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# Jet-Stirred Reactor Study of Low-Temperature Neopentane Oxidation: A Combined Theoretical, Chromatographic, Mass Spectrometric, and PEPICO Analysis

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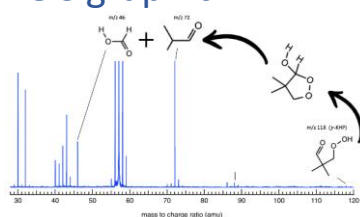
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## Abstract

The oxidation of neopentane was studied in jet-stirred reactors at atmospheric pressure over a temperature range 500 - 850 K and  $\phi = 0.5$ . The products were analyzed with chromatographic, mass spectrometric, and photoelectron spectroscopic setups complemented with theoretical calculations. This combination provides a comparison of photoionization mass spectrometry and gas chromatography for the quantification of mole fractions and highlights the relevant differences between them, while mass-tagged photoelectron spectroscopy sheds light onto the isomeric distribution. The new data and corresponding analyses are expected to provide valuable guidance for an extension of the kinetic model and the choice of experimental methods.

The main first and second O<sub>2</sub>-addition products were observed in agreement with the literature (e.g., 3,3-dimethyloxetane, acetone, isobutene, and  $\gamma$ -ketohydroperoxide). The simulated mole fractions of the products using a literature kinetic model were compared to the experimental results. Even though the kinetic model has been validated previously, significant discrepancies between the measured and simulated mole fractions of 2-methylpropanal and methacrolein, two fuel-specific low-temperature oxidation products, were found. Furthermore, some experimentally observed species related to  $\gamma$ -ketohydroperoxide decomposition were not predicted indicating that the model is incomplete. The detection of 2-methylpropanal and formic acid highlighted the importance of the Korcek-type pathway.

## 45 TOC graphic



46  
47

## 48 Introduction

49 Understanding the chemistry of auto-ignition of a fuel-air mixture, especially at low  
50 temperature ( $< 1,000$  K) is mandatory for the design and optimization of low-emission and  
51 high-efficiency internal combustion engines (ICEs). The low-temperature oxidation of  
52 hydrocarbon fuels is governed by successive additions of radicals to  $O_2$ , intramolecular  
53 migration reactions of H-atoms, and bimolecular dissociation channels leading to chain  
54 branching or propagation. This chemistry leads to the formation of numerous oxygenated  
55 intermediates among which hydroperoxides play an important role because the reactivity of  
56 the hydroperoxides is central to auto-ignition in ICEs. The overall mechanism for low-  
57 temperature combustion of hydrocarbon fuels is relatively well understood and implemented  
58 in detailed chemical kinetic models, but quantitative agreement between measurements and  
59 simulations is not always achieved. One reason for this is that not all products formed during  
60 low temperature oxidation have unequivocally been identified<sup>1</sup>.

61 Given its unique highly symmetric molecular structure, neopentane ( $C_5H_{12}$ ) is an ideal  
62 candidate to study the oxidation chemistry of alkanes. With all the primary H atoms being  
63 equivalent, only one type of alkyl radical is formed in H abstraction reactions. Similarly, the  
64 initiation through C-C bond scission leads only to one set of products (methyl and *tert*butyl  
65 radicals). These limited consumption pathways for neopentane restrict the diversity of initial  
66 product channels compared to other pentane isomers. Nevertheless, successive reactions,  
67 especially  $O_2$ -addition, lead to large variety of oxygenated species through isomerization and  
68 dissociation reactions including intermediates and reactive species such as free radicals, which  
69 play a crucial role in the formation of ketohydroperoxides (KHPs). KHPs are chain branching  
70 agents, which contain carbonyl ( $C=O$ ) and hydroperoxy ( $-OOH$ ) functional groups. Their  
71 thermal decomposition promotes the release of OH radicals as well as other reactive species,  
72 which increase the reactivity of a combustible mixture.

73 Numerous studies in the literature have investigated the oxidation chemistry of  
74 neopentane in static low pressure reactors<sup>2-7</sup>, rapid compression machines, shock tubes<sup>8-12</sup>,  
75 as well as in flow tubes<sup>13-17</sup> and in jet-stirred reactors (JSR)<sup>18-20</sup>. These techniques allowed the  
76 identification of primary and secondary products over a temperature range from 550 K to  
77 1,718 K. The analysis of these measurements was supported by ab initio calculations<sup>21</sup> and the  
78 development of chemical kinetic models<sup>14,18,22</sup>. Predictions in particular with the most recent  
79 model are generally good but significant discrepancies on specific species such as  
80 2-methylpropanal suggest that some chain-branching reactions might be missing. KHPs have  
81 not been observed until very recently by Eskola et al.<sup>17</sup> in time-resolved, Cl-atom initiated  
82 neopentane oxidation experiments. Using a synchrotron photoionization time-of-flight mass  
83 spectrometer, the KHP 3-hydroperoxy-2,2-dimethylpropanal was identified and its  
84 decomposition mechanisms explored. Based on some oxidation products found in  
85 neopentane oxidation, Eskola et al.<sup>17</sup> suggested that 3-hydroperoxy-2,2-dimethylpropanal,  
86 undergoes the so-called Korcek reaction<sup>23</sup>. The KHP in neopentane oxidation was also

87 observed by Hansen et al.<sup>20</sup> in a JSR and its maximum mole fraction was measured at T = 590  
88 K. However, their work focused on the products of the third O<sub>2</sub>-addition rather than the  
89 elementary steps leading to KHP formation and decomposition. The only other known JSR  
90 study of neopentane oxidation was performed by Dagaut et al.<sup>18</sup> over a temperature range  
91 from 800 K to 1,230 K, which is however not favorable for KHP formation.

92 This current work studies the oxidation of neopentane in a JSR in the T = 500 K - 850 K  
93 temperature range in order to identify and quantify the main oxidation products up to KHP  
94 formation and decomposition. Three JSR setups were used, each connected to different  
95 analytic equipment. The aim of this collaborative effort is twofold. First, to generate  
96 redundant data to validate the different quantification procedures used or to identify cases  
97 for which these methods lead to notable differences. Second, to generate a comprehensive  
98 data set for neopentane oxidation to provide a challenge for existing models and by doing so  
99 to enhance the current understanding of this chemistry. The three analytic systems used are:

100 (1) On-line gas chromatography (GC) at LRGP (Nancy, France) by connecting the outline  
101 of the JSR to two GC analyzers<sup>24</sup>. This setup allows to measure mole fractions as a function of  
102 temperature for neopentane, stable intermediates, and final products as a function of  
103 temperature.

104 (2) Time-of-flight mass spectrometry analysis using tunable synchrotron vacuum  
105 ultraviolet for photoionization (SVUV-PIMS) at the NSRL synchrotron (Hefei, China) by  
106 sampling the reaction mixture in the JSR through the formation of a molecular beam<sup>25</sup>. This  
107 device provides mass-resolved photoion yield (PIY) curves. The spectra are converted with the  
108 help of internal standards to species mole fractions. This device is able to detect intermediates  
109 that cannot be detected by GC analysis and therefore complementary data.

110 (3) Photoelectron photoion coincidence spectroscopy using tunable synchrotron  
111 vacuum ultraviolet light from the VUV DESIRS beamline at the SOLEIL synchrotron (Saint-  
112 Aubin, France) for photoionization (SVUV-PEPICO) of molecular beam sampled reaction  
113 mixture extracted from a JSR<sup>26</sup>. This facility allows the acquisition of mass-resolved slow  
114 photoelectron spectra (SPES)<sup>27,28</sup> on top of PIY, which provide information on the isomeric  
115 structures of oxidation products.

116 The SPES analyses are supported by high-level theoretical quantum calculations which  
117 provide simulated PES of molecular species, for which such spectra are not yet reported in the  
118 literature<sup>26,29</sup>. The detailed kinetic model developed at the Combustion Chemical Centre of  
119 the National University of Ireland (Galway, Ireland)<sup>11</sup> has been used to simulate the current  
120 neopentane experiments and to identify the major oxidation products and their dominant  
121 formation/decomposition pathways.

122 This paper is organized as follows. The first section presents the different experimental  
123 setups that were used as well as the theoretical methods employed to support the  
124 experimental data analysis. The kinetic model from the literature, used to simulate the  
125 chemistry of neopentane oxidation, is also briefly described. In the second section, the  
126 experimental results are presented according to the molecular growth pathway leading to the  
127 formation and decomposition of KHP. Throughout this section, the results are compared to  
128 the predictions of the used kinetic model and to available experimental results from the  
129 literature. The last section summarizes the main results of this study and proposes  
130 perspectives to improve the kinetic models for alkane oxidation at low temperature.

131

## 132 Experimental facilities, theoretical methods, and kinetic model

133 Neopentane oxidation was studied under steady state and atmospheric pressure  
134 conditions at the equivalence ratio ( $\phi$ ) of 0.5. The flow rates were adjusted at each  
135 temperature to achieve a  $\tau = 3$  s residence time in the JSR. He and O<sub>2</sub> were provided by Messer  
136 in LRGP (both 99.999 % pure) and by Air Liquide at SOLEIL. Ar and O<sub>2</sub> were provided by Air  
137 Liquide in NSRL with a purity of 99.999 %. The LRGP and SOLEIL experiments used a  
138 neopentane mixture provided by Air Liquide with a 3% dilution in He. The purity of  
139 neopentane was found to be > 99 % based on GC analysis and was used without further  
140 purification. NSRL experiments used liquid neopentane supplied by Nanjing Special Gas  
141 Factory Co. Ltd. with a claimed purity of 99.8 %. The purity was also verified by GC analysis.  
142 Calibrated mass flow controllers were used to measure gas flow rates with a 0.5 % uncertainty.  
143 A Coriolis flow controller was used in the NSRL facility to control the fuel liquid flow rate.  
144

### 145 JSR experiments

146 The experiments at LRGP and NSRL allowed obtaining mole fraction profiles of  
147 products and reactants over a wide temperature range. The measurement campaign at the  
148 SOLEIL synchrotron focused on recording SPES of species at specific temperatures near the  
149 peak mole fraction of KHP. Experiments at SOLEIL were also performed without O<sub>2</sub> to study  
150 the stability of neopentane during photoionization to discriminate oxidation products and  
151 dissociative ionization fragments in SPES. The experimental conditions used at the three  
152 locations are summarized in Table 1.  
153

Location	T(K)	P(Bar)	$\tau$ (s)	$\phi$	mole fractions		
					neopentane	O <sub>2</sub>	He/Ar
NSRL	500 – 825	1.07	3	0.5	0.015	0.24	0.745
LRGP	500 – 850	1.07	3	0.5	0.015	0.24	0.745
SOLEIL	580 – 650	1.07	3	0.5	0.015	0.24	0.745
	580	1.07	3	$\infty$	0.015	0	0.985

154 Table 1. Summary of JSR experimental conditions used in the present study.  
155

### 156 JSR coupled to GC-TCD/FID/MS

157 The JSR used to investigate neopentane oxidation at LRGP is a fused silica spherical  
158 reactor ( $\sim 81.2$  cm<sup>3</sup>) working under isothermal and isobaric conditions with a reactive gas  
159 mixture (fuel + O<sub>2</sub>) continuously flowing into it, with a high dilution of inert gas to avoid  
160 temperature gradients due to the oxidation exothermicity. Reactants (neopentane and O<sub>2</sub>),  
161 with helium as the carrier gas, entered the spherical JSR through four cross-shaped nozzles  
162 positioned at the center to promote turbulence and mixture homogenization. The JSR has a  
163 preheating zone upstream of the reactor inlet to reduce the temperature gradient inside of it.  
164 The JSR and the preheating zone are heated using resistances, and the reactor temperature  
165 was measured with a K-type thermocouple positioned in a glass finger close to the JSR center  
166 with an uncertainty of around 1%. The oxidation gas mixture exiting the JSR is transferred, via  
167 heated lines, to two GCs for analysis. **The length of the heating lines is  $\sim 5$  m of 1/8 in outside**  
168 **diameter stainless tube.**

169 The first GC is equipped with a Carbosphere-packed column and a thermal conductivity  
170 detector (TCD) to quantify lightweight and permanent gas species. The second GC is equipped  
171 with a Q-Bond capillary column and a flame ionization detector (FID) preceded by a  
172 methanizer. This GC is used for the quantification of organic compounds. The methanizer is

173 composed of a hydrogenation Ni bed catalyst, through which a buffer gas and H<sub>2</sub> (also used  
174 for the FID) is flowed to reduce species containing carbonyl groups to the corresponding  
175 alkanes, and CO and CO<sub>2</sub> to methane. For species identification the GC equipped with a Q-  
176 Bond capillary column was coupled to a quadrupole mass spectrometer. Ions were generated  
177 via electron impact ionization at 70 eV.

178 FID and TCD calibrations were performed using gaseous standards provided by Air  
179 Liquide for O<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub>. All other species detected with the FID were calibrated using  
180 the effective carbon number (ECN) method. Their calibration factors were deduced from  
181 those of the calibrated species by taking into account their effective carbon number. The  
182 relative uncertainties of the mole fractions of the species calibrated using gaseous standards  
183 were estimated to be ±5% while the relative uncertainties of the species calibrated using the  
184 ECN method were estimated to be ±10%.

185

### 186 JSR coupled to SVUV-PIMS

187 The PIMS experimental setup used at the VUV beamline of the NSRL synchrotron has  
188 been newly developed at the Atomic & Molecular Physics Beamline (BL09U). A detailed  
189 discussion of the experimental setup and the validation of the system will be the subject of a  
190 separate publication. Here, only a brief description of the experimental method is given. The  
191 design of the JSR is based on the KAUST JSR<sup>30</sup>, while the design of the nozzle sampling is similar  
192 to that described by Battin-Leclerc et al.<sup>25</sup>. Specifically, a tapered quartz nozzle with a 100 μm  
193 orifice is used. The tip of the quartz nozzle is inserted into the JSR to sample the gas and create  
194 a molecular beam, which enters the ionization chamber through a skimmer and is crossed by  
195 the undulator generated VUV light. The ions resulting from photoionization are then detected  
196 with a reflectron time-of-flight mass spectrometer with a mass resolution of ~4,000.

197 In the experiment, temperature dependence curves of the product's signal are  
198 obtained at fixed photon energies, and the species mole fraction can be obtained from the  
199 signal. For species *i*, the mole fraction at the different temperatures is calculated with the  
200 equation :

$$201 \quad X_i(T) = X_i(T_0) \times \frac{S_i(T)}{S_i(T_0)} \times \frac{\lambda(T_0)}{\lambda(T)}$$

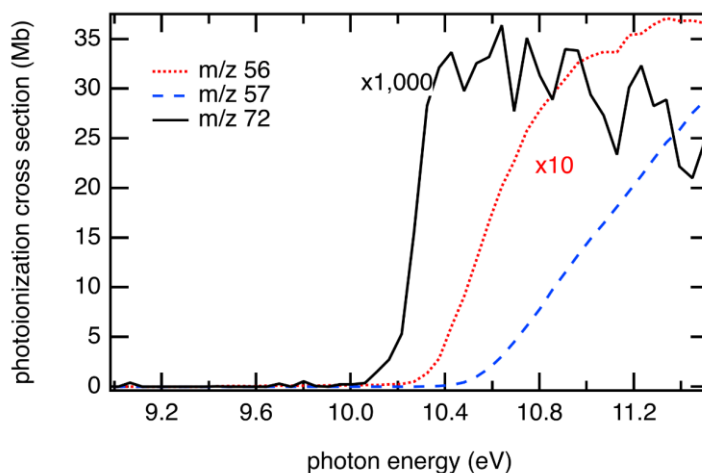
202  $X_i(T)$ ,  $\lambda(T)$  and  $S_i(T)$  represent, respectively, the mole fraction of species *i* at temperature  
203 *T*, the coefficient of gas expansion at temperature *T* depending on the bulk property of the  
204 system and the signal of species *i* at temperature *T*. Similarly,  $X_i(T_0)$ ,  $\lambda(T_0)$  and  $S_i(T_0)$  are  
205 known information at temperature *T*<sub>0</sub>, which is usually chosen as the temperature at which  
206 no reaction occurs. It is worth noting that the gas expansion factor is obtained through  
207 measurements of the change of Ar signal during the experiment.

208 Species from the low-temperature oxidation experiment of neopentane were ionized  
209 at 11.5 eV, 10.5 eV, 9.8 eV and 9.3 eV. An internal standard with a known mole fraction was  
210 used at each photon energy to convert the normalized ion signal of a given species to its mole  
211 fraction. At the same photon energy, the mole fractions of reaction products can be calculated  
212 with the fuel as a reference:

$$213 \quad X_i(T) = X_{fuel}(T) \times \frac{S_i(T)}{S_{fuel}(T)} \times \frac{\sigma_{fuel}(E)}{\sigma_i(E)} \times \frac{D_{fuel}}{D_i}$$

214  $\sigma_i(E)$  is the photoionization cross-section of species *i* at the photon energy *E*.  $D_i$  is the mass  
215 discrimination factor of species *i*. Neopentane has a very small photoionization cross section  
216 (PICS) at the onset of the parent signal at *m/z* 72 (see Figure 1). Therefore, its daughter ion at  
217 *m/z* 57 was chosen as the internal standard of 11.5 eV. The *m/z* 57 signal at conditions of no

218 reaction is used as the signal of internal standards. This ensures that there is no interference  
219 from the  $m/z$  57 signal caused by low-temperature reaction products. The PICS of the  
220 neopentane daughter ion is very small or zero at 10.5 eV and 9.8 eV. For these ionization  
221 energies ketene was chosen as the internal standard. The reason for selecting ketene as the  
222 internal standard is that its PICS is available in the literature<sup>31</sup> and its ionization energy is 9.67  
223 eV. For experiments employing 9.3 eV for ionization, 1,3-butadiene was used as the internal  
224 standard because its PICS is also available in the literature<sup>31</sup> and its ionization energy is 9.07  
225 eV. The mole fractions of ketene and 1,3-butadiene were in turn quantified at 11.5 eV using  
226  $m/z$  57 as the internal standard. Note that the use of ketene and 1,3-butadiene as internal  
227 standard may introduce additional uncertainties of the quantified mole fraction. Result shows  
228 that for the intermediates that could be quantified at different energies, mole fractions are in  
229 good agreement at the selected energies. The uncertainty in the mole fraction was evaluated  
230 to be within  $\pm 10\%$  for the reactants, within  $\pm 20\%$  for the intermediates with experimentally  
231 measured PICS, and estimated to a factor of 2 for the intermediates with calculated PICS. Note  
232 that in the rare occasions where experimental and simulated cross-sections are available,  
233 larger differences have been reported<sup>32,33</sup>.  
234



235  
236 Figure 1. Photoionization cross section of neopentane (solid black line) and its fragments at  
237  $m/z$  56 (dotted red line), and 57 (dashed blue line) from dissociative ionization, recorded at  
238 the NSRL.  
239

#### 240 JSR coupled to SVUV-PEPICO

241 Inside the SAPHIRS chamber<sup>34</sup> permanent end-station, located at one of the  
242 monochromatized branches of the DESIRS beamline at the SOLEIL synchrotron a 100 $\mu$ m  
243 sampling nozzle is connected to the JSR, which is operated at a pressure of 1.07bar. The  
244 resulting molecular beam passes through two skimmers before entering the ionization  
245 chamber where it is crossed by the VUV beam focused at the center of the double-imaging  
246 photoelectron/photoion coincidence ( $i^2$ PEPICO) spectrometer DELICIOUS III. The  
247 spectrometer is able to detect electrons and cations in coincidence<sup>35</sup>. Here, this scheme allows  
248 the photoelectrons to be filtered by ion mass and ion arrival position, where the latter  
249 ensures that only neutrals produced within the reactor are considered, discarding, by ion  
250 imaging filtering, the contribution from background gases impinging on a different spatial  
251 region of the ion position sensitive detector<sup>36</sup>. The mass spectra obtained with this apparatus  
252 have a typical mass resolving power of  $\sim 1,700$  (FWHM). The photoelectron spectroscopy of



253 any given mass, a footprint of the electronic structure of the species, can be obtained in the  
254 form of a SPES by scanning the photon energy while analyzing the photoelectron energies,  
255 using a method previously described<sup>27</sup>, with a typical overall resolution of about 20 meV. PIY  
256 can also be obtained through integration over all electron energies, even in cases for which  
257 the signal-to-background ratio does not allow an electron kinetic energy analysis. Note that  
258 time restrictions related to limited synchrotron access prevented the recording of mole  
259 fractions at SOLEIL.

260 The error bars shown in PES are obtained assuming a Poisson distribution on the image  
261 pixel counts, which is then propagated throughout all operations using standard formulae.  
262 Note that these errors are taken into account when fitting isomer distributions to obtain  
263 branching ratios.

## 264 265 Theoretical methods

266 The equilibrium structures have been determined for neutral and ionic species using  
267 the PBE0 density functional<sup>37</sup> as implemented in GAUSSIAN09<sup>38</sup>, using the augmented  
268 correlation-consistent aug-cc-pVDZ basis set<sup>39,40</sup>. To ensure that the geometries correspond  
269 to minima, the conformation space of neutral and cationic species was explored by scanning  
270 the dihedral angles responsible for rotor orientation at wB97XD/6-311G(2d,p) level.<sup>41</sup> Zero  
271 point vibrational energies (ZPVE) are determined at the anharmonic level as implemented in  
272 GAUSSIAN09. A Franck Condon (FC) analysis is performed to simulate the vibrationally  
273 resolved electronic spectra at 0 K by means of the Time-Independent Adiabatic Hessian  
274 Franck–Condon (TI-AH|FC) model<sup>42–45</sup>. The resulting stick spectrum was convolved with a 20  
275 meV bandwidth Gaussian profile to match the experimental resolution.

276 For the determination of the adiabatic ionization energy (AIE), the CBS-QB3 zero-point  
277 vibrational energy (ZPE)-corrected total electronic energies for the neutral and cation ground  
278 states have been used in the first place<sup>46,47</sup>. When further clarification was required, the  
279 geometry optimizations were followed by single point computations on the optimized  
280 structures using the explicitly correlated coupled cluster with single, double and perturbative  
281 triple excitations ((R)CCSD(T)-F12)<sup>48–51</sup> together with the aug-cc-pVDZ basis set in conjunction  
282 with the corresponding resolutions of the identity and density fitting functions<sup>52</sup> as generated  
283 by MOLPRO<sup>53</sup>. Afterwards, the computed spectra at the PBE0/aug-cc-pVDZ(opt)//(R)CCSD(T)-  
284 F12/aug-cc-pVDZ(SP) level were shifted in energy so that it best matches the experimental  
285 spectra. When available, comparison between experimental reference spectra and the  
286 simulated spectra is presented to provide a benchmark of the theoretical methodology. Note  
287 that only the most stable conformer of each isomer at a given m/z has been taken into account  
288 to simulate the spectrum.

## 289 290 Kinetic model

291 The experimental mole fractions measured during the oxidation of neopentane were  
292 compared to numerical predictions with the detailed kinetic model of pentane isomers  
293 developed at NUI Galway<sup>11</sup>. This model was used without any modifications. It predicts the  
294 auto-ignition delay times of pentane isomers measured in a rapid compression machine and  
295 a shock tube well<sup>11</sup>, and it was also previously used to reproduce experimental oxidation data  
296 of n-pentane obtained in JSRs at 1 and 10 bar<sup>54</sup>. All simulations described in this work were  
297 performed using the openSMOKE++ software package<sup>55,56</sup>.

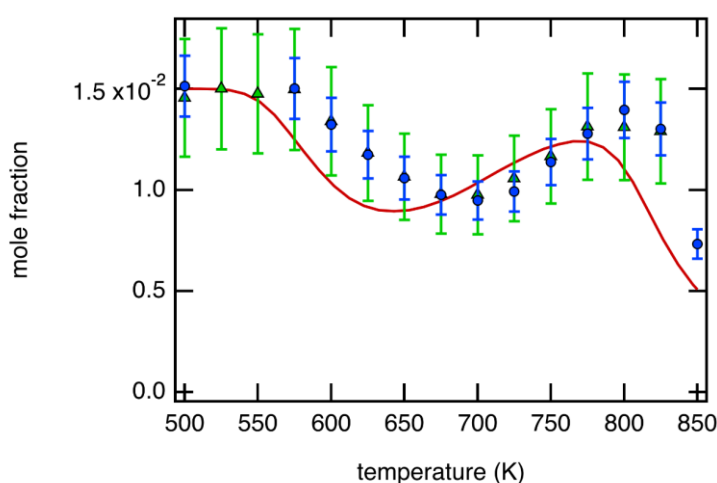
298



## 299 Results and Discussion

### 300 Neopentane conversion

301 In all figures, except for SPES, the mole fractions represented by blue circles were  
302 obtained by GC analysis at LRGP and green triangles by PIMS at NSRL. The red line correspond  
303 to numerical simulations. Figure 2 presents the conversion of neopentane measured at  $\phi = 0.5$   
304 and the temperature range  $T = 500 - 850$  K, and it compares the experimental data with  
305 predictions by the kinetic model. It should be noted that neopentane oxidation was studied  
306 for temperatures up to 1,100 K. However, oscillatory behaviors was observed at temperatures  
307 above 1,000 K. This transient evolution of the mole fractions of reactants and products during  
308 oscillating limited cycles have already been observed in the literature during fuel combustion  
309 at high temperatures<sup>57-59</sup>. As oscillatory chemistry is not the subject of this work only data up  
310 to 850 K are considered.  
311



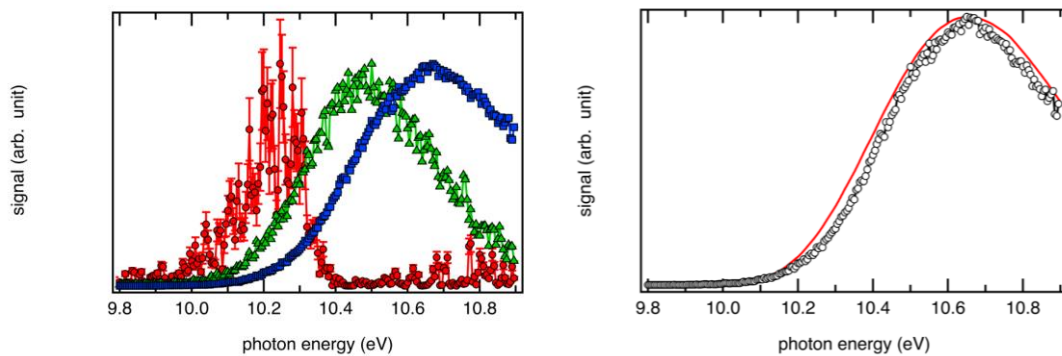
312 Figure 2. Fuel conversion during neopentane JSR oxidation between experimental  
313 measurements (GC and PIMS) and numerical predictions (neopentane 1.5 %,  $\phi = 0.5$ ,  $\tau = 3$  s).  
314  
315

316 In Figure 2, the experimental data for the conversion of neopentane show a notable  
317 low temperature reactivity and a marked negative temperature (NTC) zone which are  
318 reproduced by the kinetic model. The degree of conversion and the width of the NTC region  
319 are well captured by the kinetic model. However, in the model prediction the fuel conversion  
320 starts at a temperature  $\sim 60$  K lower than observed in the NSRL and LRGP experiments. The  
321 good agreement between both experimental measurements (GC and PIMS) suggests that the  
322 fuel reactivity is overestimated by the kinetic model and that the initiation chemistry need to  
323 be revised. The overprediction of the neopentane reactivity by the kinetic model was also  
324 observed in the experimental conditions used by Hansen et al.<sup>20</sup> (see SM of this paper). Note  
325 that the same JSR has been used at SOLEIL and LRGP, while the NSRL JSR has a different design  
326 but both of them have been used for numerous oxidation studies in the past and temperature  
327 shifts were never observed.

328 At LRGP, the mole fraction of neopentane is proportional to the FID signal measured  
329 after GC separation, of the species contained in the effluent gas mixture. In contrast, as  
330 mentioned in the experimental methods section, at NSRL the quantification was done  
331 indirectly through the dissociative ionization fragment of neopentane at  $m/z$  57 ( $C_4H_9^+$ ), which  
332 has a much higher photoionization cross section than the parent ion (see Figure 1). The

333 observed good agreement demonstrates the reliability of this indirect quantification  
334 procedure when the photoionization cross section is known.

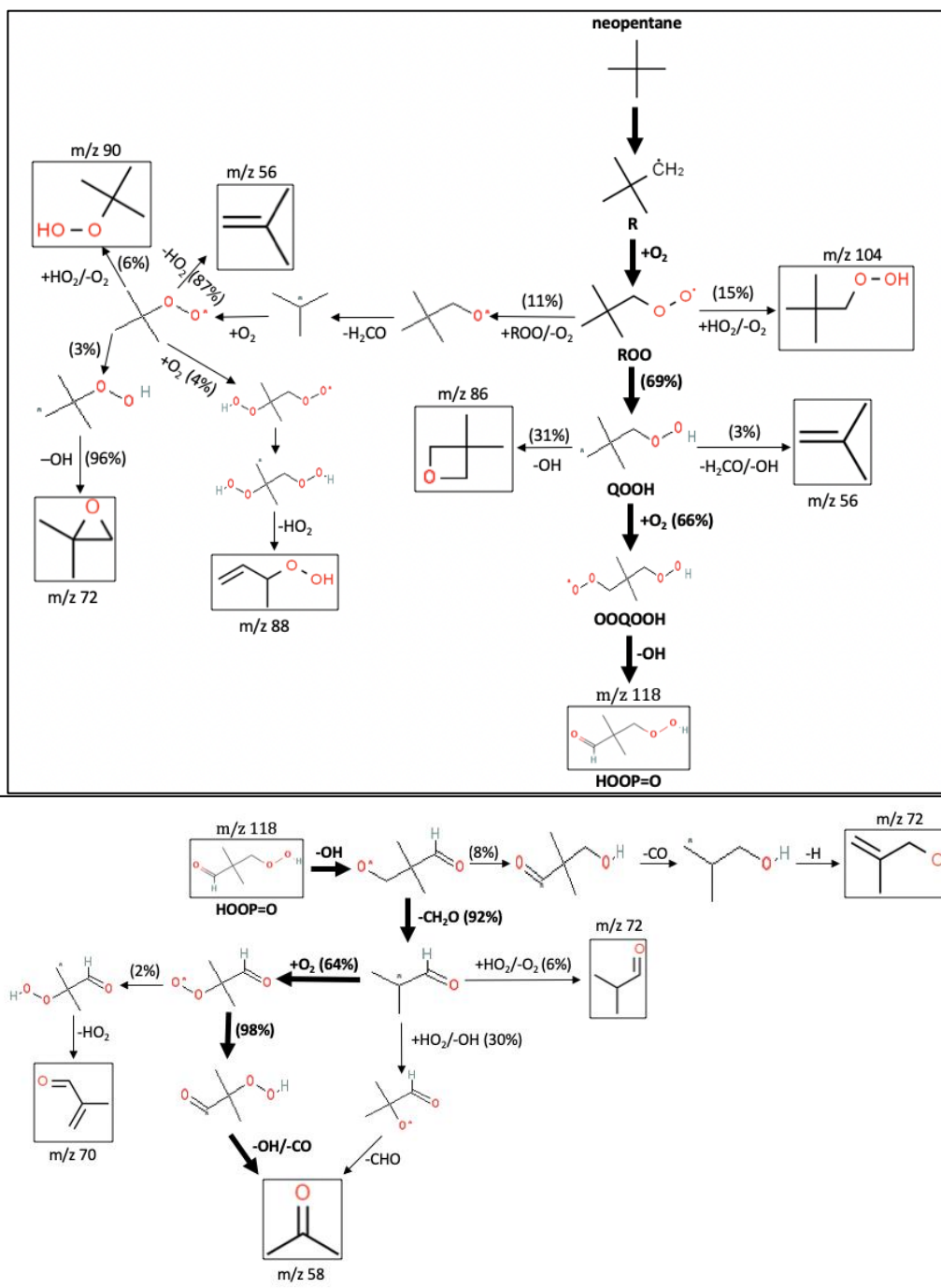
335 The dissociation of the neopentane cation to  $m/z$  56 ( $\text{CH}_4$  loss) and 57 ( $\text{CH}_3$  loss)  
336 fragment ions has been recorded without  $\text{O}_2$  addition using the  $i^2$ PEPICO spectrometer, in  
337 order to deconvolve the fuel contribution to these mass channels in oxidation conditions from  
338 contributions by product species. The mass-selected normalized SPES of the parent and the  
339 fragments are shown in the left panel of Figure 3. They agree with the previously reported  
340 breakdown diagram and appearance energies<sup>60</sup>. Figure 3 (right panel) shows the total SPES  
341 associated to neopentane, i.e. summing the non-normalized signals from  $m/z$  72, 56, and 57.  
342 As a benchmark of the theoretical methodology, the PES for electronic ground state  
343 neopentane ionization was simulated. The simulated PES shows a broad and unstructured  
344 vibrational envelop due to the geometry changes upon ionization caused by the Jahn-Teller  
345 distortion<sup>61</sup>, in good agreement with the experimental data. An AIE = 10.05 eV is obtained  
346 from matching the calculated and experimental envelopes, 160 meV lower than existing  
347 values<sup>62</sup>.  
348



349 Figure 3. (left) Normalized SPES of  $m/z$  56 (green triangles), 57 (blue squares), and 72 (red  
350 dots) obtained at SOLEIL in experiments in which neat neopentane is flowed through the JSR  
351 at 580 K. (right) Sum of non-normalized SPES of  $m/z$  56, 57, and 72 (dots) compared to  
352 simulated PES of neopentane (red line). The simulated PES has been shifted by 77 meV to  
353 match the experimental curve.  
354  
355

### 356 Products from the first $\text{O}_2$ -addition

357 Figure 4 reports a rate of production analysis carried out at 600 K for JSR experiments  
358 at  $\phi = 0.5$  using the kinetic model by Bugler et al.<sup>11</sup>. Based on the literature<sup>17</sup>, the low-  
359 temperature oxidation of neopentane is controlled by the formation of a neopentyl radical (R)  
360 that further reacts with  $\text{O}_2$  to form a neopentylperoxy radical (ROO). The predicted dominant  
361 fate of the ROO radical is isomerization to give the hydroperoxyneopentyl radical (QOOH) via  
362 a cyclic 6-membered transition state. According to the model, at 600 K, 31% of  
363 hydroperoxyneopentyl converts to 3,3-dimethyloxetane ( $\text{CC1}(\text{COC1})\text{C}$ ,  $m/z$  86) through ring-  
364 closure of the hydroperoxy neopentyl radical and simultaneous OH elimination.  
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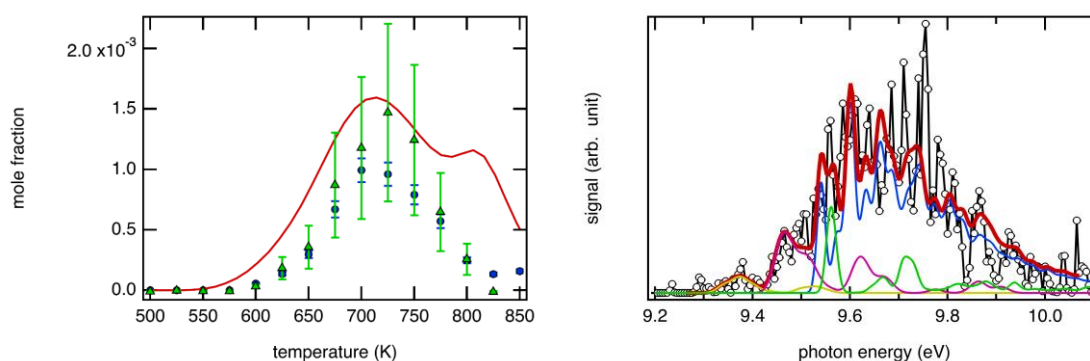
379

Figure 4. Rate of production analysis for neopentane oxidation ( $\phi = 0.5$ , 1.5 % in He) at 600 K,  $P = 1.07$  bar and  $\tau = 3$  s. Bold arrows indicate the dominant pathways. Pathways with small branching ratios ( $< 1\%$ ) to or from intermediates are omitted for clarity. The upper panel shows the reactions leading to the formation of KHP. The lower panel shows the decomposition pathways of KHP.

The right panel in Figure 5 compares the SPES of m/z 86 recorded at 580 K compared to simulated SPES of 3,3-dimethyloxetane and three isomers: 2,2-dimethylpropanal CC(C)(C)C=O, trans-2,4-dimethyloxetane CC1CC(O1)C, and pentan-3-one CCC(=O)CC. The deconvolution of the SPES leads to a 3,3-dimethyloxetane:2,2-dimethylpropanal:trans-2,4-dimethyloxetane:pentan-3-one signal branching ratio of 0.5:1.0:0.1:0.3. 3,3-dimethyloxetane and 2,2-dimethylpropanal spectra have their bands overlapping, but the SPES is found to be

380 mostly similar to that of 2,2-dimethylpropanal. A small contribution is also found from trans-  
381 2,4-dimethyloxetane and pentan-3-one but the congestion of the spectra in such out of  
382 equilibrium environment make the conclusion to be taken with care. The photoionization  
383 cross section of 2,2-dimethylpropanal could not be found in the literature making it  
384 impossible, at this time, to validate the calculations through experimental branching ratios.  
385 2,2-dimethylpropanal is known to fragment to  $m/z$  57 ( $C_3H_5O^+$ ) with an AIE = 9.51 eV<sup>63</sup>. The  
386 observed increase in the SPES signal of  $m/z$  57 under oxidizing conditions in the region, in  
387 which the 2,2-dimethylpropanal fragment is expected, supports the formation of 2,2-  
388 dimethylpropanal (see Figure S1).

389 The left panel in Figure 5 shows the recorded mole fraction profiles of 3,3-  
390 dimethyloxetane using either GC or PIMS detection and quantification. Taking into account an  
391 uncertainty estimated to be  $\pm 50\%$  for 3,3-dimethyloxetane in PIMS measurements, the GC  
392 and PIMS data agree well. In the PIMS experiments, 3,3-dimethyloxetane has been quantified  
393 using the ion fragment ( $m/z$  56) at 9.8 eV. This required the contribution of isobutene to be  
394 subtracted from the signal of  $m/z$  56, which explains the rather high uncertainty of the 3,3-  
395 dimethyloxetane mole fractions.  
396



397  
398 Figure 5. (left) Mole fraction profile of 3,3-dimethyloxetane measured during neopentane  
399 oxidation ( $\phi = 0.5$ , 1.5 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s. **The model prediction is also**  
400 **presented.** (right) SPES of  $m/z$  86 at 580 K (dots) compared to simulated spectra of trans-  
401 2,4-dimethyloxetane (yellow line), pentan-3-one (purple line), 3,3-dimethyloxetane (green  
402 line), and 2,2-dimethylpropanal (blue line). The red line shows the results of the fit (see text  
403 for details).  
404

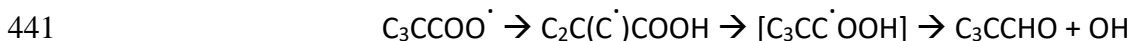
405 Note that at 600 K very little 3,3-dimethyloxetane is detected. The GC yields at LRGP  
406 are only slightly outside of the noise level and the yields determined by PIMS are essentially  
407 around zero level. The kinetic model predicts higher yields because of the temperature shift.  
408 Taking the shift into account, at best a very small amount of 3,3-dimethyloxetane is predicted  
409 at this temperature. Overall, the kinetic model satisfactorily reproduces the 3,3-  
410 dimethyloxetane mole fraction profile (shape) and peak value, except for the highest  
411 temperatures at which 3,3-dimethyloxetane is overpredicted.

412 In the study by Eskola et al.<sup>17</sup>, 3,3-dimethyloxetane was shown to hardly produces a  
413 signal at  $m/z$  86 but instead fragments to  $m/z$  56. The signal of the fragment is more than  
414 1,000 times stronger than that of the parent ion. If the 2,2-dimethylpropanal cation does not  
415 significantly fragment, then it is clear that essentially all signal at  $m/z$  86 arises from 2,2-  
416 dimethylpropanal, in agreement with the analysis presented above. Eskola et al.<sup>17</sup> also  
417 determined relative yields for 3,3-dimethyloxetane and 2,2-dimethylpropanal for three  
418 temperatures: 575 K, 625 K, and 675 K. They found the 2,2-dimethylpropanal yield to decline

419 with increasing temperature while the highest 3,3-dimethyloxetane yield relative to isobutene  
420 was found at 625 K. From their data, the 3,3-dimethyloxetane:2,2-dimethylpropanal ratios for  
421 the three temperatures are 2.8, 10.1 and 21.3. Since the PIMS and GC measured mole  
422 fractions are already at the detection limit for 3,3-dimethyloxetane at temperatures below  
423 600 K, this explains why 2,2-dimethylpropanal was not detected with these devices at low  
424 temperatures.

425 At higher temperatures, the 2,2-dimethylpropanal concentration should reach around  
426 100 ppm if the relative yields reported by Eskola et al.<sup>17</sup> for Cl initiated oxidation are applicable  
427 to the thermal oxidation of neopentane under the conditions of this study. This is not  
428 guaranteed since Eskola et al.<sup>17</sup> speculate that 2,2-dimethylpropanal “could originate at least  
429 partly from radical-radical reactions” and the radical concentrations in their work likely differ  
430 substantially from those in the JSR experiments reported here. In any case, the expected yields  
431 of 2,2-dimethylpropanal compared to 3,3-dimethyloxetane are so low that any missing signal  
432 of 2,2-dimethylpropanal has no notable impact on the mass balance or total ion counts in the  
433 PIMS experiment. Future SPES measurements ( $m/z$  86 and 56) as a function of temperature  
434 would be helpful to verify the branching ratio reported by Eskola et al.<sup>17</sup>. Any further attempts  
435 to search for 2,2-dimethylpropanal should focus on the temperature range above 625 K.

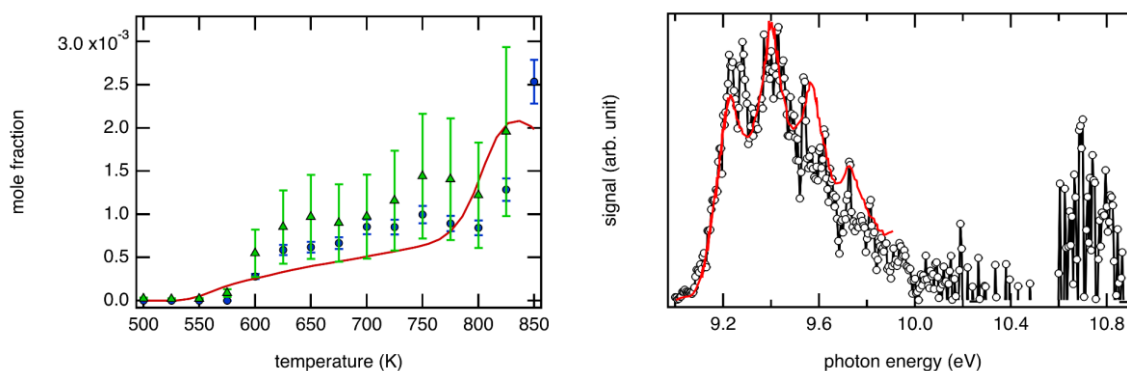
436 Although the formation of 2,2-dimethylpropanal is not predicted by the kinetic model,  
437 the work by Eskola et al.<sup>17</sup> as well as this study has clearly proven its presence. Besides the  
438 possibility to be formed in radical-radical reactions (Eskola et al.<sup>17</sup>), another reaction sequence  
439 could be a successive migration of two H atoms starting from the ROO radical, followed by the  
440 removal of an OH group:



442 This sequence may be competitive to the oxetane formation channel and should be  
443 investigated to ensure that all 2,2-dimethylpropanal related chemistry is properly included in  
444 the kinetic model.

445 Eskola et al.<sup>17</sup> recorded the photoionization signal at  $m/z$  56 to address the formation  
446 of 3,3-dimethyloxetane. The signal at  $m/z$  56 is a combination of signals originated from  
447 isobutene ( $\text{C}_4\text{H}_8$ ) and fragments from dissociative ionization of 3,3-dimethyloxetane ( $m/z$  86)  
448 and neopentane ( $m/z$  72). The right panel of Figure 6 compares the difference between SPES  
449 of  $m/z$  56 at 580 K with and without  $\text{O}_2$  addition to a reference PES of isobutene. The low  
450 photon energy region overlaps with the isobutene reference PES while above 10.5 eV,  
451 according to the results of Eskola et al.<sup>17</sup>, the spectral signature arises from the fragmentation  
452 of 3,3-dimethyloxetane.

453



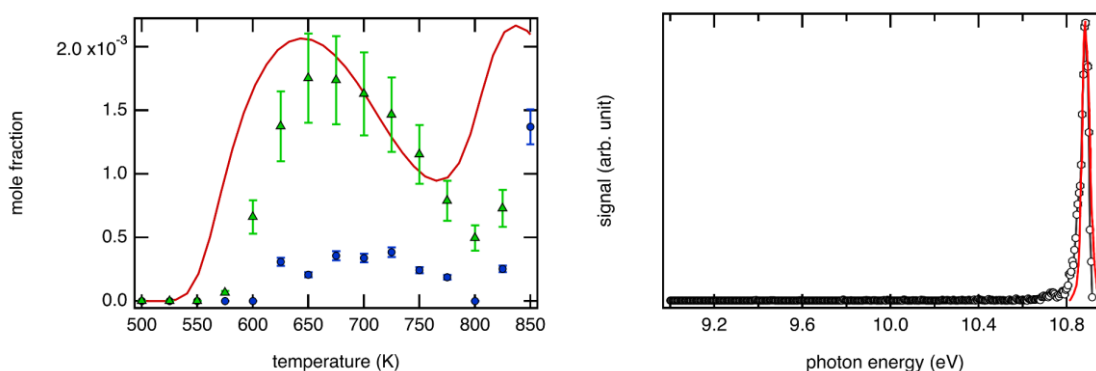
454 Figure 6. (left) Mole fraction profile of isobutene measured during neopentane oxidation ( $\phi$   
455 = 0.5, 1.5 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s. The model prediction is also presented. (right)  
456



457 Difference between SPES of  $m/z$  56 at 580 K with and without  $O_2$  addition (dots). The PES of  
458 isobutene (red line) from Mintz & Kuppermann<sup>64</sup>, scaled to match the peak, is shown too.  
459

460 Isobutene is formed in a pathway competing with 3,3-dimethyloxetane formation  
461 during the QOOH radical decomposition (see Figure 4). The left panel in Figure 6 shows good  
462 agreement between simulated and experimental isobutene mole fractions obtained at LRGP  
463 when the 60 K shift is taken into account. In order to eliminate the interference of 3,3-  
464 dimethyloxetane ion fragment ( $m/z$  56), the mole fraction of isobutene has been determined  
465 in the PIMS experiments at 9.3 eV. As mentioned above, 1,3-butadiene was used as the  
466 internal standard to quantify the mole fraction of isobutene and the uncertainty of the  
467 isobutene mole fraction is estimated to be  $\pm 50\%$ . Taking the uncertainties into account, PIMS  
468 and GC data are in good agreement. The more straightforward GC quantification makes this  
469 data more reliable, though. Isobutene formation from QOOH releases an OH radical and  
470 formaldehyde ( $CH_2O$ ,  $m/z$  30) as by-products but the modeled profiles of isobutene and  $CH_2O$   
471 are clearly different, suggesting that  $CH_2O$  is mainly produced by a different channel.

472  $CH_2O$  was detected in the GC, PIMS, and PEPICO experiments (see Figure 7). While  
473 PIMS derived mole fractions are in relatively satisfactory agreement with numerical  
474 predictions, again if one accounts for 60 K shift in neopentane conversion, the concentrations  
475 measured by GC and PIMS differ by as much as a factor of 40 as highlighted in the left panel  
476 of Figure 7, even though the overall shapes are in agreement. At the highest temperatures  
477 reached in this work, the model overpredicts  $CH_2O$  but the shape follows that of the  
478 experimental trends.  
479



480  
481 Figure 7. (left) Mole fraction profile of  $CH_2O$  measured during neopentane oxidation  
482 ( $\phi = 0.5$ , 1.5 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s. GC mole fractions (blue dots) have been  
483 multiplied by 10. The model prediction is also presented. (right) SPES of  $m/z$  30 at 580 K  
484 (dots) compared to the PES of  $CH_2O$  (red line) from Baker et al.<sup>65</sup>.  
485

486 Formaldehyde is one most important intermediate in low-temperature oxidation, thus  
487 PIMS mole fractions at a level of  $10^{-3}$  seems thus reasonable. Note that, because of the larger  
488 deviation with GC data for this species, in order to verify the reliability and rationality of  
489 experimental results for neopentane, experiments have been repeated also in the  
490 Combustion and Flame Beamline (BL03U) of NSRL. The JSR used at BL03U is the same as the  
491 one used in LRGP. Good agreement with the data obtained at BL09U is observed for the  
492 species presented, so that the PIMS experimental methodology is considered reliable. In the  
493 meantime, to ensure the reliability of the measurements obtained by GC, GC measurements  
494 have been also repeated at the same conditions with the unaltered setup but a different

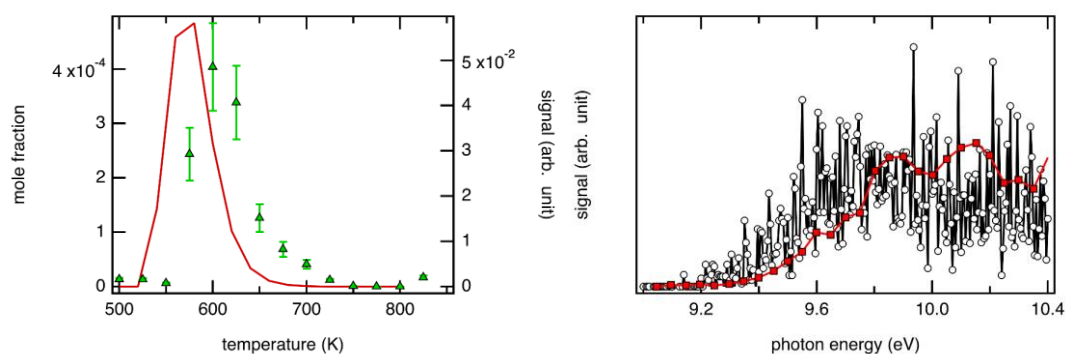


495 operator. The mole fraction results were very close to the original data, with relative  
496 deviations of less than 2%. However, the unexpected large presence of formic acid (see further  
497 more explanation below) might cause polymerization problems of CH<sub>2</sub>O in the GC transfer  
498 lines.

499 The disagreement of the formaldehyde data – although unfortunate – show the value  
500 of collaborations with complementary independent detection systems. Without these  
501 redundant data sets, there would have been no incentive to double-check the results as the  
502 good reproducibility of the individual measurements obscures the existence of a problem.  
503 Further studies are necessary to confirm our current interpretation that the PIMS data are  
504 correct and the GC data suffer from formaldehyde polymerization issues.  
505

### 506 KHP formation from the second O<sub>2</sub>-addition

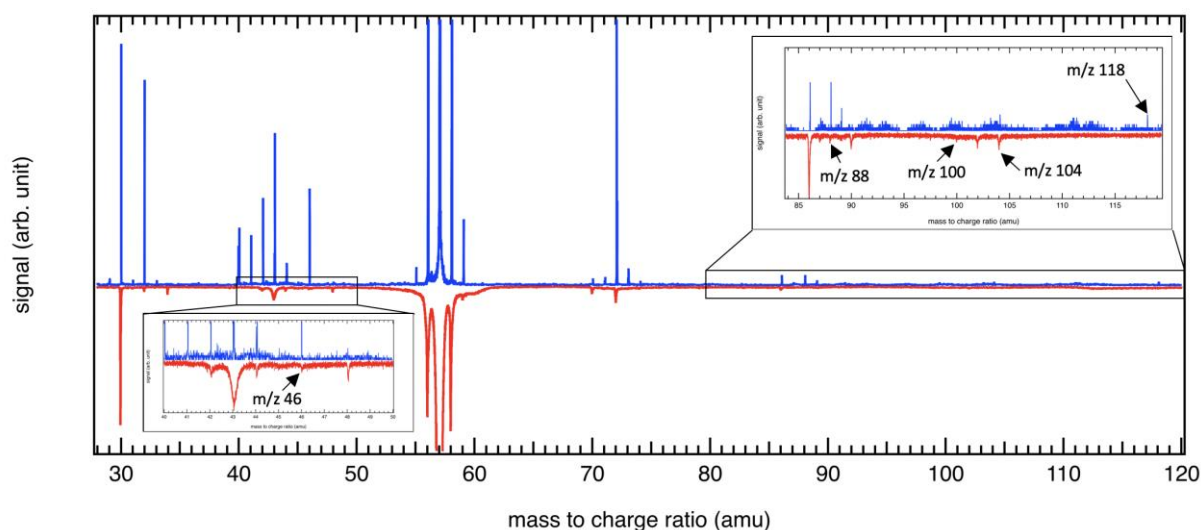
507 The second addition of O<sub>2</sub> leads to the formation of a hydroperoxyalkylperoxy radical  
508 (OOQOOH), especially at high pressures and high O<sub>2</sub> mole fractions, such as in practical  
509 combustion systems. This radical subsequently decomposes to 3-hydroperoxy-2,2-  
510 dimethylpropanal CC(C)(COO)C=O, a KHP, and an OH radical. The KHP was detected directly  
511 at m/z 118 in the NRSL experiments and the signal profile at  $\phi = 0.5$  is displayed in the left  
512 panel of Figure 8 along with the predicted mole fractions. Both profiles are in relatively good  
513 agreement (shape and position) if the systematic shift of the predictions by 60 K is taken into  
514 account. The mole fraction profile peaks over a small temperature range centered at 600 K,  
515 which is in good agreement with the measured 590 K maximum at  $\phi = 0.9$  in Hansen et al.<sup>20</sup>.  
516



517  
518 Figure 8. (left) Simulated mole fraction profile of  $\gamma$ -KHP compared to signal of m/z 118  
519 measured in PIMS during neopentane oxidation ( $\phi = 0.5$ , 1.5 % in He) at P = 1.07 bar and  $\tau =$   
520 3 s. (right) PIY of m/z 90 at 580 K (black dots) compared to a PIY curve of m/z 90 from  
521 Hansen et al.<sup>20</sup> (red line).  
522

523 The formation of KHP could not be observed directly at m/z 118 of the parent ion in  
524 the SOLEIL experiments (see Figure 9 for typical mass spectra obtained during SOLEIL and NRSL  
525 experiments). This was due to an insufficient signal to noise ratio in the SOLEIL setup, which  
526 might be caused by the relatively long (14 cm) distance between the nozzle tip to the point of  
527 ionization. The density in a molecular beam decreases quasi-linearly with distance. Even  
528 though similar gas mixtures were used, a straightforward interpretation of the differences  
529 between mass spectra is difficult because, among other reasons, the mass spectra were  
530 recorded at different temperatures and the extraction electric fields used in the both setups  
531 differed. The detection of KHPs at m/z 118 is also complicated by fragmentation of the parent  
532 ion upon photoionization. Hansen et al.<sup>20</sup> mentioned that the first fragment of KHPs is formed  
533 at a photon energy in the range 9.3 - 9.5 eV leading to the HOOCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>H<sup>+</sup> daughter ion at

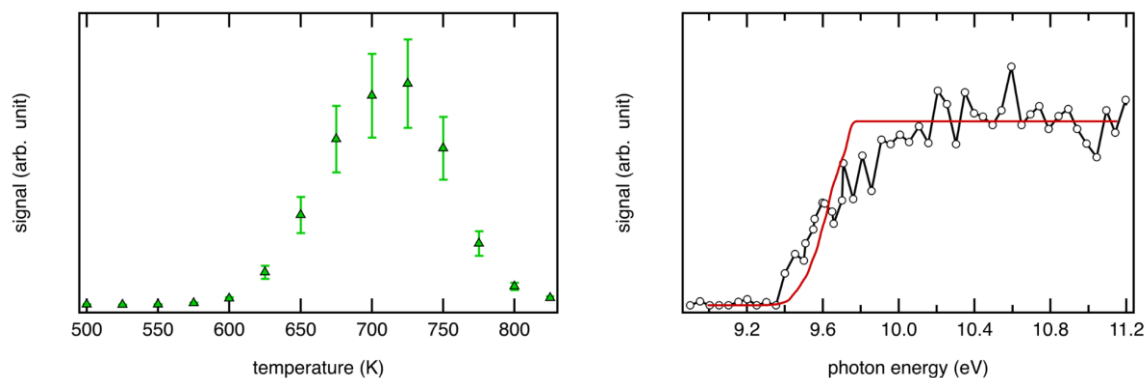
534 m/z 90. A signal at m/z 90 was observed with the SOLEIL device and the PIY is displayed in the  
 535 right panel of Figure 8. The derived appearance energy of 9.2 eV is in relatively good  
 536 agreement with that mentioned by Hansen et al.<sup>20</sup>  
 537



538  
 539 Figure 9. Typical mass spectra: NSRL at 575 K (blue line) and SOLEIL at 600 K (red line) for a  
 540 photon energy of 11.5 eV and  $\phi = 0.5$  during the low temperature oxidation of neopentane.  
 541

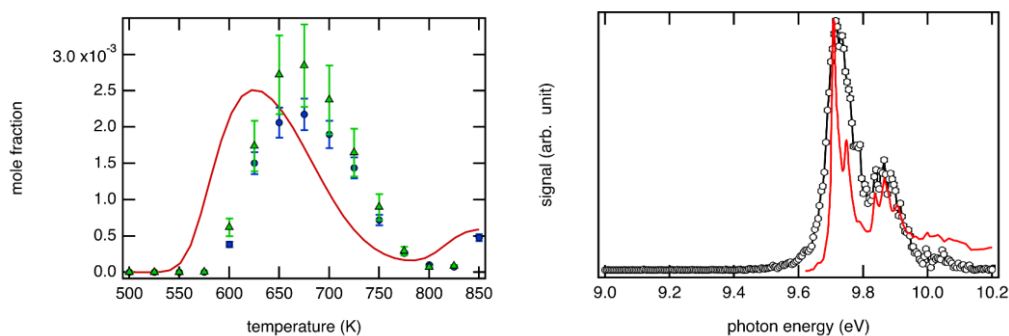
#### 542 Products from KHP decomposition

543 Once formed, KHPs decompose through dissociation pathways that remain to be  
 544 clarified. Eskola et al.<sup>17</sup> observed a peak at m/z 100 which can be attributed to 2,2-  
 545 dimethylpropanedial CC(C)(C=O)C=O. They hypothesized that it could be formed directly by  
 546 elimination of a water molecule from KHP. No dialdehyde was detected by GC analysis, but a  
 547 weak signal at m/z 100 was detected in both, the experiments at SOLEIL and at NSRL  
 548 experiments (see Figure 9). The signal-to-noise ratio was too low in the PEPICO experiments  
 549 to measure a sufficiently resolved signal, but the PIY of NSRL fits reasonably well with the  
 550 simulated PIY of 2,2-dimethylpropanedial (see right panel in Figure 10). The ionization  
 551 threshold is in good agreement with the AIE = 9.39 eV calculated in Eskola et al.<sup>17</sup> at the CBS-  
 552 QB3 level of theory. These agreements would support assignment of the m/z 100 signal to  
 553 2,2-dimethylpropanedial but new experiments with a better signal to noise ratio are necessary  
 554 to record an experimental photoelectron spectrum and to compare it with the theoretical  
 555 one. The signal of m/z 100 as a function of temperature is displayed in the left panel in Figure  
 556 10. The maximum of the mole fraction is reached above 700 K. This temperature is rather  
 557 high for the m/z species to be formed from a KHP since KHP's start to decompose at  
 558 significantly lower temperatures (see Figure 8). The kinetic model does not contain 2,2-  
 559 dimethylpropanedial chemistry and thus cannot support the assignment of the data. If the  
 560 formation of 2,2-dimethylpropanedial were confirmed experimentally, then the neopentane  
 561 oxidation model would be incomplete and would require an upgrade. Possible missing  
 562 reactions could be of the type  $\text{KHP} + \text{CH}_3 \rightarrow \text{C}_2\text{C}(\text{COOH})\dot{\text{C}}=\text{O} + \text{CH}_4$  and  $\text{KHP} + \text{CH}_3 \rightarrow \text{C}_2\text{C}(\text{CHO})_2$   
 563  $+ \text{OH} + \text{CH}_4$ .  
 564



565  
 566 Figure 10. (left) PIMS signal profile of  $m/z$  100 during neopentane oxidation ( $\phi = 0.5$ , 1.5 % in  
 567 He) at  $P = 1.07$  bar and  $\tau = 3$  s. (right) PIY of  $m/z$  100 derived from NSRL (dots) to simulated  
 568 PIY of 2,2-dimethylpropanedial (red line).  
 569

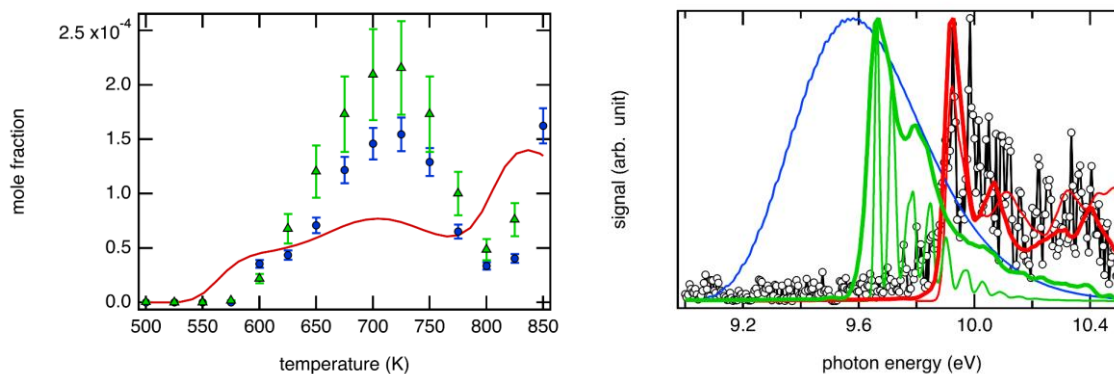
570 KHPs (HOOP=O) mainly decompose via -O-OH bond rupture, which leads to chain-  
 571 branching due to the reactivity of the O-centered isobutanal-2-methoxy radical (OPO).  
 572 Subsequent reactions form species with atomic masses of 58, 70, and 72 (see Figure 4). The  
 573 dominant decomposition pathways consist of  $\text{CH}_2\text{O}$ -loss, mainly leading to acetone ( $m/z$  58).  
 574 The acetone profiles measured by NSRL and LRGP agree reasonably well given the  
 575 uncertainties of the calibrations (see left panel in Figure 11). Good agreement is also found  
 576 between predicted and experimental mole fractions of acetone. The SPES of  $m/z$  58 (see right  
 577 panel in Figure 11) confirms the assignment of the spectral features to the acetone cation, in  
 578 agreement with the results from Eskola et al.<sup>17</sup> Consequently, other potential isomers  
 579 (propanal, methyloxirane) can be safely be ruled out.  
 580



581  
 582 Figure 11. (left) Mole fraction of acetone measured during neopentane oxidation ( $\phi = 0.5$ ,  
 583 1.5 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s. The model prediction is also presented. (right) SPES  
 584 of  $m/z$  58 at 580 K (dots) compared to TPES of acetone (red line) from Rennie et al.<sup>67</sup>.  
 585

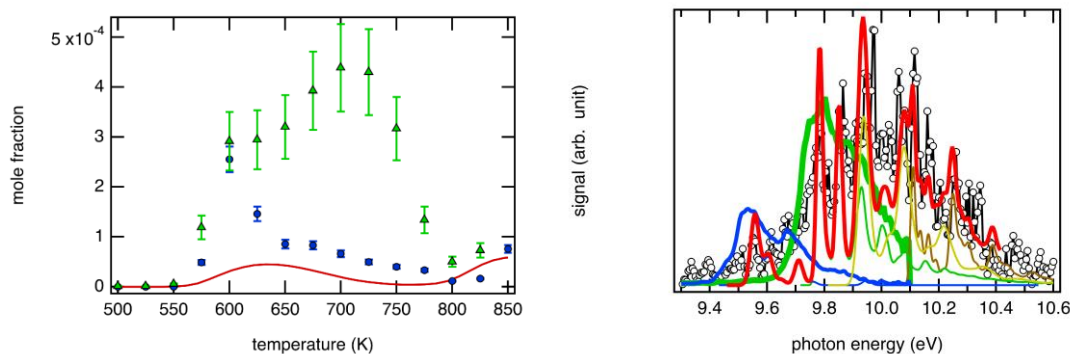
586 According to the kinetic model, a minor decomposition pathway of the KHP leads to  
 587 methacrolein ( $\text{CC}(\text{=C})\text{C}=\text{O}$ ,  $m/z$  70). The left panel in Figure 12 shows that the simulation  
 588 predicts for the central temperature regime studied lower methacrolein mole fractions than  
 589 measured in both setups. At 700 K, at which the methacrolein mole fraction peaks, the  
 590 deviation is about a factor of two. The agreement between PIMS and GC is good considering  
 591 that the PICS of 2-butenal has been used to estimate the PICS of methacrolein. The PICS of 2-  
 592 butenal is generally considered to have an uncertainty factor of 2. The SPES of  $m/z$  70 is  
 593 displayed in the right panel of Figure 12 and the simulated PES of methacrolein matches the  
 594 first band fits rather well with the simulated PES of methacrolein. The AIE calculated in this

595 work is 9.91 eV which is in very good agreement with the experimental AIE of 9.92 eV reported  
596 in the literature<sup>66</sup>. The contribution of other potential isomers (1,1-dimethyl cyclopropane  
597 CC1(CC1)C, methyl vinyl ketone CC(=O)C=C) can be safely ruled out based on their simulated  
598 or experimental photoelectron spectra.  
599



600  
601 Figure 12. (left) mole fraction of methacrolein measured during neopentane oxidation ( $\phi =$   
602  $0.5, 1.5\%$  in He) at  $P = 1.07$  bar and  $\tau = 3$  s. The model prediction is also presented. (right)  
603 SPES of  $m/z$  70 at 580 K (dots) compared to simulated PES of methacrolein (red line), methyl  
604 vinyl ketone (green line), and 1,1-dimethyl cyclopropane (blue line). Reference experimental  
605 PES of methyl vinyl ketone (bold green line) and methacrolein (bold red line) recorded at low  
606 resolution and at photon energy of 10.4 eV with the PEPICO facility are also plotted as a  
607 gauge of the simulation quality.  
608

609 Reported in Figure 4, another minor pathway involving the loss of CH2O and a  
610 successive HO2-addition/O2-elimination leads to 2-methylpropanal (CC(C)C=O,  $m/z$  72). The  
611 left panel of Figure 13 shows a reasonably good agreement between the numerical and LRGP  
612 experimental mole fractions, except at 600 K where the discrepancy is significant (almost an  
613 order of magnitude difference). The PIMS data shown in Figure 13 are significantly higher than  
614 the GC measurements. This is likely due to contribution of additional species, such as 2,2-  
615 dimethyloxirane, to the  $m/z$  72 signal. This explanation is supported by the right panel of  
616 Figure 13 which clearly shows that the  $m/z$  72 spectrum cannot be reproduced by 2-  
617 methylpropanal alone. See also the next section for further explanations. Eskola et al.<sup>17</sup>  
618 proposed a parallel decomposition pathway for KHP via intermediate cyclic peroxide  
619 formation rather than direct OH-loss. This mechanism, called Korcek reaction, is known to lead  
620 through subsequent decomposition to a carbonyl compound and an organic acid<sup>23</sup>. In the case  
621 of neopentane, the Korcek reaction of its KHP produces 2-methylpropanal as carbonyl  
622 component accompanied by formic acid (HCOOH,  $m/z$  46) (see Figure 14). The maximum  
623 deviation between numerical and experimental mole fractions of 2-methylpropanal coincides  
624 with the maximum mole fraction of KHP (600 K, see Figure 8), which supports the idea that  
625 the missing Korcek reaction in the model causes the discrepancy between experiment and  
626 model.  
627



628  
 629 Figure 13. (left) Mole fraction of 2-methylpropanal measured by GC and  $m/z$  72 measured by  
 630 PIMS during neopentane oxidation ( $\phi = 0.5$ , 1.5 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s compared  
 631 to literature model predictions. (right) SPES of  $m/z$  72 at 580 K (dots) compared to simulated  
 632 spectra of butan-2-one (blue line), 2-methylpropanal (green line), trans-2,3-dimethyloxirane  
 633 (yellow line), and 2,2-dimethyloxirane (brown line). Reference experimental PES of butan-2-  
 634 one (bold blue line) and 2-methylpropanal (bold green line) from Pieper et al.<sup>68</sup> are also  
 635 plotted as a gauge of the simulation quality. The bold red line shows the results of the fit  
 636 (see text for details).  
 637

638 In agreement with this Korcek-type pathway interpretation, a signal at  $m/z$  46 was  
 639 recorded in the NSRL experiments (see NSRL mass spectrum reported in Figure 9). A signal at  
 640  $m/z$  46 was also observed in a SOLEIL mass spectrum recorded at 11.5 eV (see the insert in  
 641 Figure 9) supporting the formation of formic acid (AIE = 11.31 eV)<sup>63</sup>. A SPES is not available  
 642 since the AIE falls outside the energy range of the scans performed at SOLEIL. However, the  
 643 PIY measured in PIMS experiments shown in the left panel of Figure 15 fits well with a  
 644 reference PIY of formic acid from Battin-Leclerc et al.<sup>29</sup>. Note that the FID detector is usually  
 645 not sensitive to formic acid, which makes it difficult to identify this species in GC experiments.  
 646 The observed formation of formic acid is in agreement with the higher pressure work of Wang  
 647 et al.<sup>14</sup> at  $\phi=0.3$ , who measured experimentally a significant mole fraction of HCOOH with a  
 648 maximum yield at 645 K. Their model does not predict any reaction until the temperature  
 649 reaches 630 K and Wang et al.<sup>14</sup> introduced a HCOOH production pathway from CH<sub>2</sub>O but  
 650 mentioned the possibility of another unknown formation pathway. This pathway could be  
 651 related to the Korcek reaction, which is not included in the current kinetic model (see Figure  
 652 4) and would provide a plausible explanation for the underestimation of 2-methylpropanal  
 653 (see left panel in Figure 13) and the detection of HCOOH. It would also provide a parallel  
 654 decomposition mechanism for KHP in competition with the OH-elimination channel. It means  
 655 that if KHP were consumed by the Korcek pathway, less CH<sub>2</sub>O would be produced (see Figure  
 656 4) and the predicted CH<sub>2</sub>O yields would be lower. Because the Korcek reaction competes with  
 657 OH forming reactions, it should reduce the reactivity at low temperatures through the  
 658 formation of closed-shell species. Therefore, this reaction should be included in an updated  
 659 neopentane low temperature oxidation model.  
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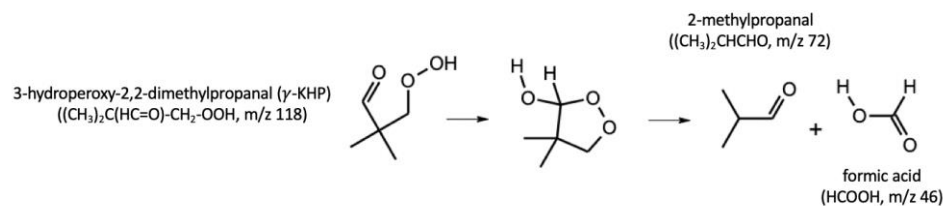


Figure 14. Potential Korcek reaction from  $\gamma$ KHP leading to 2-methylpropanal and formic acid.

A weak signal was detected for m/z 88 in both, PIMS and PEPICO experiments but the signal-to-noise ratio was too low in the PEPICO measurements to get a sufficiently resolved signal. The PIMS PIY of m/z 88 is displayed in the right panel of Figure 15. The PIMS PIY is compared to a reference PIY of isobutyric acid ((CH<sub>3</sub>)<sub>2</sub>CHCOOH)<sup>69</sup> and simulated spectra of two isomers 3-hydroperoxybut-1-ene CC(C=C)OO and 3-hydroperoxy-2-methylprop-1-ene CC(=C)COO. The reference spectrum of isobutyric acid does not seem to correspond to the PIMS PIY. Furthermore, even though the ionization threshold is difficult to distinguish (between 9.8 and 10.2 eV) because of the low signal to noise ratio, it seems to be slightly lower than that of isobutyric acid. Moreover, the spectrum of isobutyric acid does not have a plateau as pronounced as in the PIMS PIY and increases from 11.4 eV, which does not seem to be the case for the PIMS PIY. Another possibility is that the observed signal at m/z = 88 corresponds to 3-hydroperoxy-2-methylprop-1-ene, which can be formed by a termination reaction between the allylic isobutenyl radical and HO<sub>2</sub>. This reaction is now routinely incorporated in the alkene submechanisms<sup>70</sup>, and the resulting hydroperoxide can then yield the conjugated unsaturated aldehyde (in this case, methacrolein). This would be consistent with the high mole fractions of isobutene and methacrolein observed. The calculated AIE is 9.45 eV at the CBS-QB3 level. However, the PIMS PIY better matches the simulated spectrum of 3-hydroperoxybut-1-ene (see right panel in Figure 15). The AIE is calculated to be 9.38 eV at the CBS-QB3 level. 3-hydroperoxybut-1-ene is predicted by the kinetic model as a product in the sequence of reactions initiated by the ROO + ROO reaction (see Figure 4).

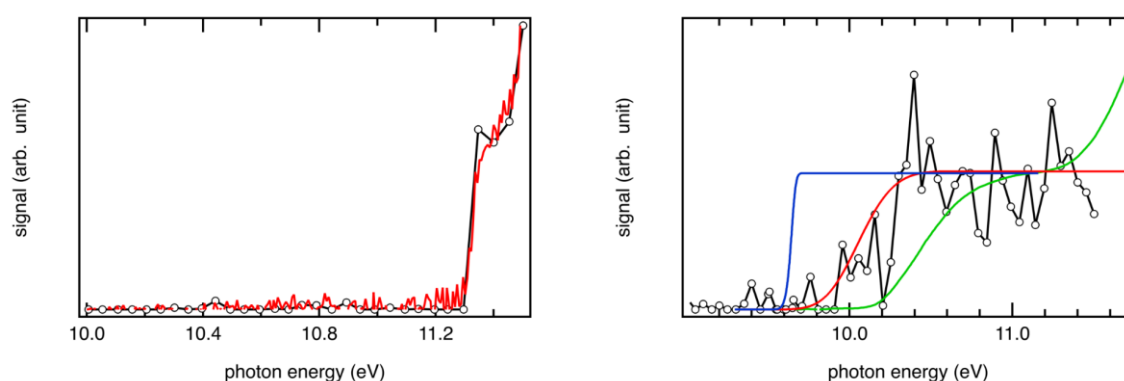


Figure 15. (left) PIY of m/z 46 registered in PIMS measurements at 600 K (dots) compared to a reference PIY of formic acid from Battin-Leclerc et al.<sup>29</sup> (red line). (right) PIY of m/z 88 registered in PIMS at 600 K (dots) compared to a reference PIY of isobutyric acid from Watanabe et al.<sup>69</sup> (green line) and simulated PIY of 3-hydroperoxybut-1-ene (red line) and 3-hydroperoxy-2-methylprop-1-ene (blue line). Note that the PIY of 3-hydroperoxybut-1-ene has been shifted by 100 meV.



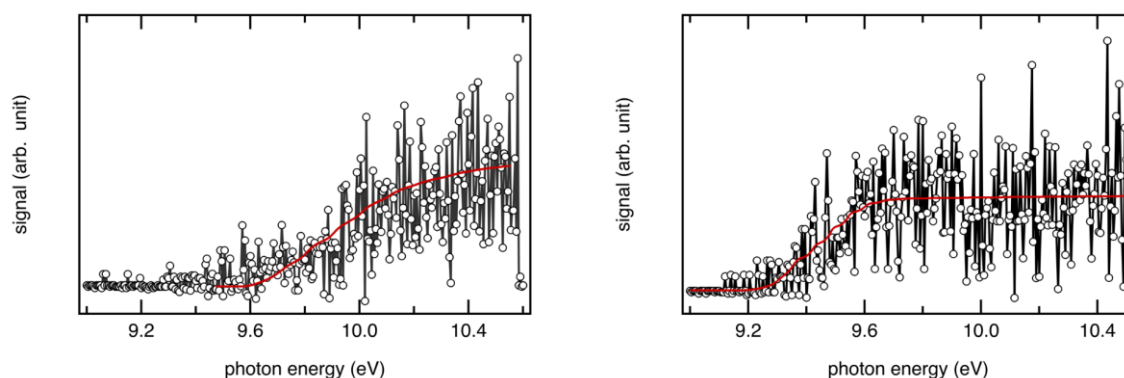
694 New experiments over a wider energy range and leading to better signal to noise  
695 detection of m/z 88 would be necessary to confirm this result. Based on the currently available  
696 data, m/z 88 does not appear to correspond to isobutyric acid but rather to 3-hydroperoxybut-  
697 1-ene. The identification of isobutyric acid next to formic acid, and 2-methylpropanal would  
698 have been an additional argument for the Korcek reaction to play a role in the neopentane  
699 oxidation, because a second decomposition pathway of the Korcek reaction may lead to the  
700 formation of isobutyric acid and CH<sub>2</sub>O. However, 3-hydroperoxybut-1-ene is also a reasonable  
701 species as it is predicted by the kinetic model as a product in the sequence of reactions  
702 initiated by the ROO + ROO reaction.

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#### 704 Side products from neopentane oxidation

705 In the right panel of Figure 13, the SPES deconvolution of m/z 72 using simulated  
706 spectra gives a butan-2-one:2-methylpropanal:trans-2,3-dimethyloxirane:2,2-  
707 dimethyloxirane signal branching ratio of 0.3:1.0:0.7:0.5. Besides the dominant contribution  
708 of 2-methylpropanal, the signature of two oxirane isomers (2,2-dimethyloxirane CC1(CO1)C  
709 and trans-2,3-dimethyloxirane CC1C(O1)C) and butan-2-one CCC(=O)C fits with the ones of  
710 the SPES. From the kinetic model simulations obtained at the relatively low temperature of  
711 600 K, 2,2-dimethyloxirane results from the direct addition of HO<sub>2</sub> to isobutene<sup>15</sup> and a  
712 sequence of reactions initiated by the ROO + ROO. As the temperature increases, the  
713 unimolecular decomposition of the radical R to isobutene + CH<sub>3</sub> will counterbalance the  
714 reaction R + O<sub>2</sub> → RO<sub>2</sub>. The kinetic model also predicts 2-methyl-2-propen-1-ol CC(=C)CO as  
715 minor product (see Figure 4) from a parallel decomposition mechanism of the OPO radical via  
716 a loss of CO after isomerization of the radical. However, this is not compatible with the  
717 experimental m/z 72 SPES shown in Figure 13, which lacks signal around the first ionization  
718 energy of 2-methyl-2-propen-1-ol (9.24 eV)<sup>71</sup>. Additionally, 2-methyl-2-propen-1-ol fragments  
719 to give C<sub>2</sub>H<sub>3</sub>O<sup>+</sup> above 9.7 eV. The signal at m/z 43 starts distinctly below 9.5 eV (see Figure S2)  
720 with no sign for an additional contribution above 9.7 eV, which confirms the absence of 2-  
721 methyl-2-propen-1-ol. The PIMS and GC data in Figure 13 start to disagree at 650 K because  
722 the PIMS data are derived from the m/z 72 signal, which does not only originate from 2-  
723 methylpropanal but also includes contributions from at least one other species. These species  
724 likely have different photoionization cross sections and thus the quantification is  
725 questionable.

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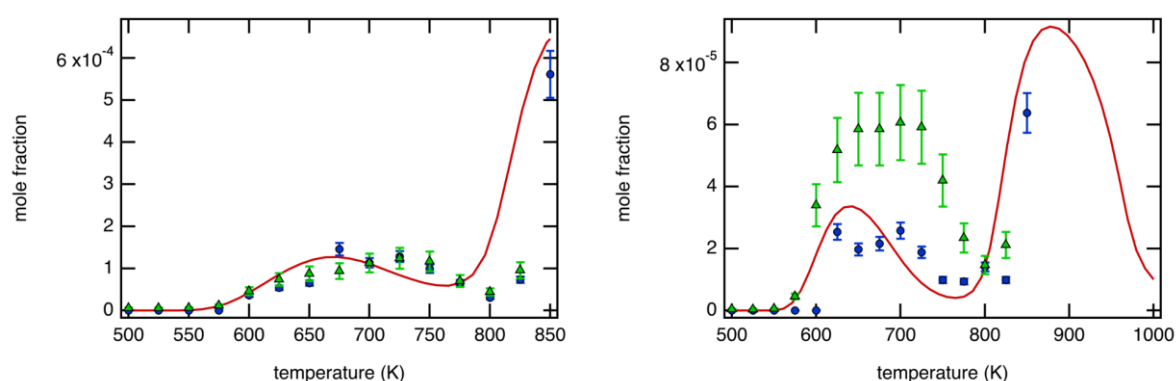
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728 Figure 16. PIY of m/z 102 (left) and 104 (right) registered in PEPICO measurements at 570 K  
729 (dots) compared to simulated PIY of 2-methyl-3-methylperoxyprop-1-ene and 1-  
730 hydroperoxy-2,2-dimethylpropane (red lines) respectively. Note that the simulated spectra  
731 were shifted (see text for explanation).

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*Tert*-butylhydroperoxide  $\text{CC(C)(C)OO}$  (tBuOOH,  $m/z$  90) is predicted by the kinetic model but not detected in this work. The ionization threshold observed in the PIY of  $m/z$  90 (see right panel in Figure 8), identified as the main KHP fragment, does not coincide with the one of tBuOOH<sup>72</sup>. The kinetic model also predicts that a minor fraction of ROO may be consumed by disproportionation with an  $\text{HO}_2$  radical to form 1-hydroperoxy-2,2-dimethylpropane ( $\text{CC(C)(C)COO}$ ,  $m/z$  104) and an  $\text{O}_2$  molecule. A signal was recorded at  $m/z$  104 in both NSRL and SOLEIL experiments (see Figure 9). However, the signal of  $m/z$  104 obtained with the PIMS setup does not have the temperature dependence expected for an intermediate. The PIY of  $m/z$  104 recorded in  $i^2$ PEPICO compared to simulated PIY of 1-hydroperoxy-2,2-dimethylpropane would support this statement though (see right panel in Figure 16). However, the simulated PIY requires an excessively large energy shift (450 meV) to match the PIY curve. Finally, a peak at  $m/z$  102 is also observed in the PEPICO but not in the PIMS mass spectrum (see Figure 9). The kinetic model predicts the formation of 2-methyl-3-methylperoxyprop-1-ene  $\text{CC(=C)COOC}$  with a maximum mole fraction of 3.5 ppm at 600 K by radical reaction  $i\text{C}_4\text{H}_7 + \text{CH}_3\text{OO}$ .  $i\text{C}_4\text{H}_7$  is formed by H-abstraction from isobutene and  $\text{CH}_3\text{OO}$  by  $\text{O}_2$ -addition on a methyl radical. The PIY of  $m/z$  102 obtained in PEPICO measurements agrees well with the simulated spectrum of 2-methyl-3-methylperoxyprop-1-ene (see left panel in Figure 16). However, as for  $m/z$  104 an excessively large energy shift (600 meV) to match the PIY curve is required.

#### Chemistry from KHP decomposition products

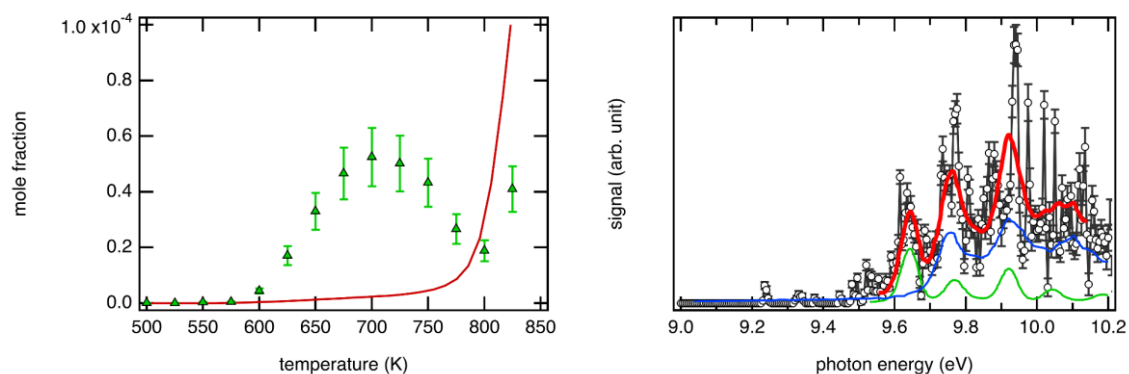
Other species were detected and quantified by GC and PIMS. Propene ( $\text{C}_3\text{H}_6$ ,  $m/z$  42) was quantified by raw mass separation due to a high mass resolving power at NSRL and its experimental mole fraction is in good agreement with the numerical predictions (see left panel of Figure 17). Propene is produced according to the model from 2-methylpropanal, which reacts by H-abstraction with OH followed by CO elimination and H atom loss. Subsequent reaction of propene leads to acetaldehyde ( $\text{CH}_3\text{CHO}$ ,  $m/z$  44), for which experimental measurements and numerical predictions of the mole fraction are in relatively good agreement (see right panel in Figure 17) with those measured by LRGP, while the mole fractions derived from NSRL are two times larger.



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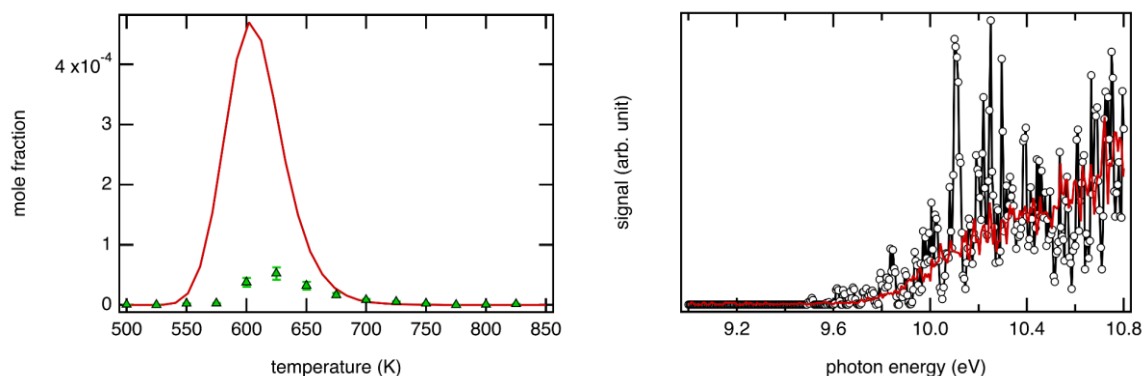
Figure 17. mole fraction of propene (left) and acetaldehyde (right) measured during neopentane oxidation ( $\phi = 0.5$ , 1.5 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s. The model prediction is also presented.

769 The SPES of  $m/z$  42 in the right panel of Figure 18 shows, in addition to propene, the  
 770 presence of ketene ( $\text{H}_2\text{C}=\text{C}=\text{O}$ ), which cannot be detected with good sensitivity by GC. The PES  
 771 of ketene and propene and the SPES were integrated and normalized. A least-squares fit of  
 772 the photoelectron spectra of both isomers to the experimental SPES gives an equivalent signal  
 773 ratio of 0.6:1.0. Relative mole fractions could then be estimated by weighting the branching  
 774 ratio using the absolute photoionization cross sections at 10.0 eV from Yang et al. for ketene  
 775 ( $22.4 \text{ Mb}$ )<sup>31</sup> and Person et al. for propene ( $7.2 \text{ Mb}$ )<sup>73</sup>. The weighting leads to a ketene:propene  
 776 mole fraction (MF) ratio of 0.2:1.0, which is in disagreement with the one derived from  
 777 simulations. Based on Figure 17 and 18, the predicted ratio would be 0.01:1.0. Since the  
 778 agreement between the kinetic model and the experiment is good for propene, and using a  
 779 reference value of 40 ppm for propene at 600 K (see Figure 17), the mole fraction of ketene  
 780 based on SPES derived MF ratio would be around  $\sim 8$  ppm. This is in agreement within a factor  
 781 2 with the NSRL-derived 4.4 ppm mole fraction at 600 K and shows that the quantification by  
 782 the SPES method is relatively robust.  
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 785 Figure 18. (left) mole fraction of ketene measured during neopentane oxidation ( $\phi = 0.5, 1.5$   
 786 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s compared to literature model predictions. (right) SPES of  
 787  $m/z$  42 at  $T = 580$  K (dots) compared to PES of ketene (green) from Niu et al.<sup>74</sup> and propene  
 788 (blue) from Bieri et al.<sup>75</sup> The red curve shows the results of the fit (see text for details).  
 789

790 Finally, methylhydroperoxide ( $\text{CH}_3\text{OOH}$ ,  $m/z$  48) has been detected in the PEPICO and  
 791 PIMS experiments. The SPES of  $m/z$  48 is presented on the right side of Figure 19 and shows a  
 792 good agreement with the SPES of  $\text{CH}_3\text{OOH}$  obtained during the oxidation of n-pentane at low  
 793 temperature by Bourgalais et al.<sup>26</sup>. According to the kinetic model,  $\text{CH}_3\text{OOH}$  is produced from  
 794 the reaction  $\text{CH}_3\text{OO} + \text{HO}_2$ , with  $\text{CH}_3\text{OO}$  being formed by the addition of an oxygen molecule  
 795 to a methyl radical. The mole fraction calculated from the PIMS measurements show that this  
 796 pathway is overestimated by the kinetic model.  
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800 Figure 19. (left) Mole fraction of methylhydroperoxide measured during neopentane  
801 oxidation ( $\phi = 0.5$ , 1.5 % in He) at  $P = 1.07$  bar and  $\tau = 3$  s compared to literature model  
802 predictions. (right) SPES of  $m/z$  48 at  $T = 580$  K (dots) compared to SPES of  
803 methylhydroperoxide from Bourgalais et al.<sup>26</sup> (red line).

## 804 Conclusion and perspectives

805 Neopentane oxidation was studied in three JSR experiments in a temperature range  
806 from 500 to 850 K, a pressure of 1.07 bar, and for  $\phi = 0.5$ . The products were identified and  
807 quantified by several analytical techniques: GC-TCD/FID/MS, SVUV-PIMS, and SVUV-PEPICO.  
808 Theoretical calculations were performed to support the assignment of SPES. The use of  
809 different techniques provided complementary and coherent results, which increased the  
810 confidence in the assignments and quantifications of intermediates. The major first and  
811 second  $O_2$  addition products were observed in agreement with the literature: 3,3-  
812 dimethyloxetane, 2-methylpropanal, methacrolein, acetone, and isobutene. The KHP was  
813 detected and quantified and a fragment of its photoionization at  $m/z$  90 was observed.

814 Simulations using the kinetic model by Bugler et al.<sup>11</sup> from the literature developed for  
815 the oxidation of pentane isomers at low temperature were compared to the experimental  
816 results. Disregarding a systematic temperature shift of the predictions, most of the mole  
817 fraction profiles are relatively well reproduced, demonstrating the robustness of the kinetic  
818 model. Within uncertainties, PIMS and GC mole fractions are in relatively good agreement  
819 except for  $CH_2O$  for which a significant difference between the mole fractions was observed  
820 between PIMS and GC measurements. Both measurements were repeated and appeared very  
821 reproducible. The unexpected large presence of formic acid might have caused some  $CH_2O$  to  
822 polymerize in the GC transfer line. Considering the differences for all aldehydes even taking  
823 into account uncertainty, a polymerization effect on this class of compound cannot be  
824 excluded at this point. Additional measurements with other analytical tools would be  
825 necessary in the future to obtain the accurate mole fraction profiles required for the  
826 improvement of the kinetic model. Calibration with known gas quantities at all three sites  
827 would be necessary in the future to benchmark the measured mole fraction at the different  
828 facilities at the same conditions.

829 A few significant discrepancies between experimental and predicted mole fractions are  
830 observed and related to the possibility that the model is incomplete. The PEPICO  
831 measurements indicate the formation of 2,2-dimethylpropanal which is a product not  
832 predicted by the kinetic model and not detected by PIMS or GC. However, it was detected by  
833 Eskola et al.<sup>17</sup>. The seemingly contradicting results are explained by the fact that 2,2-  
834 dimethylpropanal is mainly formed at low temperatures while its isomer 3,3-dimethyloxetane  
835 dominates at higher temperatures. In order to confirm this explanation, the photoionization

836 cross section of 2,2-dimethylpropanal is required for quantification. Furthermore, the relative  
837 yields of both isomers should be confirmed since Eskola et al.<sup>17</sup> initiated neopentane oxidation  
838 with Cl atoms. The most likely pathways for 2,2-dimethylpropanal formation should be added  
839 to the kinetic model to be able to compare experimental and predicted 2,2-dimethylpropanal  
840 yields and to find optimized conditions to attempt its detection by GC. A potential pathway to  
841 consider would be successive reactions of H-migration from the ROO radical. This would  
842 impact the chemistry of the first oxygen addition and the formation of some hydroperoxides  
843 that are predicted by the kinetic model but not observed in this work (tBuOOH, 1-  
844 hydroperoxy-2,2-dimethylpropane) or overestimated (CH<sub>3</sub>OOH).

845 The formation of KHP could be observed directly in the m/z 118 parent ion channel at  
846 the NSRL and indirectly in the m/z 90 dissociative ionization channels at SOLEIL—and the  
847 temperature profile is similar to that predicted by the kinetic model. Information on the  
848 photoionization cross section is needed in order to compare measured and calculated KHP  
849 mole fractions. The decomposition pathways of KHP need to be thoroughly revised in an  
850 improved kinetic model. The detection of a signal at m/z 100 shows that it is necessary to  
851 consider the possibility of the formation of 2,2-dimethylpropanedial by H<sub>2</sub>O-elimination from  
852 the KHP. More importantly, the underestimation of the mole fraction measurements of 2-  
853 methylpropanal in conjunction with the observation of peaks at m/z 46 assigned to formic  
854 acid respectively, highlights the importance of the Korcek reaction, which is not included in  
855 the kinetic model.

856 Besides the Korcek model, the implementation of the isobutene + HO<sub>2</sub> chemistry  
857 should be double-checked as it could be an important source of 2,2-dimethyloxirane which  
858 was detected in this work but not quantified. Discrepancies in the measured and simulated  
859 mole fractions of intermediate yielded by specific pathways, such as  $\gamma$ -KHP decomposition and  
860 Korcek reaction, demonstrate that a careful revision of the kinetic model is needed.  
861 Development of the kinetic model would benefit from additional experiments with a better  
862 sensitivity to provide robust structural information (e.g. m/z 88, 100, 102, 104) and from  
863 additional photoionization cross section information (m/z 86, 100, and 118).

864

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