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Jérémy Bourgalais, Olivier Herbinet, Hans-Heinrich Carstensen, Janney Debleza, Gustavo Garcia, et al.. Jet-Stirred Reactor Study of Low-Temperature Neopentane Oxidation: A Combined Theoretical, Chromatographic, Mass Spectrometric, and PEPICO Analysis. *Sustainable Energy & Fuels*, 2021, 35 (23), pp.19689-19704. 10.1021/acs.energyfuels.1c02080 . hal-03444305

HAL Id: hal-03444305

<https://hal.univ-lorraine.fr/hal-03444305v1>

Submitted on 22 Oct 2022

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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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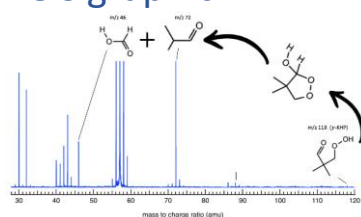
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Abstract

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 O₂-addition products were observed in agreement with the literature (e.g., 3,3-dimethyloxetane, acetone, isobutene, and γ -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 γ -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 identified¹.

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 reactors²⁻⁷, rapid compression machines, shock tubes⁸⁻¹²,
75 as well as in flow tubes¹³⁻¹⁷ and in jet-stirred reactors (JSR)¹⁸⁻²⁰. 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 calculations²¹ and the
78 development of chemical kinetic models^{14,18,22}. 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.¹⁷ 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.¹⁷ suggested that 3-hydroperoxy-2,2-dimethylpropanal,
86 undergoes the so-called Korcek reaction²³. The KHP in neopentane oxidation was also

87 observed by Hansen et al.²⁰ 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 O₂-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.¹⁸ 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 analyzers²⁴. 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 beam²⁵. 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 JSR²⁶. This facility allows the acquisition of mass-resolved slow
114 photoelectron spectra (SPES)^{27,28} 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^{26,29}. The detailed kinetic model developed at the Combustion Chemical Centre of
119 the National University of Ireland (Galway, Ireland)¹¹ 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 (ϕ) 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 O₂ were provided by Messer
136 in LRGP (both 99.999 % pure) and by Air Liquide at SOLEIL. Ar and O₂ 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 O₂ 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)	τ (s)	ϕ	mole fractions		
					neopentane	O ₂	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	∞	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 (~ 81.2 cm³) working under isothermal and isobaric conditions with a reactive gas
159 mixture (fuel + O₂) continuously flowing into it, with a high dilution of inert gas to avoid
160 temperature gradients due to the oxidation exothermicity. Reactants (neopentane and O₂),
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 ~ 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 H₂ (also used
174 for the FID) is flowed to reduce species containing carbonyl groups to the corresponding
175 alkanes, and CO and CO₂ 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 O₂, CH₄, CO, and CO₂. 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 JSR³⁰, while the design of the nozzle sampling is similar
192 to that described by Battin-Leclerc et al.²⁵. 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 :

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

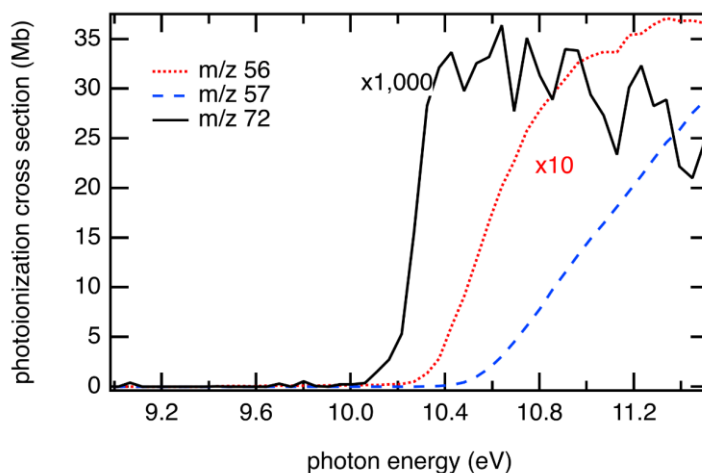
202 $X_i(T)$, $\lambda(T)$ and $S_i(T)$ represent, respectively, the mole fraction of species *i* at temperature
203 *T*, the coefficient of gas expansion at temperature *T* depending on the bulk property of the
204 system and the signal of species *i* at temperature *T*. Similarly, $X_i(T_0)$, $\lambda(T_0)$ and $S_i(T_0)$ are
205 known information at temperature *T*₀, 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 literature³¹ 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 literature³¹ 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^{32,33}.
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 chamber³⁴ permanent end-station, located at one of the
242 monochromatized branches of the DESIRS beamline at the SOLEIL synchrotron a 100 μ 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 coincidence³⁵. 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 detector³⁶. 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 described²⁷, 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 functional³⁷ as implemented in GAUSSIAN09³⁸, using the augmented
268 correlation-consistent aug-cc-pVDZ basis set^{39,40}. 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.⁴¹ 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^{42–45}. 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^{46,47}. 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)^{48–51} together with the aug-cc-pVDZ basis set in conjunction
282 with the corresponding resolutions of the identity and density fitting functions⁵² as generated
283 by MOLPRO⁵³. 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

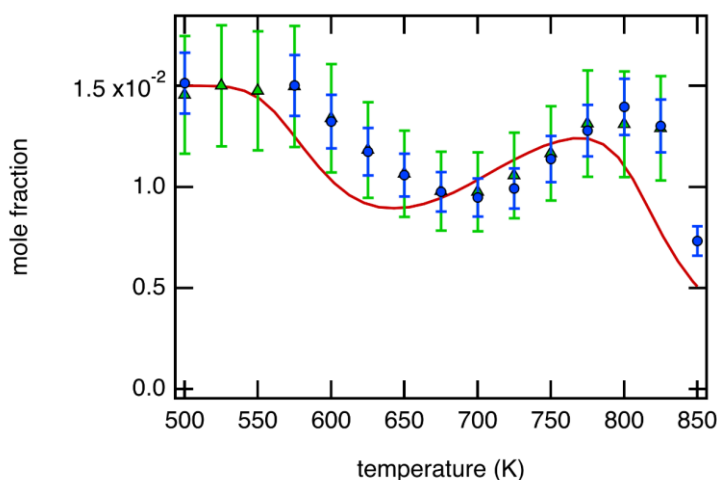
291 The experimental mole fractions measured during the oxidation of neopentane were
292 compared to numerical predictions with the detailed kinetic model of pentane isomers
293 developed at NUI Galway¹¹. This model was used without any modifications. It predicts the
294 auto-ignition delay times of pentane isomers measured in a rapid compression machine and
295 a shock tube well¹¹, and it was also previously used to reproduce experimental oxidation data
296 of n-pentane obtained in JSRs at 1 and 10 bar⁵⁴. All simulations described in this work were
297 performed using the openSMOKE++ software package^{55,56}.

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 temperatures⁵⁷⁻⁵⁹. As oscillatory chemistry is not the subject of this work only data up
310 to 850 K are considered.
311



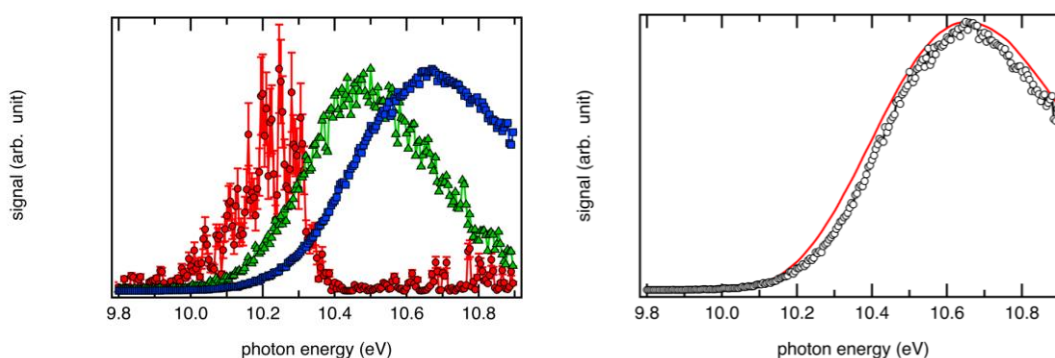
312 Figure 2. Fuel conversion during neopentane JSR oxidation between experimental
313 measurements (GC and PIMS) and numerical predictions (neopentane 1.5 %, $\phi = 0.5$, $\tau = 3$ s).
314
315

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 ~ 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.²⁰ (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.

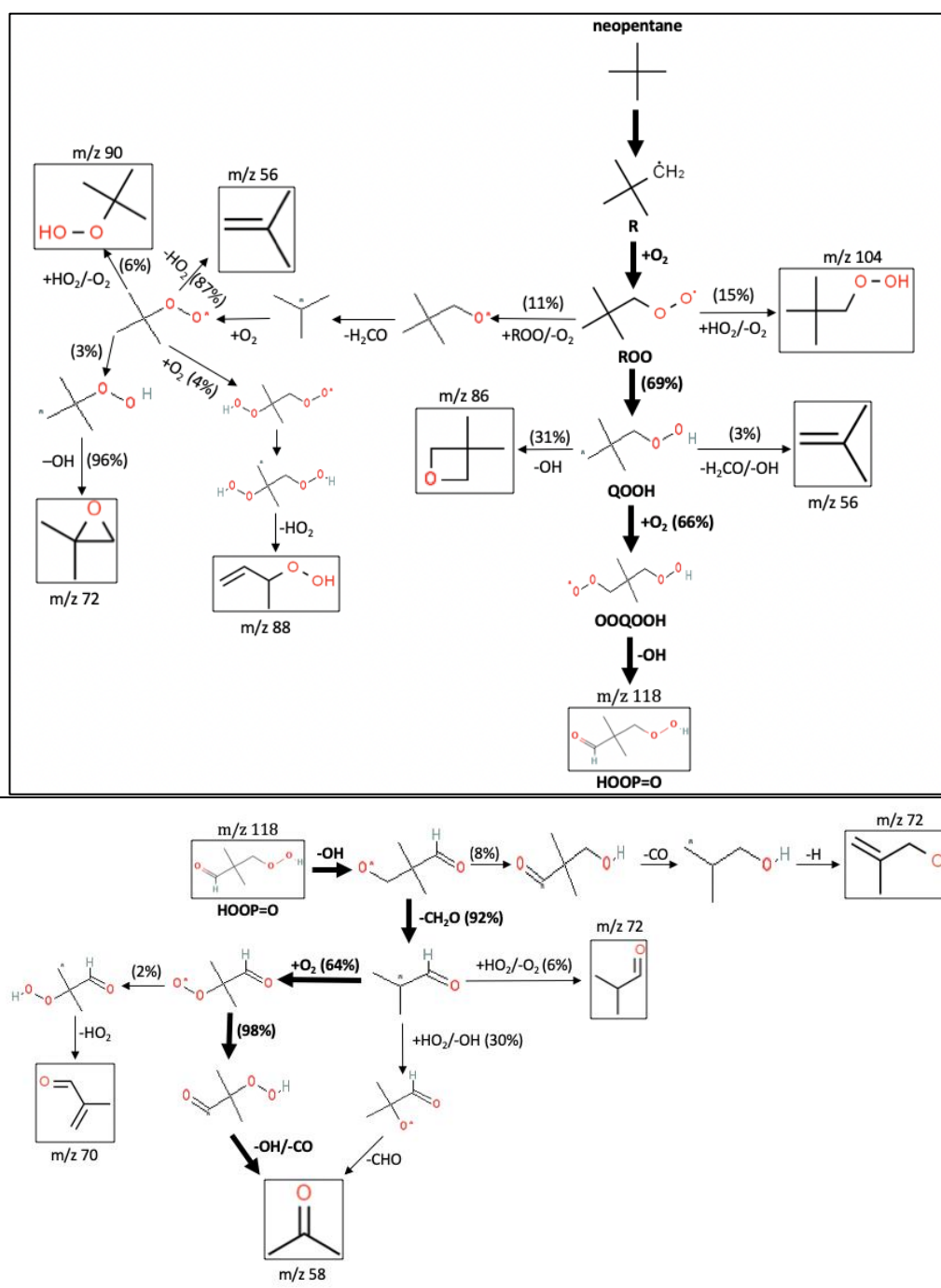
335 The dissociation of the neopentane cation to m/z 56 (CH_4 loss) and 57 (CH_3 loss)
336 fragment ions has been recorded without O_2 addition using the i^2 PEPICO spectrometer, in
337 order to deconvolve the fuel contribution to these mass channels in oxidation conditions from
338 contributions by 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 energies⁶⁰. 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 distortion⁶¹, 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 values⁶².



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.

356 Products from the first 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.¹¹. Based on the literature¹⁷, the low-
359 temperature oxidation of neopentane is controlled by the formation of a neopentyl radical (R)
360 that further reacts with 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.



366

367

368

369 Figure 4. Rate of production analysis for neopentane oxidation ($\phi = 0.5$, 1.5 % in He) at 600 K,

370 P = 1.07 bar and $\tau = 3$ s. Bold arrows indicate the dominant pathways. Pathways with small

371 branching ratios (< 1 %) to or from intermediates are omitted for clarity. The upper panel

372 shows the reactions leading to the formation of KHP. The lower panel shows the

373 decomposition pathways of KHP.

374

375 The right panel in Figure 5 compares the SPES of m/z 86 recorded at 580 K compared

376 to simulated SPES of 3,3-dimethyloxetane and three isomers: 2,2-dimethylpropanal

377 CC(C)(C)C=O, trans-2,4-dimethyloxetane CC1CC(O1)C, and pentan-3-one CCC(=O)CC. The

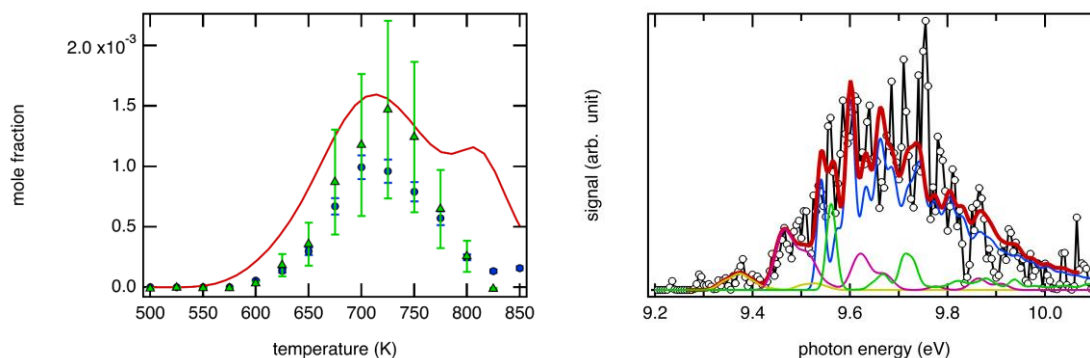
378 deconvolution of the SPES leads to a 3,3-dimethyloxetane:2,2-dimethylpropanal:trans-2,4-

379 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 eV⁶³. 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

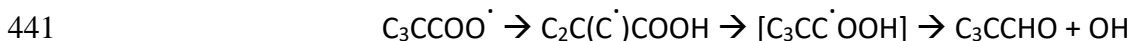
405 Note that at 600 K very little 3,3-dimethyloxetane is detected. The GC yields at LRGP
406 are only slightly outside of the noise level and the yields determined by PIMS are essentially
407 around zero level. The kinetic model predicts higher yields because of the temperature shift.
408 Taking the 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.¹⁷, 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.¹⁷ 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.¹⁷ 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.¹⁷ 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.¹⁷. Any further attempts
435 to search for 2,2-dimethylpropanal should focus on the temperature range above 625 K.

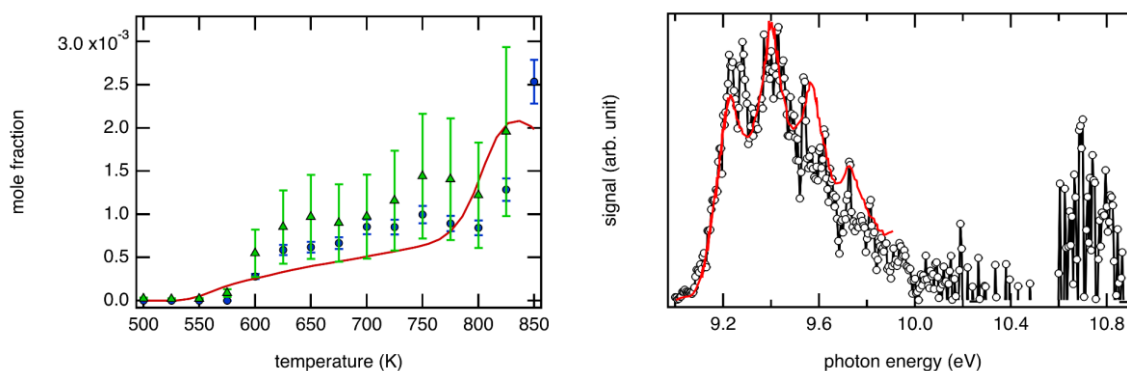
436 Although the formation of 2,2-dimethylpropanal is not predicted by the kinetic model,
437 the work by Eskola et al.¹⁷ as well as this study has clearly proven its presence. Besides the
438 possibility to be formed in radical-radical reactions (Eskola et al.¹⁷), another reaction sequence
439 could 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.¹⁷ 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 (C_4H_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 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.¹⁷, the spectral signature arises from the fragmentation
452 of 3,3-dimethyloxetane.

453

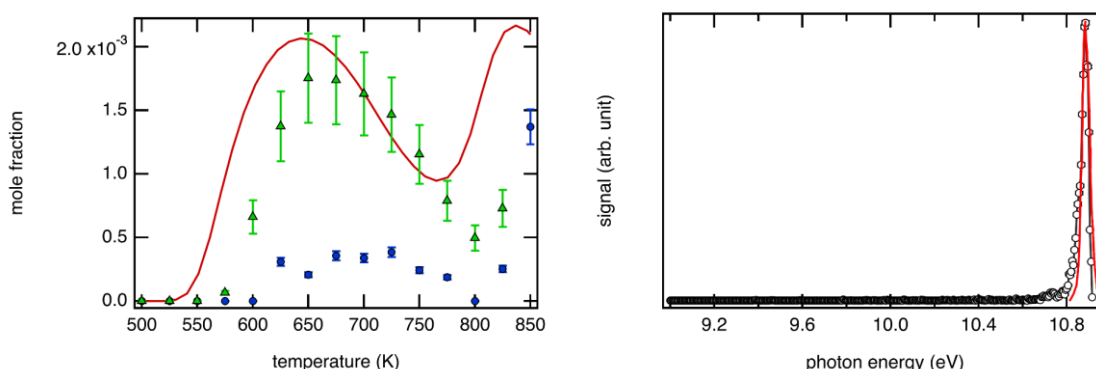


454 Figure 6. (left) Mole fraction profile of isobutene measured during neopentane oxidation (ϕ
455 = 0.5, 1.5 % in He) at $P = 1.07$ bar and $\tau = 3$ s. The model prediction is also presented. (right)
456

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 & Kuppermann⁶⁴, 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.⁶⁵.
485

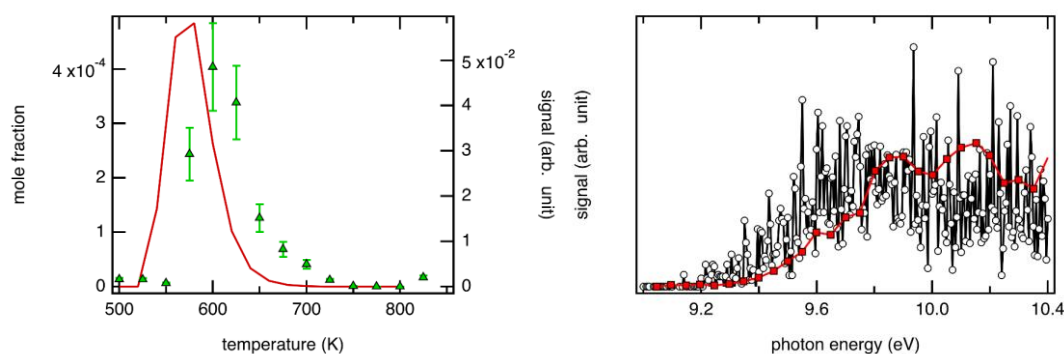
486 Formaldehyde is one most important intermediate in low-temperature oxidation, thus
487 PIMS mole fractions at a level of 10^{-3} seems thus reasonable. Note that, because of the larger
488 deviation with GC data for this species, in order to verify the reliability and rationality of
489 experimental 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 CH₂O 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 O₂-addition

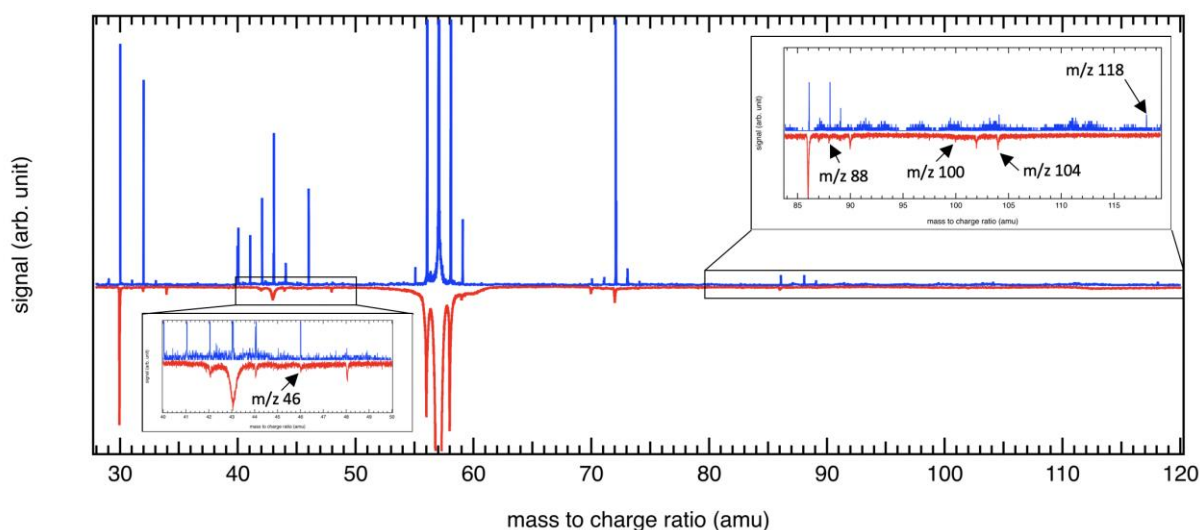
507 The second addition of O₂ leads to the formation of a hydroperoxyalkylperoxy radical
508 (OOQOOH), especially at high pressures and high O₂ mole fractions, such as in practical
509 combustion systems. This radical subsequently decomposes to 3-hydroperoxy-2,2-
510 dimethylpropanal CC(C)(COO)C=O, a 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.²⁰.
516



517
518 Figure 8. (left) Simulated mole fraction profile of γ -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.²⁰ (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 NSRL
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.²⁰ 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 HOOCH₂C(CH₃)₂H⁺ daughter ion at

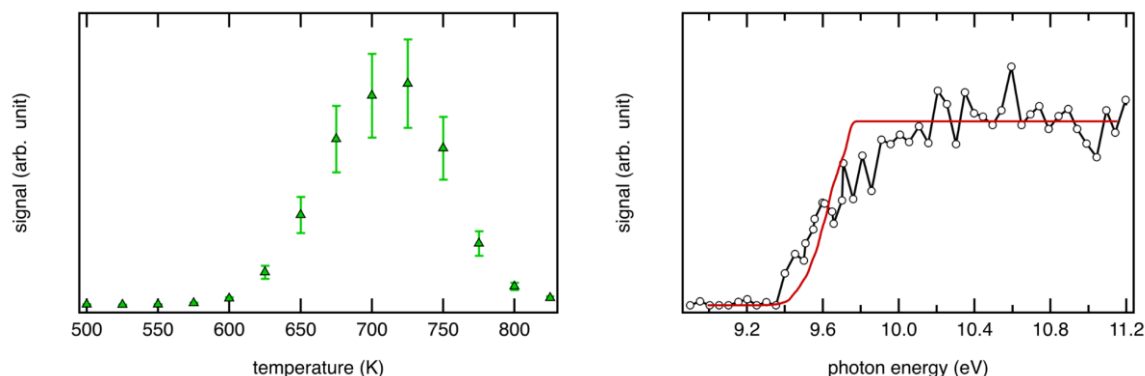
534 m/z 90. A signal at m/z 90 was observed with the SOLEIL device and the PIY is displayed in the
 535 right panel of Figure 8. The derived appearance energy of 9.2 eV is in relatively good
 536 agreement with that mentioned by Hansen et al.²⁰
 537



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

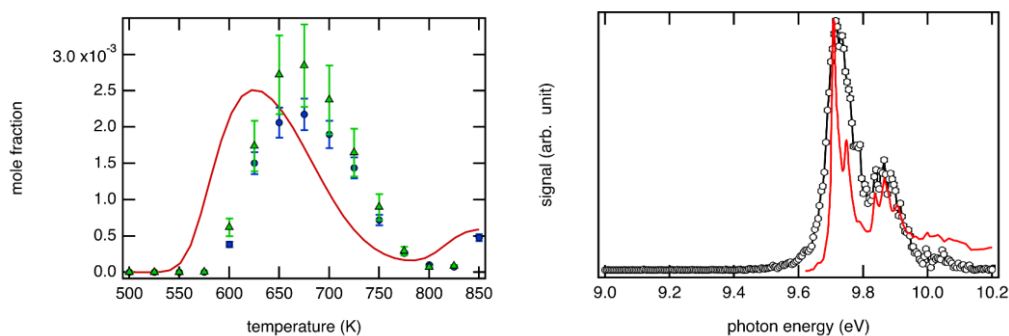
542 Products from KHP decomposition

543 Once formed, KHPs decompose through dissociation pathways that remain to be
 544 clarified. Eskola et al.¹⁷ 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.¹⁷ 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

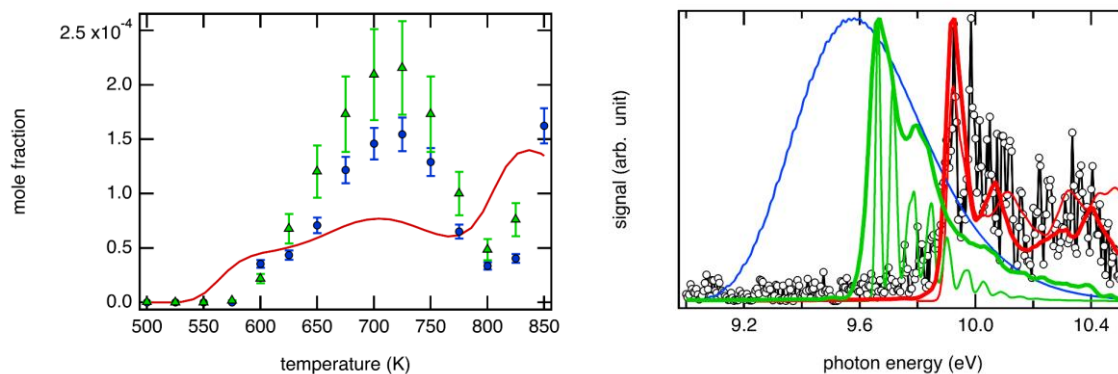
570 KHPs (HOOP=O) mainly decompose via -O-OH bond rupture, which leads to chain-
 571 branching due to the reactivity of the O-centered isobutanal-2-methoxy radical (OPO).
 572 Subsequent reactions form species with atomic masses of 58, 70, and 72 (see Figure 4). The
 573 dominant decomposition pathways consist of CH_2O -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.¹⁷ 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.⁶⁷.
 585

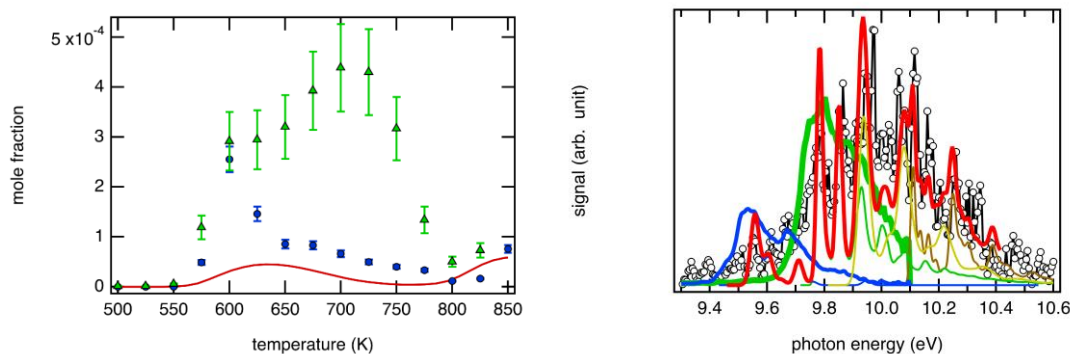
586 According to the kinetic model, a minor decomposition pathway of the KHP leads to
 587 methacrolein ($\text{CC}(\text{=C})\text{C}=\text{O}$, m/z 70). The left panel in Figure 12 shows that the simulation
 588 predicts for the central temperature regime studied lower methacrolein mole fractions than
 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 literature⁶⁶. 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
610 Reported in Figure 4, another minor pathway involving the loss of CH2O and a
611 successive HO2-addition/O2-elimination leads to 2-methylpropanal (CC(C)C=O, m/z 72). The
612 left panel of Figure 13 shows a reasonably good agreement between the numerical and LRGP
613 experimental mole fractions, except at 600 K where the discrepancy is significant (almost an
614 order of magnitude difference). The PIMS data shown in Figure 13 are significantly higher than
615 the GC measurements. This is likely due to contribution of additional species, such as 2,2-
616 dimethyloxirane, to the m/z 72 signal. This explanation is supported by the right panel of
617 Figure 13 which clearly shows that the m/z 72 spectrum cannot be reproduced by 2-
618 methylpropanal alone. See also the next section for further explanations. Eskola et al.¹⁷
619 proposed a parallel decomposition pathway for KHP via intermediate cyclic peroxide
620 formation rather than direct OH-loss. This mechanism, called Korcek reaction, is known to lead
621 through subsequent decomposition to a carbonyl compound and an organic acid²³. In the case
622 of neopentane, the Korcek reaction of its KHP produces 2-methylpropanal as carbonyl
623 component accompanied by formic acid (HCOOH, m/z 46) (see Figure 14). The maximum
624 deviation between numerical and experimental mole fractions of 2-methylpropanal coincides
625 with the maximum mole fraction of KHP (600 K, see Figure 8), which supports the idea that
626 the missing Korcek reaction in the model causes the discrepancy between experiment and
627 model.



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.⁶⁸ 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)⁶³. 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.²⁹. 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.¹⁴ 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.¹⁴ introduced a HCOOH production pathway from CH₂O 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 CH₂O would be produced (see Figure
 656 4) and the predicted CH₂O 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.
 660

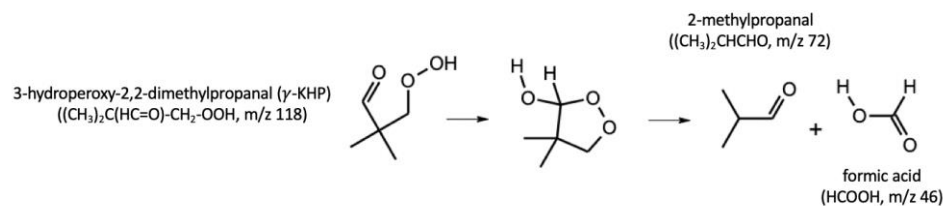


Figure 14. Potential Korcek reaction from γ KHP leading to 2-methylpropanal and formic acid.

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 $((\text{CH}_3)_2\text{CHCOOH})^{69}$ and simulated spectra of two isomers 3-hydroperoxybut-1-ene $\text{CC}(\text{C}=\text{C})\text{OO}$ and 3-hydroperoxy-2-methylprop-1-ene $\text{CC}(\text{C}=\text{C})\text{COO}$. 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_2 . This reaction is now routinely incorporated in the alkene submechanisms⁷⁰, 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 $\text{ROO} + \text{ROO}$ reaction (see Figure 4).

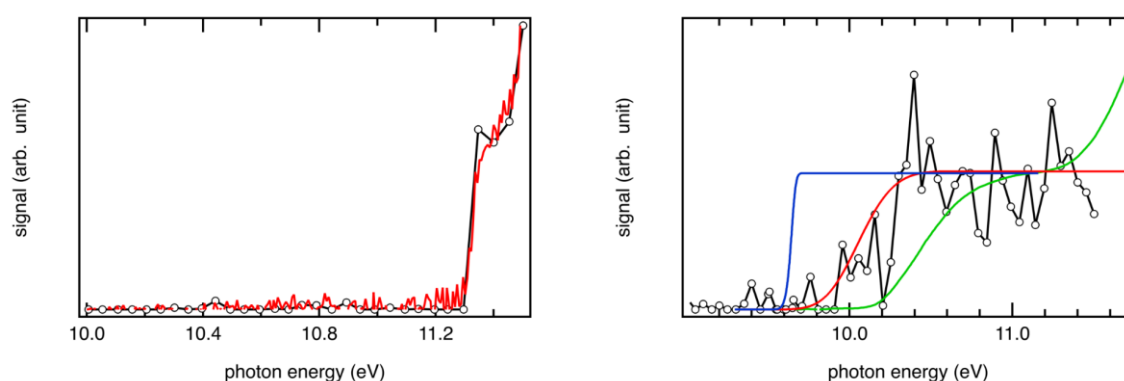


Figure 15. (left) PIY of m/z 46 registered in PIMS measurements at 600 K (dots) compared to a reference PIY of formic acid from Battin-Leclerc et al.²⁹ (red line). (right) PIY of m/z 88 registered in PIMS at 600 K (dots) compared to a reference PIY of isobutyric acid from Watanabe et al.⁶⁹ (green line) 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.

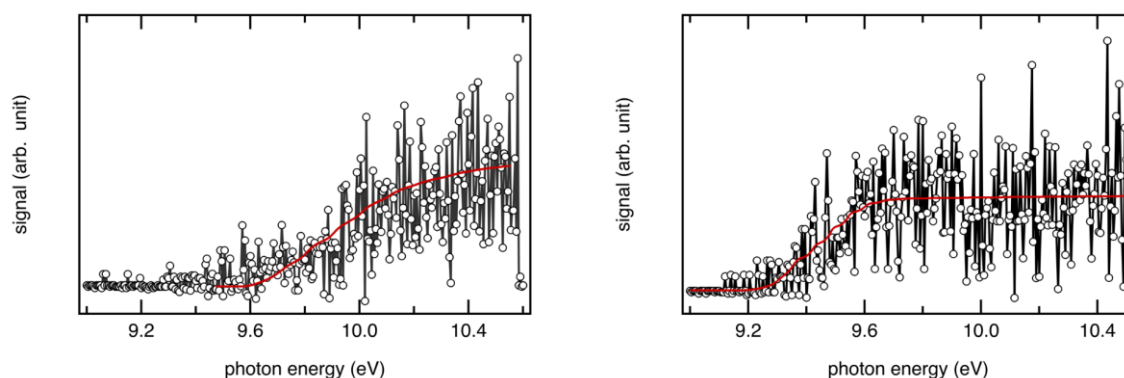
694 New experiments over a wider energy range and leading to better signal to noise
695 detection of m/z 88 would be necessary to confirm this result. Based on the currently available
696 data, m/z 88 does not appear to correspond to isobutyric acid but rather to 3-hydroperoxybut-
697 1-ene. The identification 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_2O . 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 $\text{ROO} + \text{ROO}$ 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 $\text{CC1}(\text{CO1})\text{C}$
709 and trans-2,3-dimethyloxirane $\text{CC1C}(\text{O1})\text{C}$) and butan-2-one $\text{CCC}(=\text{O})\text{C}$ 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_2 to isobutene¹⁵ and a
712 sequence of reactions initiated by the $\text{ROO} + \text{ROO}$. As the temperature increases, the
713 unimolecular decomposition of the radical R to isobutene + CH_3 will counterbalance the
714 reaction $\text{R} + \text{O}_2 \rightarrow \text{RO}_2$. The kinetic model also predicts 2-methyl-2-propen-1-ol $\text{CC}(=\text{C})\text{CO}$ 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)⁷¹. Additionally, 2-methyl-2-propen-1-ol fragments
719 to give $\text{C}_2\text{H}_3\text{O}^+$ 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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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).

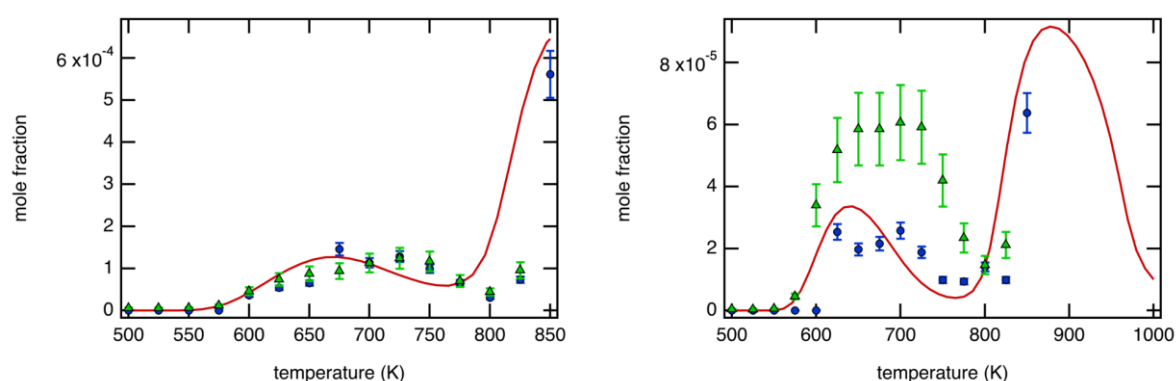
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Tert-butylhydroperoxide CC(C)(C)OO (tBuOOH, m/z 90) is predicted by the kinetic model but not detected in this work. The ionization threshold observed in the PIY of m/z 90 (see right panel in Figure 8), identified as the main KHP fragment, does not coincide with the one of tBuOOH⁷². The kinetic model also predicts that a minor fraction of ROO may be consumed by disproportionation with an HO_2 radical to form 1-hydroperoxy-2,2-dimethylpropane CC(C)(C)COO , (m/z 104) and an 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 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 CH_3OO by 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

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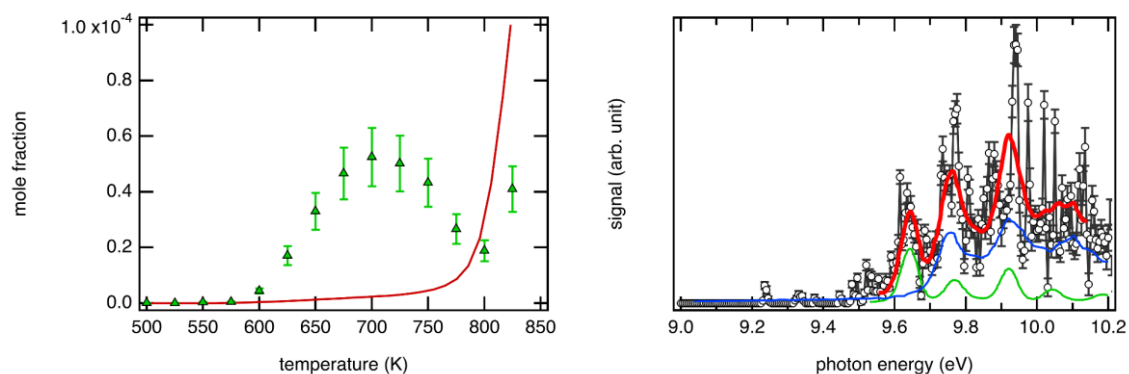
Other species were detected and quantified by GC and PIMS. Propene (C_3H_6 , m/z 42) was quantified by raw mass separation due to a high mass resolving power at NSRL and its experimental mole fraction is in good agreement with the numerical predictions (see left panel of Figure 17). Propene is produced 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 (CH_3CHO , 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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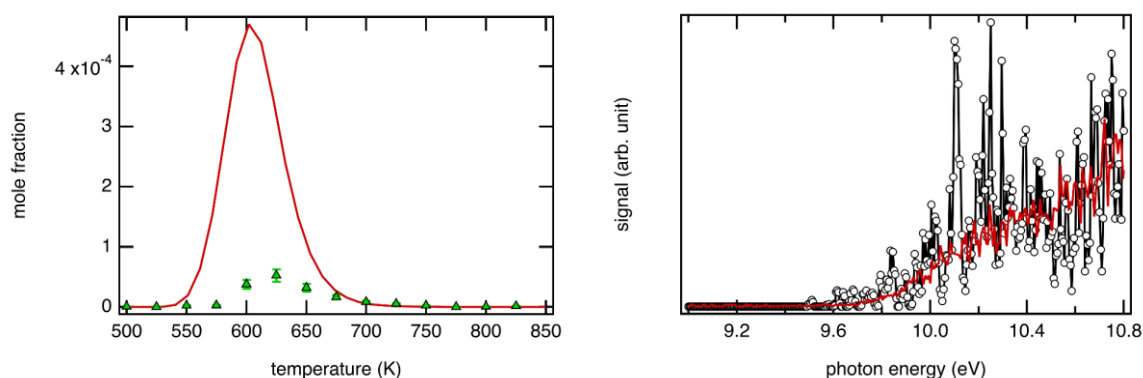
Figure 17. mole fraction of propene (left) and acetaldehyde (right) measured during neopentane oxidation ($\phi = 0.5$, 1.5 % in He) at $P = 1.07$ bar and $\tau = 3$ s. The model prediction is also presented.

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 Mb)³¹ and Person et al. for propene (7.2 Mb)⁷³. 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 ~ 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.⁷⁴ and propene
 788 (blue) from Bieri et al.⁷⁵ The red curve shows the results of the fit (see text for details).
 789

790 Finally, methylhydroperoxide (CH_3OOH , 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 CH_3OOH obtained during the oxidation of n-pentane at low
 793 temperature by Bourgalais et al.²⁶. According to the kinetic model, CH_3OOH is produced from
 794 the reaction $\text{CH}_3\text{OO} + \text{HO}_2$, with CH_3OO 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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 799 Figure 19. (left) Mole fraction of methylhydroperoxide measured during neopentane
 800 oxidation ($\phi = 0.5$, 1.5 % in He) at $P = 1.07$ bar and $\tau = 3$ s compared to literature model
 801 predictions. (right) SPES of m/z 48 at $T = 580$ K (dots) compared to SPES of
 802 methylhydroperoxide from Bourgalais et al.²⁶ (red line).
 803

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.¹¹ 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.¹⁷. 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.¹⁷ 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 (CH₃OOH).

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 H₂O-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 + HO₂ 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 γ -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

865 Acknowledgement

866 We are grateful to the whole SOLEIL staff for smoothly running the facility under
867 project 20180021. We warmly thank J-F Gil for his technical help around the SAPHIRS
868 experiment. HHC acknowledges I3A for the use of its HPC cluster HERMES and the funding
869 from the Aragón Government (Ref. T22_20R), co-funded by FEDER 2014-2020 "Construyendo
870 Europa desde Aragón".

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