<sub>3</sub> addition. The blue- and orange-colored areas indicate the  
 263 temperature ranges where specific species contribute to the increased conversion of 1-hexene when O<sub>3</sub> is  
 264 added. The green area symbolizes the LTC zone.

265

266 Without O<sub>3</sub>, the results align with literature regarding the oxidation of 1-hexene<sup>34</sup>.  
267 The beginning of reactivity is observed at 550 K, indicating the transition into the LTC region.  
268 At this point, the conversion rate peaks at 40% when the temperature reaches 650 K.  
269 Following this, as the system enters the NTC zone, the fuel conversion dropping to as low as  
270 10% at 750 K. Subsequently, the reactivity increases significantly upon entering the high-  
271 temperature (HT) zone.

272 When O<sub>3</sub> is added, the 1-hexene consumption goes to 20% between 350 and 550 K  
273 compared to the case without O<sub>3</sub> where no reactivity is observed before 550 K. This  
274 enhancement remains consistent above 550 K. Above 650 K (in the NTC zone), the  
275 enhancement increases with temperature, up to 40% at 750 K, making a significant boost in  
276 reactivity compared to the non-O<sub>3</sub> case. This enhancement is more marked than for other  
277 fuels (dimethylether<sup>24</sup>, methylhexanoate<sup>25</sup>, and propane<sup>23</sup>), for which such an O<sub>3</sub> effect was  
278 reported.

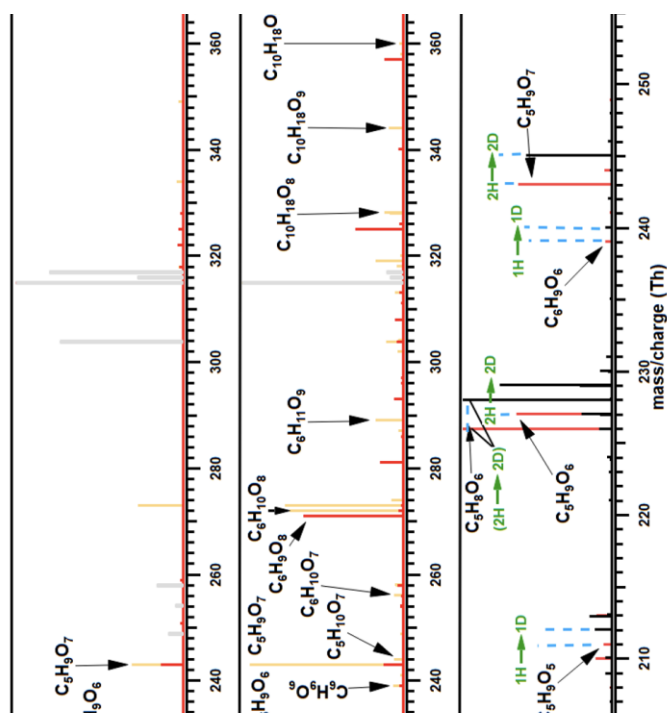
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#### 280 *1-hexene ozonolysis products in TFR*

281 To understand the 20% reactivity enhancement observed all along below 650 K,  
282 1-hexene oxidation initiated by O<sub>3</sub> was also studied at 300 K in an atmospheric pressure flow  
283 reactor coupled with an orbitrap mass spectrometer equipped with a multi-scheme chemical  
284 ionization inlet (O-MION-CIMS)<sup>41,42</sup>. A gas mixture consisting of bath gas air with various  
285 1-hexene and O<sub>3</sub> mole fractions was investigated in a TFR utilizing a moveable injector to  
286 achieve reaction times between 1.5 and 9.2 s. As shown in Figure 2, several HOMs and less  
287 oxygenated reaction products were promptly observed.

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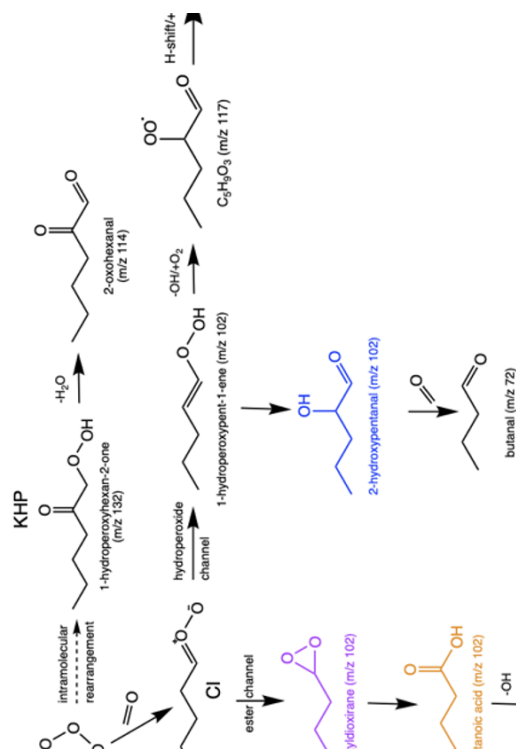


**Figure 2.**  $\text{NO}_3^-$  O-MION-CIMS mass spectra of 1-hexene +  $\text{O}_3$  oxidation products. **A)** At 1.5 seconds reaction time with  $[\text{C}_6\text{H}_{12}] = 0.5$  ppm (red) and  $[\text{C}_6\text{H}_{12}] = 1.69$  ppm (yellow). **B)** At 9.2 seconds reaction time with  $[\text{C}_6\text{H}_{12}] = 0.17$  ppm (red) and  $[\text{C}_6\text{H}_{12}] = 1.69$  ppm (yellow). **C)**  $\text{D}_2\text{O}$  addition experiments showing the expected  $\text{H} \rightarrow \text{D}$  substitution (see Figure 3). The inset shows the corresponding conversion of the reagent ion adducts  $\text{HNO}_3 \cdot \text{NO}_3^-$  to  $\text{DNO}_3 \cdot \text{NO}_3^-$  indicating the completeness of the  $\text{H}$  to  $\text{D}$  substitution. All spectra were measured at 300 K and atmospheric pressure of air with  $[\text{O}_3] = 0.2$  ppm. The  $\text{NO}_3^-$  is omitted from the given product ion-adduct labels. Gray color is used to label background peaks.

298 Under the low ROO conversion regime, *i.e.*, short reaction time and low reactant  
299 concentrations, the nitrate chemical ionization mass spectrum was dominated by a few  
300 peroxy radicals formed by autoxidation, and their apparent unimolecular termination  
301 products, *i.e.*, formed by an OH loss through abstraction from a carbon bearing an -OOH  
302 group<sup>16</sup>. While both ROO from OH and  $\text{O}_3$  initiated oxidation seemed to be apparent at  
303 longer reaction times (Figure 2b), (*i.e.*, with 6 C-atoms indicating OH involvement and 5 C-  
304 atoms signifying ozonolysis initiation, or a C-atom loss during the oxidation; Figure 3), the  
305 dominance of the ozonolysis-initiated oxidation was apparent at short timescales (Figure 2a).  
306 The most abundant ROO species observed was  $\text{C}_5\text{H}_9\text{O}_7$  and its OH termination product  
307  $\text{C}_5\text{H}_8\text{O}_6$ , formed via a pseudo-unimolecular pathway shown in Figure 3, and supported by the  
308  $\text{D}_2\text{O}$  addition experiments (see Figure 3 and the SM). At longer residence times the  
309 complexity quickly increases, leading to a multitude of radical and closed-shell reaction  
310 products including the ROO accretion products ROOR with 10 C-atoms (Figure 2b). Also, a

311  $C_6H_9O_8$  radical becomes prominent, indicating the presence of cyclohexene<sup>51,52</sup>, which was  
 312 found as a minor impurity in the 1-hexene cylinder by a proton-transfer-reaction mass  
 313 spectrometry (PTRMS) analysis.

314



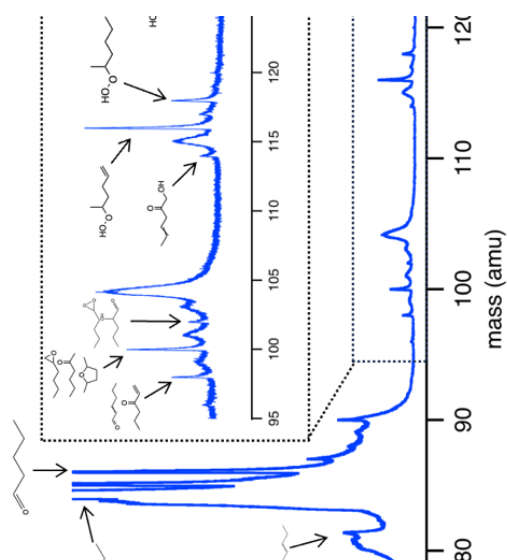
315  
 316 **Figure 3.** Simplified reaction network of 1-hexene ozonolysis proposed in this work based on experimental  
 317 observations. Cl, KHP, and POZ refer to Criegee intermediates, ketohydroperoxides, and primary ozonide  
 318 respectively. Dotted arrows refer to minor channels. The red circles indicate the H-atoms that were exchanged  
 319 in the  $D_2O$  addition experiments (see Figure 2c and SM for more details).

320

### 321 1-hexene ozonolysis products in JSR

322 The study of 1-hexene +  $O_3$  reaction between 350 K and 800 K in the JSR was also  
 323 conducted with a  $i^2$ PEPICO spectrometer available on the DESIRS VUV beamline at the  
 324 SOLEIL synchrotron (see more experimental details in SM). Figure 4 displays a typical mass  
 325 spectrum registered for a  $He/O_2/1$ -hexene mixture at 400 K. The molecular structure of the  
 326 chain-branching agents shown in Figure 4 was determined through the analysis of their  
 327 mass-selected threshold photoelectron spectra (TPES) measured using mass spectrometer  
 328 coupled with the  $i^2$ PEPICO spectroscopy.

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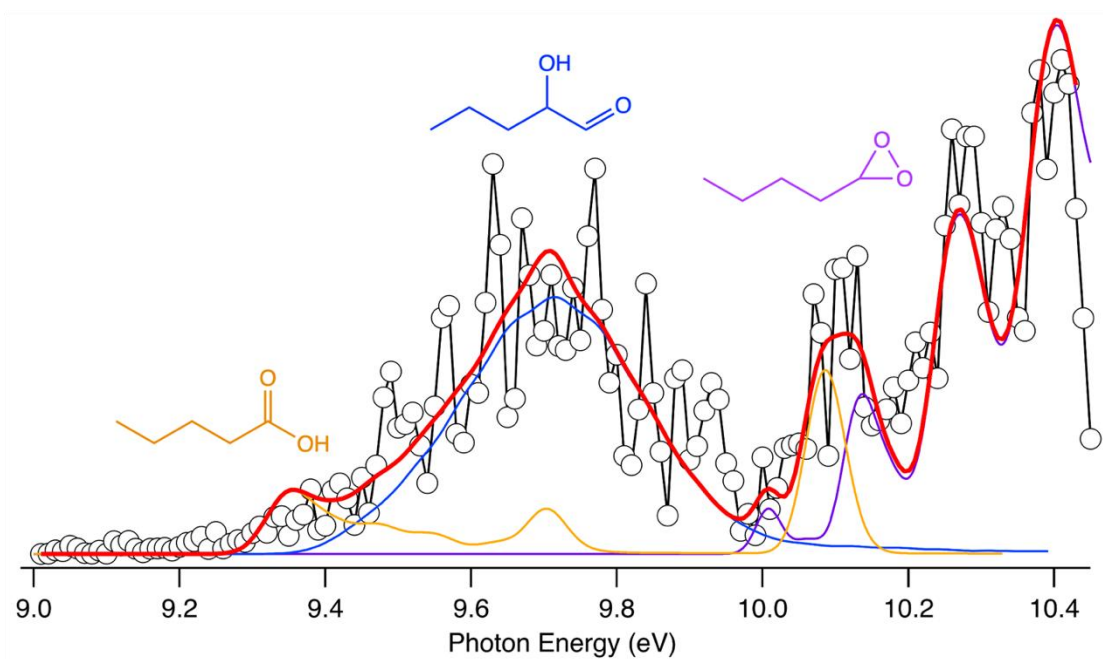


330  
 331 **Figure 4.** Typical mass spectrum recorded by synchrotron VUV photoionization of a He/O<sub>2</sub>/1-hexene gas mixture  
 332 at 400 K with the addition of 3,000 ppm of O<sub>3</sub> (blue line). The mass spectrum is integrated over the 9.0–10.4 eV  
 333 photon energy range. The inset shows a zoomed view of the expanded mass spectrum from 95 to 150 amu.  
 334 Because the vertical scale is adjusted to emphasize the low-intensity peaks, that of 1-hexene (*m/z* 84) and of its  
 335 7% <sup>13</sup>C isotopologue (*m/z* 85) are truncated. The structures of some already-known products and intermediates  
 336 based on the literature, are displayed along with combustion chain-branching agents that are the masses of  
 337 interest that have been identified in this work. See text for details.

338  
 339 Despite it was obtained at 400 K, the mass spectrum of Figure 4 reveals the presence  
 340 products and intermediates both from the O<sub>3</sub>-related kinetic network and from the LTC  
 341 chemistry, which is expected to start only above 550 K. For instance, the hydroperoxides  
 342 (*m/z* 116, 118, and 134) and ketohydroperoxides (*m/z* 130, 132, and 148) observed in Figure  
 343 4 with alkenyl (AnHP/AnKHP) or hydroxyl (HyHP/HyKHP) functional groups are well known  
 344 chain branching agents formed in the LTC of 1-hexene (see Figure S1)<sup>34,53</sup>.

345 As shown in Figure S2 in SM, the TPES for *m/z* 116, 118, 130, and 148, and the total  
 346 ion yield (TIY) of *m/z* 132 and 134, show good agreement with the simulated curves of the  
 347 isomers in Figure 4 despite low signal-to-noise ratios and the complexity related to the  
 348 simulation of vibronic transitions in floppy molecular systems<sup>54</sup>. Note that the identification  
 349 of the minor KHP, 5-hydroperoxyhexan-2-one, at *m/z* 132 is also validated by the presence  
 350 of methyl ethyl ketone at *m/z* 72 as a product of the KHP decomposition (Figure S3),  
 351 furthering confidence in the molecular structure findings.

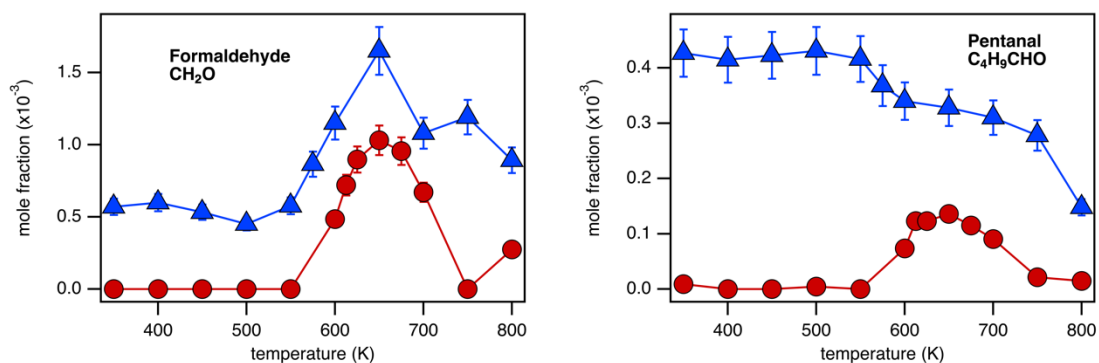
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*Figure 5. TPES of  $m/z$  102 (open dots) compared to simulated PES of the isomers considered in this work: 3-butyldioxirane (purple line), 2-hydroxypentanal (blue line), and pentanoic acid (orange line). The thick red line is a weighed combination of the simulated spectra using a 0.4:1.0:0.3 signal ratio (2-hydroxypentanal, 3-butyldioxirane, pentanoic acid).*

359 In 1-hexene ozonolysis oxidation, the formation of the primary ozonide (POZ), namely  
360 4-butyl-1,2,3-trioxolane, dissociates into two reactive Criegee Intermediates (CIs):  $\text{CH}_2\text{OO}$   
361 and  $\text{C}_4\text{H}_9\text{CHOO}$ , as seen in Figure 3. These concurrent dissociations produce formaldehyde  
362 ( $m/z$  30) and pentanal ( $m/z$  86) as co-products. The absence of a signal at  $m/z$  30 in Figure 4  
363 is due to the ionization energy of formaldehyde ( $\text{IE} = 10.88 \text{ eV}$ <sup>55</sup>) which falls outside the  
364 photon energy range explored in this study. Nevertheless, both formaldehyde and pentanal  
365 were quantified in appreciable amounts using GC (see Figure 6). There is no formation of  
366 both species without the introduction of  $\text{O}_3$  below 550 K and this acts as a direct proof of the  
367 ozonolysis mechanism.  
368

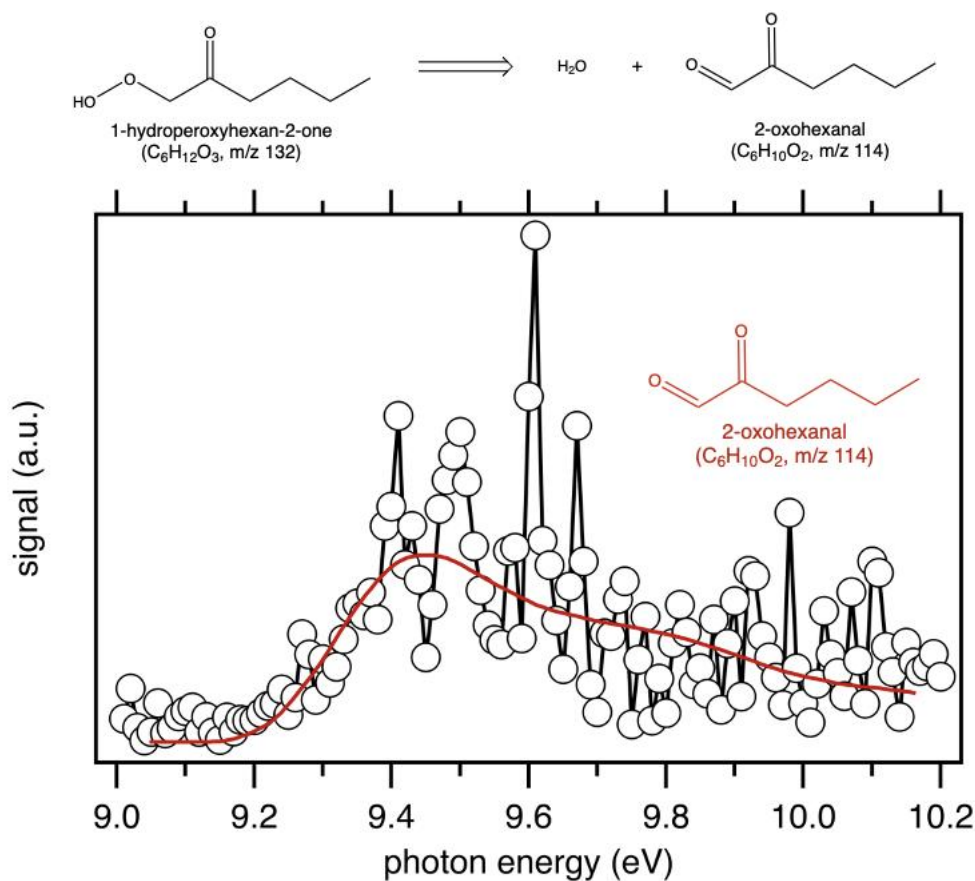


369  
 370 *Figure 6. Mole fraction of formaldehyde (left panel) and pentanal (right panel) recorded by GC as a*  
 371 *function of temperature without (red circles) and with (blue triangles) the addition of O<sub>3</sub>.*

372  
 373 Furthermore, this study highlights the detection of a KHP at  $m/z$  132 stemming from  
 374 POZ isomerization (see Figure 3) that has gained experimental validation only recently in  
 375 ozonolysis systems<sup>56,57</sup>. Besides the good agreement between the TIY of  $m/z$  132 and the  
 376 simulated one (see SI for theoretical details) for 1-hydroperoxyhexan-2-one in Figure S2,  
 377 Figure 7 depicts a strong correlation between the experimentally recorded TPES of  $m/z$  114  
 378 and a simulated spectrum of 2-oxohexanal, the product of the decomposition of  
 379 1-hydroperoxyhexan-2-one providing compelling evidence for its formation. Note that as  
 380 expected due to their short lifetime, the POZ has not been detected in this study.

381



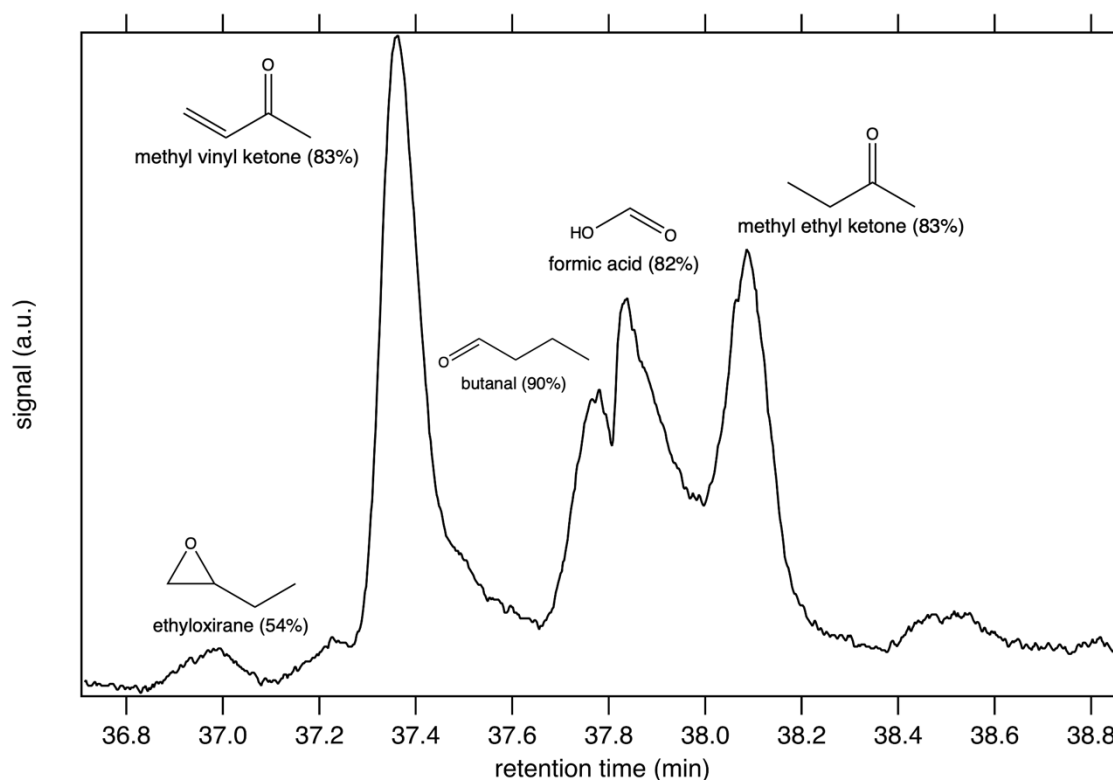


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*Figure 7. TPES of  $m/z$  114 (open dots) compared to a simulated spectrum of 2-oxohexanal (red line). The chemical reaction shows the fragmentation mechanism of the KHP, 1-hydroperoxyhexan-2-one at  $m/z$  132.*

386 Formic acid ( $HCOOH$ ,  $m/z$  46) formed via the isomerization of the Cl  $CH_2OO$  into  
387 dioxirane intermediate (see Figure 3) has also been identified via GC-MS (see Figure 8), but  
388 quantification of  $HCOOH$  remained elusive due to its low FID signal<sup>58</sup>. As for formaldehyde,  
389 no signal at  $m/z$  46 has been recorded in Figure 4 because the AIE of  $HCOOH$  falls outside the  
390 photon energy range examined in this work (11.33 eV). Note that, due to the time  
391 restrictions typical of large facilities such as the SOLEIL synchrotron, the chosen photon  
392 energy range aimed to cover the ionization energy of most organic species.

393

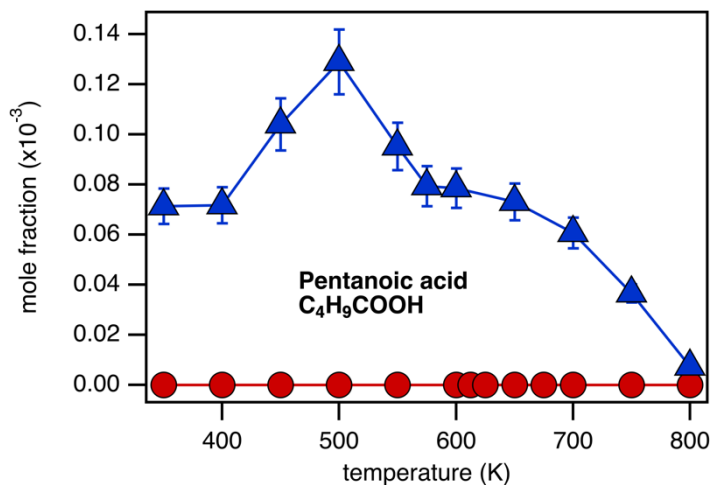


394  
 395 *Figure 8. Chromatogram obtained at 650 K with the addition of O<sub>3</sub> showing the retention peak of formic acid*  
 396 *along with other important oxidation products. The probability of match of each peak to the species according*  
 397 *to the NIST database is provided based on the respective fragmentation pattern of each peak using a mass*  
 398 *spectrometer with electron ionization.*

399  
 400 In the gas-phase, due to the large exothermicity and the succession of weakly bound  
 401 intermediates, the CI C<sub>4</sub>H<sub>9</sub>CHOO isomerization is thought to predominate. The CI is expected  
 402 to isomerize promptly to 1-hydroperoxypent-1-ene, a vinylhydroperoxide (VHP) that is  
 403 generally susceptible to dissociation into an organic oxygenated radical or subsequently  
 404 isomerize into 2-hydroxypentanal, which then dissociates into butanal by losing a  
 405 formaldehyde molecule. This oxygenated radical is the potential precursor to a sequence of  
 406 reactions leading to HOM species detected in this work. However, the CI can also result in  
 407 an oxirane, specifically 3-butyldioxirane, whose O-O bond cleavage can terminate in the  
 408 formation of pentanoic acid. The TPES of m/z 102 is showcased in Figure 5 contrasted with  
 409 simulated spectra of 3-butyldioxirane, 2-hydroxypentanal, and pentanoic acid. A least-  
 410 squares fit of the simulated spectra to the TPES spectrum of m/z 102 reveals the presence of  
 411 all the discussed species. The detection of pentanoic acid was also corroborated by GC (see

412 Figure 9) and acts also as another direct proof of the ozonolysis mechanism, as it is not  
413 formed without the addition of O<sub>3</sub>.

414



415

416 *Figure 9. Pentanoic acid mole fraction recorded by GC as a function of temperature without (red circles)*

417

*and with (blue triangles) the addition of O<sub>3</sub>.*

418

## 419 Discussion

420 The results described in the previous part show that under combustion regime,

421 various hydroperoxide intermediates like KHPs are produced already at 300 K in 1-hexene

422 ozonolysis, indicating the formation of their parent OOQOOH radicals (for example, C<sub>5</sub>H<sub>9</sub>O<sub>5</sub>

423 and C<sub>5</sub>H<sub>9</sub>O<sub>7</sub>). The rate of the O<sub>3</sub>-derived reactions, such as ROO H-shift isomerization, is likely

424 to increase significantly with temperature due to their substantial barriers enhancing the

425 quantity of oxygenated intermediates, and play a crucial role in shaping the autoxidation

426 behavior of 1-hexene. As temperature drops barrierless or low-barrier mechanisms are

427 favored such as OH-addition reactions to olefins<sup>59</sup>. At the opposite, H-abstraction by OH

428 becomes increasingly competitive as temperature rises due to the increased energy at

429 higher temperatures, facilitating overcoming the activation barriers inherent to H-

430 abstraction reactions. This is illustrated by a decrease of the m/z 130/148 signal ratio by

431 around 50% at 400 K measured in Figure 4 compared to that measured in the LTC.<sup>60,61</sup> The

432 LTC of 1-hexene is dominated by two pathways: H-abstraction and OH-addition onto the

433 double bond of the carbon chain leading respectively to m/z 130, an alkenyl

434 ketohydroperoxide and m/z 148, an hydroxyl ketohydroperoxide (see Figure S1). While the

435 H-abstraction is favored in the LTC, this result in this work emphasizing a shift in dominant  
436 reaction pathways.

437 The O<sub>3</sub>-related kinetic network operates up to at least 650 K and is responsible for  
438 the observed 20% enhancement in the conversion of 1-Hexene when O<sub>3</sub> is added. This  
439 increase is also a substantial contribution to the reactivity in the LTC region, even with the  
440 KHP branching decomposition into OH and oxy (OO=O) radicals, enhancing much more the  
441 overall combustion kinetics<sup>62</sup>. Propagation reactions from the O<sub>3</sub> side involving various  
442 oxygenated intermediates increase the pool of radicals, especially OH with the loose O-OH  
443 bonds, to trigger the LTC chemistry below 550 K. The species related to the LTC chemistry  
444 found in Figure 4 are mainly initiated by the abstraction of allylic and alkylic H-atoms, the  
445 addition of OH-radicals to the double bond, followed by the addition of an O<sub>2</sub> molecule. The  
446 addition of H-atoms to create alkyl radicals (R) also play a role, but to a lesser extent as the  
447 temperature is low (see Figure S1).

448 Importantly, the O-MION-CIMS measurements also show the detection of ROO  
449 accretion products: ROOR'<sup>63,64</sup> which have been found especially important for the  
450 formation and growth of atmospheric SOA. While the accretion products were not found in  
451 the PEPICO experiments, their involvement in shaping the autoxidation behavior of a VOC at  
452 elevated temperature could also be substantial. They form very rapidly<sup>65</sup>, the peroxide  
453 bridge connecting the R units is weak, and the R units likely contain one or two relatively  
454 weakly bound hydroperoxide functional groups each, potentially providing a cascade of  
455 reactive radicals during decomposition contributing to increasing oxidation rate.

456 Out of the two CIs that are formed, C<sub>4</sub>H<sub>9</sub>CHOO is anticipated to have a more  
457 significant impact than CH<sub>2</sub>OO in increasing the concentration of radicals. The nascent  
458 stabilization factor of CH<sub>2</sub>OO is expected to be higher than C<sub>4</sub>H<sub>9</sub>CHOO because of the larger  
459 size of the pentanal co-product which takes away more energy than formaldehyde<sup>66</sup>.  
460 However, this requires further theoretical analysis to determine the energy barriers  
461 associated with isomerization and dissociation processes in this ozonolysis system, as well as  
462 to calculate their respective branching ratios.

463 Beyond 650 K, the NTC zone begins because substantial quantities of poorly reactive  
464 OOH radicals, which are produced through reactions like the concerted elimination (ROO =  
465 olefin + HOO). However, this slowdown is expected to be counteracted by the thermal  
466 decomposition of O<sub>3</sub> into O atoms, which affects the overall radical concentration and

467 balance in the system. The thermal decomposition of  $O_3$  starts around 450-500 K and is  
468 almost complete at the temperature of 650 – 700 K<sup>27</sup>. The increase of 40% is twice the  
469 increase observed at low temperatures likely due to the biradical nature of O atoms sharing  
470 two radical sites ( $O + RH \rightarrow R + OH$ ). The contribution of the much-accelerated  $O_3 + 1$ -  
471 hexene reaction in this region remain an opening question but is likely to be minimum  
472 compared to the thermal decomposition of  $O_3$ .

473 This work reveals the concurrent operation of two distinct yet intertwined chemical  
474 systems where reaction mechanisms relevant to both atmospheric science and combustion  
475 chemistry coexist. Radicals generated from ozonolysis spark a cascade of reactions  
476 reminiscent of combustion processes at temperatures well below what they would be in the  
477 absence of  $O_3$ , establishing a distinct connection between atmospheric and combustion  
478 chemistry. What is particularly noteworthy here is that these two chemical systems —  
479 ozonolysis and combustion — do not interact. By looking at Figure 1, the fuel conversion  
480 curves are the same except for a constant offset, up to the NTC region.

481

#### 482 **Implications for Energy Efficiency, Atmospheric Sciences, and Pollution Control**

483 This work reports on the interplay of  $O_3$  and the oxidation chemistry of 1-hexene  
484 across a wide temperature range (300 – 800 K), connecting combustion engineering with  
485 atmospheric science. The results emphasize an important discovery:  $O_3$  enhances oxidation  
486 and facilitates fuel conversion under typically inhibitory combustion conditions (<500 K and  
487 > 700 K). The presence of  $O_3$  expands the initially limited range of reactivity, covering  
488 temperatures from those relevant to the atmosphere all the way up to those relevant to  
489 combustion counteracting the NTC behavior.

490 At low combustion temperatures (< 550 K), ozonolysis initiates the LTC chemistry,  
491 resulting in the formation of oxygenated reactive intermediates, including KHPs. These  
492 findings support recent research emphasizing the significance of H-migration in ROO radicals  
493 even at ambient atmospheric temperatures and in systems lacking the autocatalytic  
494 influence of oxygen containing functional groups (i.e., pristine ROO radicals)<sup>67-69</sup>. The similar  
495 sequence of reactions has been shown to lead to the formation of multitude of oxygenated  
496 compounds, and ultimately HOMs, the fuel that drives atmospheric secondary organic  
497 aerosol generation [4, 16]. Thus, the current results build an intriguing bridge between  
498 atmospheric and combustion science: The same compounds that allow the embryonic

499 molecular clusters to grow into atmospherically relevant aerosol particles provide the spark  
500 for igniting the formation of combustion intermediates at temperatures lower than has been  
501 previously thought possible.

502         Specific combustion intermediates that are common in systems sequentially oxidizing  
503 toward HOMs were here identified under intentionally increased O<sub>3</sub> concentrations but their  
504 formation is unlikely to happen at typical ambient O<sub>3</sub> levels. To modify combustion  
505 processes, significantly higher O<sub>3</sub> levels than those commonly found in the environment are  
506 necessary, but these levels are not overly difficult to attain. Furthermore, current findings  
507 suggest that for a comprehensive understanding of particle formation in areas with  
508 temperature higher than in the troposphere and high O<sub>3</sub> concentrations, sometimes  
509 exceeding ppm levels, such as in smoke plumes<sup>70</sup>, the cooling exhausts of combustion  
510 devices<sup>19</sup>, or even in certain megacities during intense pollution episodes<sup>71-73</sup>, it is essential  
511 to understand the processes resulting from both combustion and atmospheric chemistry.

512         From the industrial point of view, there is a growing interest in technologies based on  
513 plasma-assisted combustion for the development of superior air-breathing engines<sup>74</sup> in  
514 which O<sub>3</sub> can be formed in substantial amount, shading light on its potential as an efficient  
515 fuel oxidation promoter<sup>19</sup>. The ability of O<sub>3</sub> to modify autoignition chemistry and trigger  
516 unsaturated fuel autoxidation under conditions that are usually inhibitory multiplies the  
517 interest in using O<sub>3</sub> in energy conversion devices, opening new possibilities ranging from the  
518 refinement of fuel composition for optimization of current processes working at  
519 intermediate combustion temperatures. The current research underscored a remarkable  
520 influence of O<sub>3</sub> on the occurrence of NTC, that had been so far intuited in alkane oxidation  
521 systems but with very limited effect<sup>24,25</sup>. It also makes opportunities for the development of  
522 new combustion techniques working at extremely low temperature and pollution mitigation  
523 strategies.

524         By counteracting the NTC behavior and enabling more efficient fuel conversion across  
525 a broader temperature range, engineers and scientists gain increased flexibility in designing  
526 advanced energy conversion devices. This newfound flexibility means that temperature  
527 constraints, which may have previously limited device development, are no longer a barrier.  
528 Energy conversion devices can now be tailored and optimized for operation across a wider  
529 spectrum of temperatures, offering a more adaptable and versatile approach.

530

531 **Conclusion**

532 This work highlights the dual role of O<sub>3</sub> at both low and high temperatures,  
533 emphasizing its potential usefulness for fuel optimization and pollution reduction. Moreover,  
534 the importance of atmospheric molecular mechanisms in triggering autoignition and  
535 autoxidation under conditions that normally prevent it is also underlined. The combination  
536 of two advanced analytical tools in mass spectrometry and spectroscopy has enabled the  
537 detection of different species that are part of the same kinetic network; this suggests  
538 promising prospects for using this analytical pairing to study even more complex chemical  
539 systems.

540

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550

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