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1 Enhancing 1-Hexene Reactivity under Inhibitive
2 Temperatures using Ozone

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7

8 **KEYWORDS:** Ozone; Jet-stirred Reactor; Kinetic Modeling; Gas Chromatography; Negative
9 Temperature Coefficient.

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18 **ABSTRACT:** This research delved into the oxidation chemistry of 1-hexene with and without the
19 addition of O₃ within a 350 – 800 K temperature range using a near-atmospheric pressure jet-
20 stirred reactor. Using gas chromatography and mass spectrometry, the products were identified,
21 revealing O₃ ability to enhance fuel oxidation and enabling its significant conversion in typically
22 inhibitive conditions (< 500 K and > 700 K). Due to the addition of O₃, an efficient fuel conversion
23 is noticed at the lowest temperatures, while a significant fuel reactivity persists in the high
24 temperature zone where the negative temperature coefficient behavior is almost fully suppresses.
25 The addition of O₃ induces an increased production of aldehydes (formaldehyde, acetaldehyde,
26 propanal, butanal and pentanal) and acids (pentanoic acid) at the lowest temperatures and amplifies
27 the formation of several products (CO₂, CO, butene, butyl-oxirane, 2-butanone, ethylene,
28 methanol, ethanol, furan, acrolein, acetone, propene, butadiene, methyloxirane, ethyloxirane,
29 pentane, methylvinylketone) at higher temperatures. A significant concentration of
30 ketohydroperoxides is also formed below 500 K. Our experimental findings, compared to the
31 simulations of an updated kinetic model, suggest that ozonolysis at low temperatures and the
32 interaction of O-atoms from the thermal decomposition of O₃ with oxidation products at high
33 temperature are responsible of the fuel conversion enhancement by enriching the radical pool. The
34 implications of this study spanning both combustion and atmospheric chemistry domains show
35 that the incorporation of O₃ promises enhanced combustion fuel efficiency and strengthen its
36 potential in optimizing fuel blends, pioneering combustion strategies, and pollution control.

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41 INTRODUCTION

42 Plasma-assisted combustion offers potential advancements in the development of superior air-
43 breathing engines. This is due to its ability to significantly change both kinetic and transport
44 attributes, leading to improved ignition, better emission control, and stable flame ¹. Yet, achieving
45 uniform plasmas in the high-pressure environments typical of combustion processes presents a
46 challenge ². As a result, there is a growing interest in using ozone (O₃), an electrically produced
47 and long-lasting species that can be introduced upstream of the combustion chamber. The presence
48 of O₃ also facilitates low-temperature reactions, enabling fuel conversion at temperatures beneath
49 traditional low-temperature combustion (LTC) conditions. This conversion happens either through
50 O-atoms generated from O₃ thermal decomposition or via O₃-addition to the fuel skeleton,
51 depending on the fuel molecular structure ³.

52 While oxidation by O-atoms mainly speeds up chain-branching reactions ⁴⁻⁸, ozonolysis initiate
53 fuel conversion at ambient temperatures. This process yields different oxidation products, thereby
54 altering the overall reaction network. Such changes can significantly influence fuel combustion
55 properties. However, there is a limited amount of research that delves into the elementary reactions
56 and resultant products of ozonolysis at combustion-relevant temperatures. This knowledge gap
57 means that uncertainties persist in understanding the chemistry of O₃ in combustion, essential for
58 enhancing emission control and efficiency in new technological designs. Existing experiments at
59 combustion-relevant temperatures have mostly been limited to flow reactors using few reactants
60 ⁹⁻¹². These efforts have given insights into kinetic mechanisms and preliminary modeling based on
61 global ozonolysis reactions that qualitatively capture the profiles of the main products ^{8,10,12}.

62 In the literature, 1-hexene (C_6H_{12}), is often proposed as a representative alkene component in
63 gasoline surrogate fuels^{13–15}. However, there is only one study about the reactions of this fuel with
64 O_3 under combustion-relevant conditions. This was performed in an homogeneous charge
65 compression ignition (HCCI) engine by reacting a variable fuel portion with O_3 -containing air by
66 Schöborn et al.¹⁶. These measurements indicate an increase in pressure and heat release in
67 presence of O_3 , as well as earlier ignition. There was also a notable decrease in particle emissions
68 and an increase in combustion efficiency under elevated pressure and temperature conditions.

69 Our study explores the impact of O_3 on the oxidation of 1-hexene, known for its pronounced LTC
70 chemistry¹⁷, over a large temperature span (300—800 K). We found that O_3 does not just intensify
71 oxidation but also alters the fuel temperature-driven reactivity; at both low (< 500 K) and high
72 temperatures (> 700 K), thus eliminating the conventional restrictions of LTC. Our results
73 highlight the potential of O_3 to counteract the negative temperature-coefficient (NTC) behavior
74 usual in combustion, where reactivity decreases as the temperature increases^{18,19}. Additionally,
75 we show that the effect of O-atoms in O_3 -driven oxidation differs from those in the oxidation of
76 saturated fuels^{5,20}.

77 In this research, conducted using a Jet-Stirred Reactor (JSR), we identified and quantified main
78 products and stable intermediates using gas chromatographs (GCs) and mass spectrometry (MS),
79 both with and without O_3 introduction. Then our findings were compared with a kinetic model of
80 1-hexene oxidation from literature, updated in order to integrate global ozonolysis reactions. This
81 allowed us to identify pivotal elementary processes when O_3 is incorporated.

82 The manuscript is structured into five sections:

83 (1&2) The first two present the experimental setup and the kinetic model used in this work.

84 (3) A section describing the experimental results confronted to the predictions of the kinetic
85 model.

86 (4) A section presenting a kinetic analysis using the kinetic model at three relevant
87 temperatures into a respective sub-section: (a) 400 K, the ozonolysis zone, (b) 650 K, the
88 maximum of fuel conversion, (c) 750 K, the LTC minimum; a final sub-section on the
89 impact of O-atoms at high temperature is closing the section.

90 (5) A conclusion summarizing the main results and take-home messages.

91

92 **EXPERIMENTAL METHOD**

93 The JSR experimental setup and the GC method used to quantify oxidation products are similar to
94 those mentioned in earlier studies. Therefore, we will provide only a brief summary with details
95 unique to this study. For more in-depth details on the GC method, refer to the JSR study of
96 1-hexene LTC performed by Meng et al. ¹⁷. Specifics regarding the use of JSR with O₃ are
97 available in Smith Lewin et al. ¹⁰.

98 We conducted the oxidation of 1-hexene with or without O₃ in a near-atmospheric JSR that is
99 heated by shaped electric resistances. This spherical reactor, made from fused silica with a volume
100 of around 81.2 cm³, ensures stable temperature and pressure conditions ²¹. We continuously fed
101 gas mixtures consisting of 1-hexene, O₂, and optionally O₃, into the reactor. To stabilize
102 temperature fluctuations in the JSR due to exothermic reactions, we introduced a significant
103 amount of inert helium gas. The reactor temperature was measured using a K-type thermocouple
104 positioned in a glass finger close to the JSR center indicating a temperature uncertainty of around

105 1%.²¹ For all experiments, we kept the pressure, equivalence ratio, and inlet mole fraction of 1-
106 hexene constant at 800 Torr (1.067 kPa), 0.5, and 0.01. The flow rates were adjusted according to
107 temperature, ensuring a constant residence time of 2.0 s (without O₃) or 2.5 s (with O₃). The
108 increased residence time for the case with O₃ is explained by the need to perform more experiments
109 in the very low temperature region, which leads to higher flow rates into the JSR than the one
110 considered maximum ideally (2 NL/min). However, simulations using 2 and 2.5 s as residence
111 time for the case without O₃ showed no significant changes. When initiating oxidation with O₃,
112 we used an O₃ generator to impose a mole fraction of 1,000 ppm that was blended with the fuel
113 just before entering the JSR. Since O₃ is highly reactive even at room temperatures, the reaction
114 time between the fuel and O₃ has been minimized before the reactor preheating stage by mixing
115 the reactants just at the entrance.¹⁰

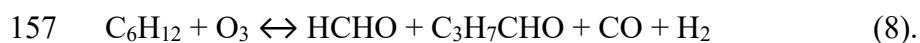
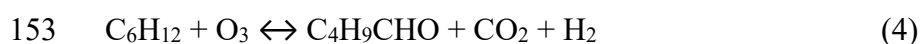
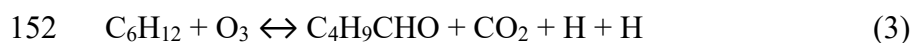
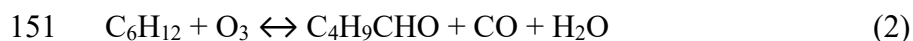
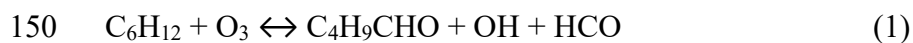
116 The gases resulting from oxidation in the JSR were directed through heated stainless-steel tubes
117 to three GCs to quantify the stable and intermediate products. The first GC, equipped with a
118 Carbosphere-packed column and a thermal conductivity detector (TCD), measures lightweight and
119 permanent gases. The second GC, paired with a Q-Bond capillary column and a flame ionization
120 detector (FID) preceded by a methanizer, was used primarily to quantify organic compounds
121 containing from 1 to 5 carbon atoms. This methanizer contains a hydrogenation nickel catalyst. A
122 third GC equipped with a HP-5 column and an FID was used to quantify organic compounds
123 containing more than 5 carbon atoms. To identify species, a GC with either the Q-Bond or the HP-
124 5 capillary columns was paired with a quadrupole mass spectrometer, achieving ion generation
125 using electron ionization at 70 eV. The identification of the species was determined by comparing
126 the fragmentation pattern of each peak, associated with a specific retention time, to the NIST
127 database²².

128 The calibration factors for both GC-FIDs were derived from injection of the fuel in non-reactive
129 conditions. For the GC with the HP-5 column (without the methanizer), the effective carbon
130 number (ECN) method ²³ was employed to obtain the mole fractions of the detected species in
131 comparison to the one of the fuel. The estimated uncertainties were $\pm 5\%$ for the fuel and about
132 $\pm 10\%$ for species quantified using conversion factors from the fuel mole fraction. We calibrated
133 the TCD using gaseous standards from Air Liquide for O₂ with the estimated uncertainty of $\pm 5\%$.
134 The mole fractions of all the quantified products are provided in the excel spreadsheet in
135 Supplementary Information (SI).

136

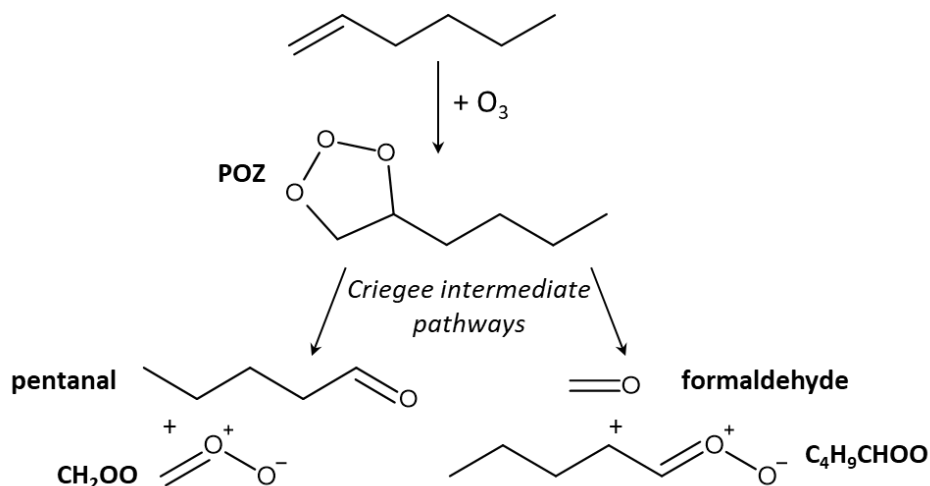
137 **KINETIC MODEL**

138 The detailed kinetic model used in this work is a upspring of the kinetic model developed and
139 validated by Meng et al.¹⁷ to simulate the JSR oxidation of 1-hexene. The new kinetic model
140 includes 1134 species and 4887 reactions and is provided in SI along with its thermochemical data.
141 In this work, we added an O₃ sub-mechanism ²⁴ to model the O₃-initiated oxidation experiments.
142 Due to a lack of information regarding the details of the elementary reactions following ozonolysis
143 and their kinetic parameters, we implemented 8 lumped reactions using the same kinetic
144 parameters taken from Avzanovia et al. ²⁵ for 1-hexene global ozonolysis reaction ($A=1.39E+09$
145 $\text{cm}^3 \text{mole}^{-1} \text{s}^{-1}$, $n=0.00$, $E_a=3140.5 \text{ cal mole}^{-1}$) assuming the same contribution of the 8 channels.
146 The following reactions, (1) to (8), which lump the several elementary steps involving Criegee
147 intermediates (CIs), were written to model the detected products, pentanal (C₄H₉CHO),
148 formaldehyde (HCHO), 2-hydroxypentanal (C₄H₈OHCHO), pentanoic acid (C₄H₉COOH), butene
149 (C₄H₈), butanal (C₃H₇CHO), and other stable products:



158 The presence of formaldehyde and pentanal aligns with the typical ozonolysis mechanism, which
159 starts with O_3 adding to the double bond of 1-hexene, resulting in a primary ozonide (POZ), known
160 as 4-butyl-1,2,3-trioxolane. For 1-hexene, the POZ can break down into two reactive CIs: CH_2OO
161 and C_4H_9CHOO , with formaldehyde and pentanal as their co-products (see Fig. 1). Further
162 unimolecular CI decomposition, isomerization, bimolecular reactions lead to other significant
163 species such as butanal, butene, acetaldehyde, propanal, pentanoic acid, butyl-oxirane, and
164 2-butanone considered in the globalized reactions 1 to 8. The detailed analysis of these complex
165 chemical pathways at very low temperatures is currently the subject of a specific study.²⁶

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167

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Figure 1. 1-hexene ozonolysis scheme

169

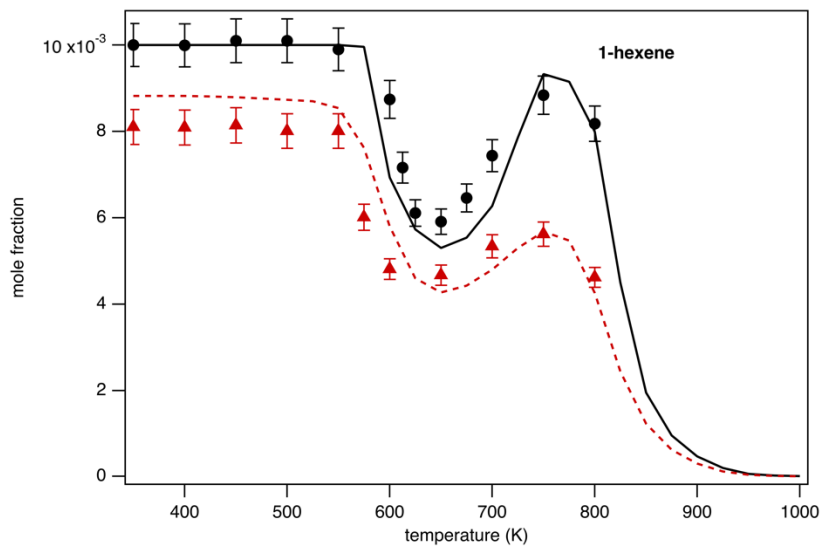
170 Using the CHEMKINPro software²⁷, we modeled the 1-hexene oxidation without O_3 considering
 171 a perfectly stirred reactor (PSR), typical for JSR models, given that the residence time in the
 172 preheating zone can be neglected compared to that in the JSR. For the O_3 -assisted oxidation, we
 173 included two plug flow reactors (PFR) before the JSR, replicating the two-stage experimental
 174 preheating zone. Earlier research emphasized the significance of modeling this preheating section,
 175 noting that O_3 partially converts in this area.^{10,28,29} According to simulations (see Fig. S1), out of
 176 the 1,000 ppm injected at 350 K, 149 and 26 ppm of O_3 enter the second PFR and the PSR,
 177 respectively, whereas those numbers decrease to 20 and 0 ppm at 700 K. PFR simulations used the
 178 same dimensions and temperatures as the preheating quartz tube preceding the JSR in experiments.

179

180 EXPERIMENTAL RESULTS COMPARED TO KINETIC PREDICTIONS

181 The mole fraction profile of 1-hexene resulting from its oxidation, both with and without O_3 , are
 182 shown in Fig. 2. Carbon balance varied from 78% to 101% for the case without O_3 and from 70%

183 to 90% for the O₃-assisted oxidation case. Those values are included in the tabulated experimental
184 data in the SI. The experimental data without O₃ aligns well with the earlier ones by Meng et al.¹⁷
185 as illustrated in Fig. S2 in SI. The O₃ mole fraction is not shown because it is nearly 0 at 350 K.
186 Based on Fig. 2, introducing a small amount of O₃ enables the fuel to start reacting at room
187 temperature. Between temperatures from 300 to 550 K, about 20% of the fuel is converted when
188 O₃ is incorporated. Although the temperature of the start of the LTC remains about the same at
189 550 K, the conversion rate is still 20% higher at the peak conversion temperature of 650 K.
190 Notably, in the NTC region (temperatures exceeding 650 K), where the fuel conversion drops
191 sharply from 44% to 10% without O₃, the conversion rate remains significantly higher, above 50%
192 in presence of O₃. This is near the highest conversion rate observed at 650 K in the LTC range in
193 ozone-less conditions. The addition of O₃ does not cause a shift of the NTC region. The difference
194 in mole fractions between scenarios with and without O₃ amplifies to 44% at 750 K, which is more
195 than the 20% increase seen at lower temperatures. These findings indicate that besides just
196 enhancing oxidation, O₃ also triggers fuel conversion under conditions that typically inhibit it
197 under standard oxidation conditions. This starts from room temperature and extends to higher
198 temperatures, diminishing the usual NTC patterns, until it reaches the high temperature zone
199 (above 800 K) where all the fuel gets consumed. A similar effect was intuited in the literature,
200 although it was not as obvious as the one observed in this study^{30,31}.

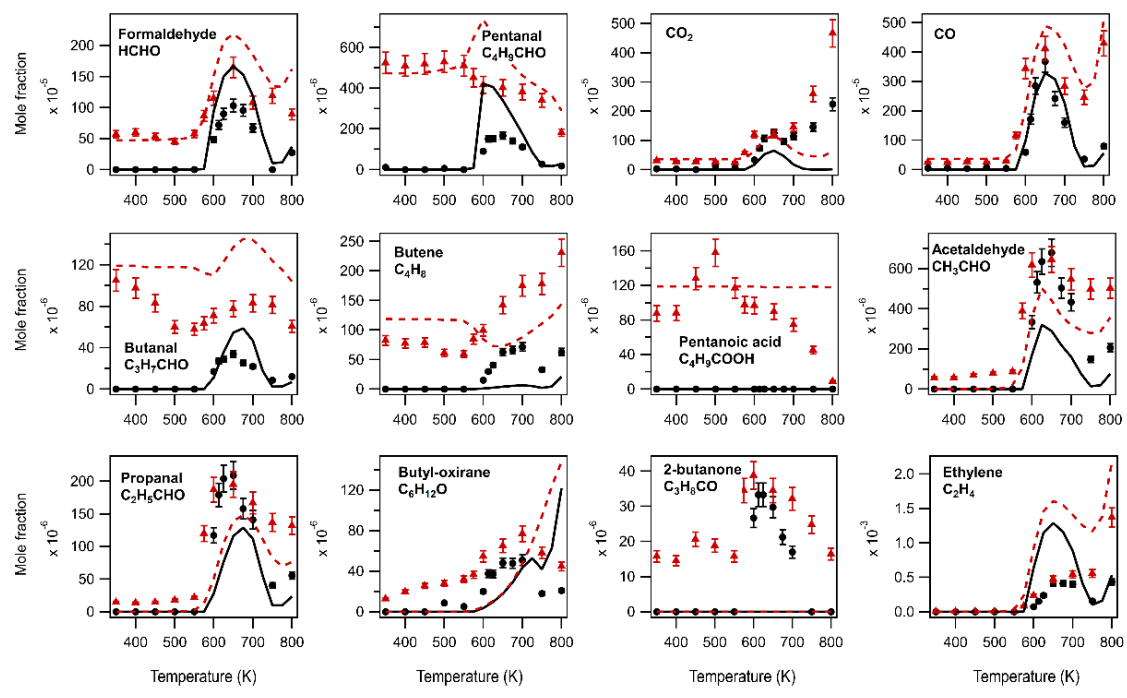


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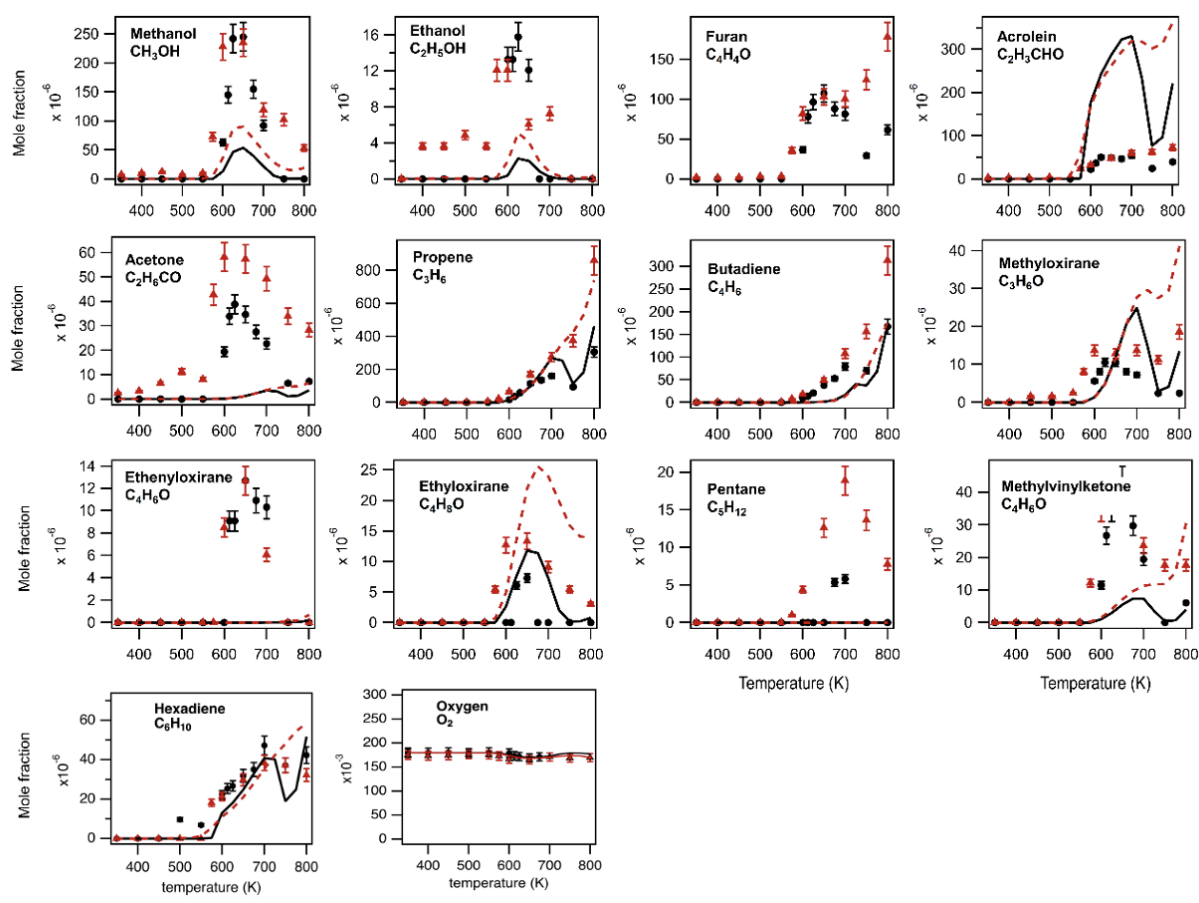
202 *Figure 2. Comparison of experimental (symbols) and predicted (lines) mole fraction profiles for the conventional (black dots and*
 203 *solid lines) and O₃-initiated (red triangles and dashed lines) oxidation of 1-hexene. The condition of pressure, equivalence ratio,*
 204 *and inlet mole fraction of 1-hexene was kept constant at 800 Torr (1.067 kPa), 0.5, and 0.01 respectively. The residence time*
 205 *was 2.0 s (without O₃) or 2.5 s (with O₃).*

206

207 Fig. 3 displays the mole fraction of all the observed products produced during 1-hexene oxidation
 208 below 500 K as determined by GC measurements. Without O₃, the results for the four key products,
 209 namely CO, formaldehyde, CO₂, and pentanal generally align well with the previous findings of
 210 Meng et al.¹⁷ as shown in Fig. S2. However, we observed that the mole fractions for formaldehyde
 211 and pentanal are consistently lower than Meng et al.'s data. In contrast, the mole fraction of CO₂
 212 at high temperatures is higher than Meng et al.'s results.



213



214

215 *Figure 3. Comparison of experimental and predicted mole fraction profiles of all the observed products for the conventional*
216 *(black dots and solid lines) and O₃-initiated (red triangles and dashed lines) oxidation of 1-hexene. The condition of pressure,*
217 *equivalence ratio, and inlet mole fraction of 1-hexene was kept constant at 800 Torr (1.067 kPa), 0.5, and 0.01 respectively. The*
218 *residence time was 2.0 s (without O₃) or 2.5 s (with O₃).*

219

220 According to Fig. 3, with O₃ at temperatures below 600 K, the dominant products are formaldehyde
221 (around 500 ppm) and pentanal (roughly 500 ppm). CO and CO₂ become prevalent at higher
222 temperatures. Significant amounts (measured in ppm) of other species were detected, including
223 butanal, butene, acetaldehyde, propanal, pentanoic acid, butyl-oxirane, 2-butanone, and ethylene.
224 Notably, pentanoic acid is unique in that it is not formed during standard oxidation but appears
225 only when O₃ is added across all temperatures studied.

226 Additional minor species present at low temperatures were also identified using GCs: these include
227 methanol, ethanol, furan, acrolein, and acetone. Note that the discrepancy regarding methanol
228 between the model and the experimental data, which is a significant byproduct (approximately 200
229 ppm), had already been observed during the oxidation of 1-hexene.¹⁷ The co-elution of methanol
230 and acetaldehyde, which is also a main species in the LTC region (see Fig. 3), likely contributed
231 to a degradation in the accuracy of both measurement species. At higher temperatures, other
232 detected minor species include propene, 1,3-butadiene, methyloxirane, ethenyloxirane,
233 ethyloxirane, pentane, methylvinylketone, and 2,4-hexadiene. In summary, adding O₃ boosts the
234 production of carbonyls and acids, especially at cooler temperatures. Additionally, there is a
235 notable increase in CO production at higher temperatures, with it being four times higher at 800
236 K.

237 When we compare the experimental mole fraction of fuel and products with predictions from the
238 kinetic model (as seen in Fig. 3), they align fairly well at low temperature for the main species.

239 The proposed model allows the fuel conversion trends to be well simulated at both low and high
240 temperatures. Looking closely at Fig. 3, the inlet mole fractions of formaldehyde and pentanal
241 from model simulations agree well with experimental data at low temperatures, at higher
242 temperature the model overpredict the mole fraction of both species, which could also be seen
243 under conventional oxidation conditions. The CO and CO₂ mole fraction profiles are also
244 reasonably reproduced by the model at low temperature, while CO₂ is clearly underestimated at
245 the highest temperatures. Butanal mole fraction at low temperatures is overestimated, while butene
246 profile is reasonably predicted assuming a 100 K shift, mirroring the trend in conventional
247 oxidation. Pentanoic acid mole fraction remains stable, even with recent modeling insights into its
248 oxidation kinetics³². Though the order of magnitude is accurate, the maximum deviation is about
249 three times over the entire temperature range.

250 For minor species like acetaldehyde, propanal, and butyl-oxirane, the model predictions are
251 reasonable at high temperature, but their mole fractions at low temperatures are slightly
252 underestimated. The notable deviations in the prediction of butyl-oxirane highlights the limitation
253 of the global reactions for ozonolysis as could be a product of the isomerization of the CI formed
254 by ozonolysis (see section regarding the kinetic model) for which no kinetic data is available in
255 the literature, explaining that the kinetic model does not produce butyl-oxirane at low temperature.
256 The production of 2-butanone is the worst predicted one because no formation reaction for this
257 ketone was identified, even if experimental data show ppm-level mole fractions, even at the lowest
258 temperatures. In general, the kinetic model predictions fairly match with the experimental mole
259 fraction profiles of the main species at low temperature considering that only global ozonolysis
260 reactions have been implemented due to a lack of kinetic data in literature. Especially the trend of
261 O₃ effect is well captured for the fuel. However, it is essential to approach the interpretation of the

262 modeling results with caution, recognizing the need for further validation in a near future
263 especially across different experimental conditions to address the robustness of the model.

264

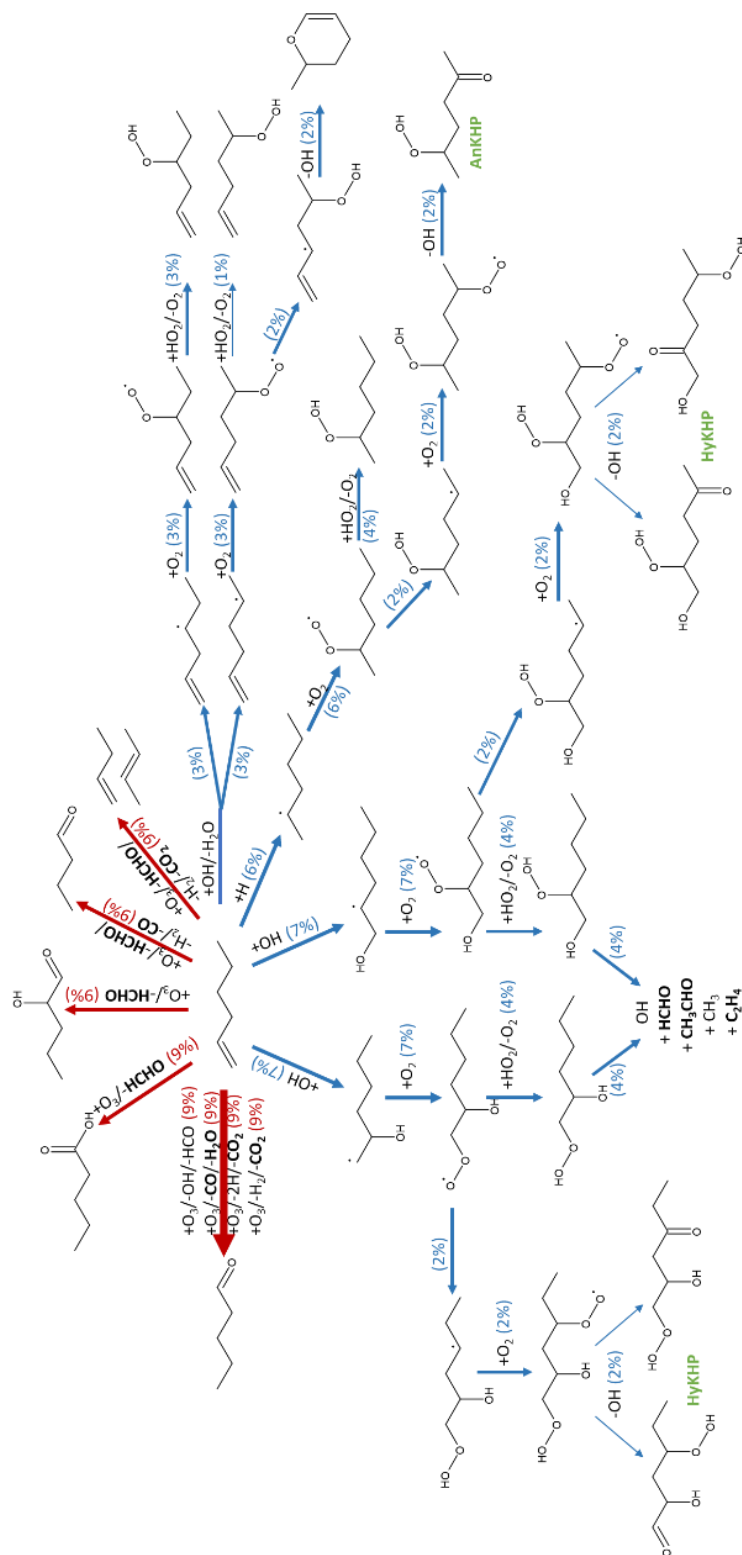
265 **KINETIC ANALYSIS OF THE DIFFERENT TEMPERATURE ZONE**

266 This part describes the kinetic analysis based on the present model in the three considered
267 temperature zone and discuss the effect of O-atoms generated by O₃ decomposition.

268

269 *At 400 K, the ozonolysis zone*

270 Fig. 4 displays a flow rate analysis at 400 K. At this temperature, the primary reactions involve the
271 fuel interacting with O₃, yielding distinct ozonolysis products.



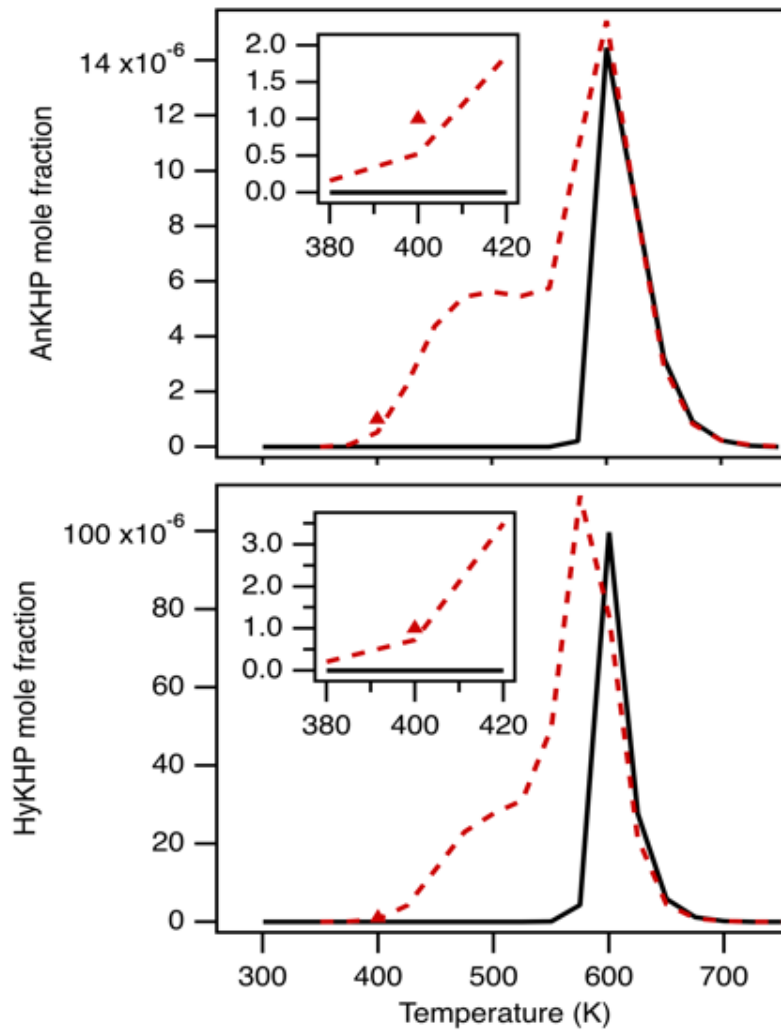
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275

Figure 4. Flow rate analysis for 1-hexene oxidation assisted by O_3 (1,000 ppm), at 400 K under the current experimental conditions of Fig. 2, obtained by simulations. Each arrow denotes the percentage of fuel consumption in the corresponding pathway. For the sake of clarity, only pathways above 1% are displayed.

276 As shown in Fig. 4, at 400 K ozonolysis reactions (reactions (1-8)) consume 72% of the fuel. The
277 sensitivity analysis on the fuel in Fig. S3 supports this observation, emphasizing the primary
278 importance of reaction between O_3 and 1-hexene. The remaining conversion is due to reaction
279 pathways related to the conventional low-temperature oxidation kinetics, initiated by reactions
280 between the fuel and radicals that are produced through the ozonolysis channels.

281 Another interesting observation based on Fig. 4 is that the addition of O_3 induces the formation of
282 alkenyl ketohydroperoxides (AnKHP) and hydroxyl ketohydroperoxides (HyKHP) at temperature
283 as low as 400 K. Those KHPs were detected and characterized experimentally in Smith Lewin et
284 al.²⁶: a typical mass spectrum registered at 400 K showing the peaks of KHPs is given in Fig. S4.
285 Fig. 5 presents the simulated mole fraction profiles of AnKHP and HyKHP and highlights that the
286 formation of KHPs starts to be significant just above 400 K. Around 20-25% of the amount of
287 KHPs formed in the LTC region is reached below 500 K. However, due to the needed activation
288 energy, around 42 kcal/mol, despite the formation from 400 K, HyKHP and AnKHP cannot
289 decompose significantly before 550 K. Consequently, the acceleration of the reactivity due to the
290 branching step cannot occur before this temperature. The 0.7 AnKHP/HyKHP ratio predicted at
291 400 K is in good agreement with the experimental ~ 1.0 AnKHP/HyKHP ratio at 400 K (see the
292 inserts in Fig. 5). This value is based on experimental mole fractions calculated from the mass
293 spectrum signals in Fig. S4 using the method described in Bourgalais et al.³³.



294

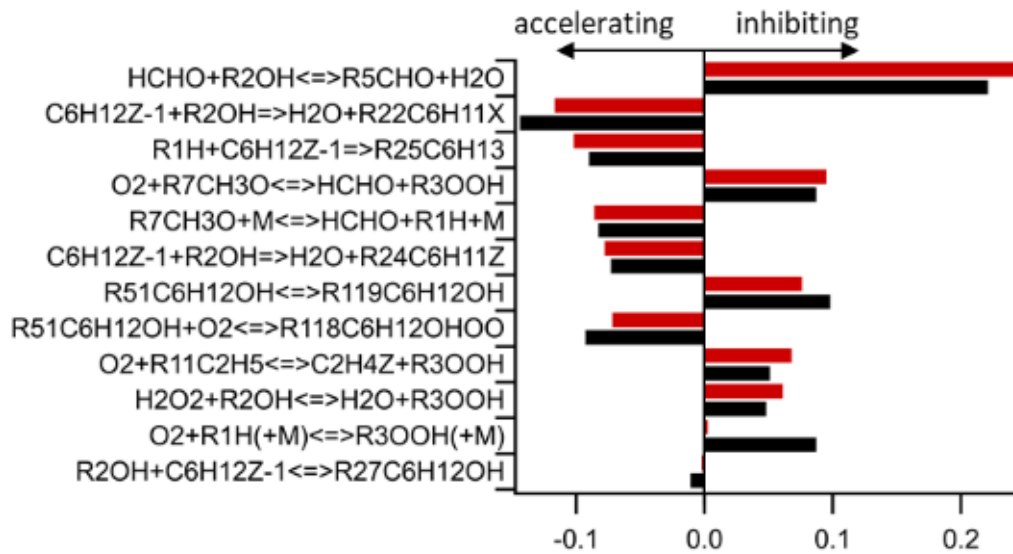
295 *Figure 5. Simulated mole fractions of AnKHP (upper panel) and HyKHP (lower panel) under the experimental conditions of Fig. 2.*
 296 *Black and red lines correspond to the cases without and with O₃, respectively. The red dots are experimental mole fraction*
 297 *calculated from Fig. S3.*

298

299 ***At 650 K, the maximum of fuel conversion***

300 A second flow rate analysis, at 650 K, with 1,000 ppm and without O₃, is shown in Figure S6 and
 301 aligns with the pathway distribution reported by Meng et al.¹⁷. The sensitivity analysis shown in
 302 Fig. 6 on fuel mole fraction, denoted as C₆H₁₂Z-1, shows reactions ordered by importance for the
 303 case with O₃ and does not indicate much difference with or without O₃. It suggests that the

304 enhanced fuel conversion observed in Fig. 2 results from the same reaction pathways but with a
 305 slight sensitivity boost of some reactions between the fuel and radicals like H and OH in the
 306 presence of O₃.

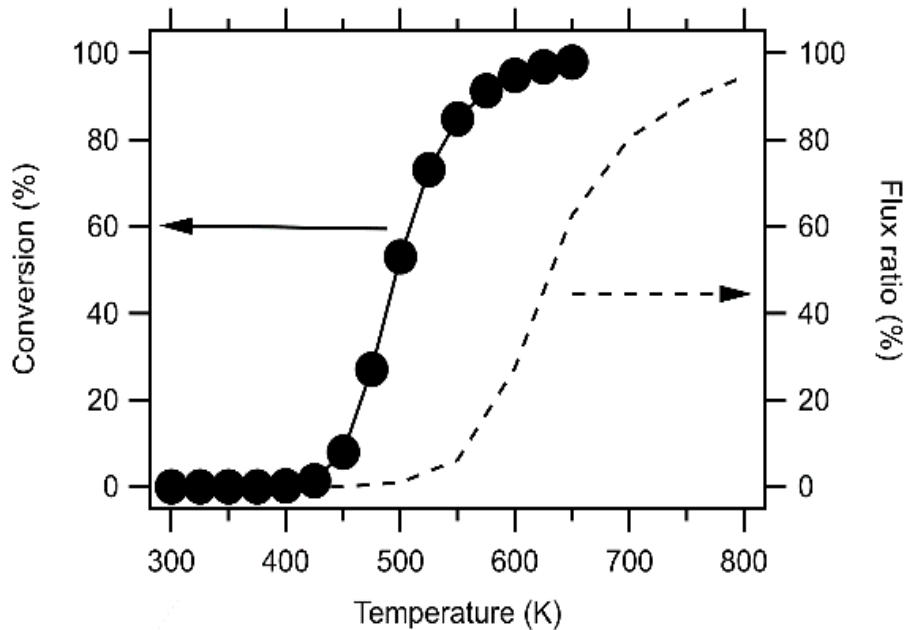


307

308 *Figure 6. Sensitivity analysis at 650 K for the fuel mole fraction without (black) and with O₃ (red) under the experimental*
 309 *conditions of Fig. 2.*

310

311 This increased sensitivity stems from the growing radical pool as the temperature increases due to
 312 the thermal decomposition of O₃ into O-atoms and O₂. Fig. 7 shows predictions from the kinetic
 313 model under our current experimental conditions of the ratio of the O₃ flux going through the O-
 314 formation pathway in the total O₃ consumed flux. The thermal decomposition of O₃ competes with
 315 ozonolysis starting from around 550 K, a temperature about 100 K higher than that the start of
 316 thermal decomposition of neat O₃ (450 K in Fig. 7).



317

318 *Figure 7. Comparison between the thermal decomposition of neat O₃ in the JSR [10] (black dots) compared to the predictions of*
 319 *the ratio of O₃ flux leading to the formation of O-atoms in the total O₃ flux consumed under the experimental conditions of Fig. 2*
 320 *(dotted line).*

321

322 The predictions of the kinetic model show that the thermal decomposition of O₃ becomes more
 323 significant than the O₃ direct addition to the fuel unsaturation only above 600 K. However, one
 324 should note that even if 40% of O₃ reacts with the fuel at 650 K, this flux corresponds to less than
 325 1% for the fuel consumption, explaining why no ozonolysis reaction appears in Fig. S5.

326

327 ***At 750 K, the LTC minimum***

328 The impact of thermal decomposition of O₃ is anticipated to be more pronounced at elevated
 329 temperatures, with more than 90% of O₃ resulting in O-atoms at 750 K, as depicted in Fig. 7. A
 330 surge in the radical mole fractions is observed from 550 K, with an increase by up to ten times of
 331 the radical mole fractions at 750 K, as illustrated in Fig. S6. Consequently, the sensitivity analysis

332 for the fuel mole fraction displayed in Fig. S7, emphasizes that the most sensitive reactions remain
333 quite the same at both 650 K and 750 K when O₃ is introduced, while they significantly differ in
334 absence of O₃. Additionally, we can notice that the sensitivity coefficients at 750 K are
335 significantly larger in the presence of O₃ than without it. The fact that the inclusion of O₃ makes
336 the sensitivity coefficients at 750 K to align closely with those at 650 K is consistent with the near-
337 constant fuel conversion with O₃ within the NTC region observed in Fig. 2. However, at 750 K,
338 the chemical pathways of fuel consumption are very much the same with and without O₃, as
339 illustrated in Fig. S8.

340

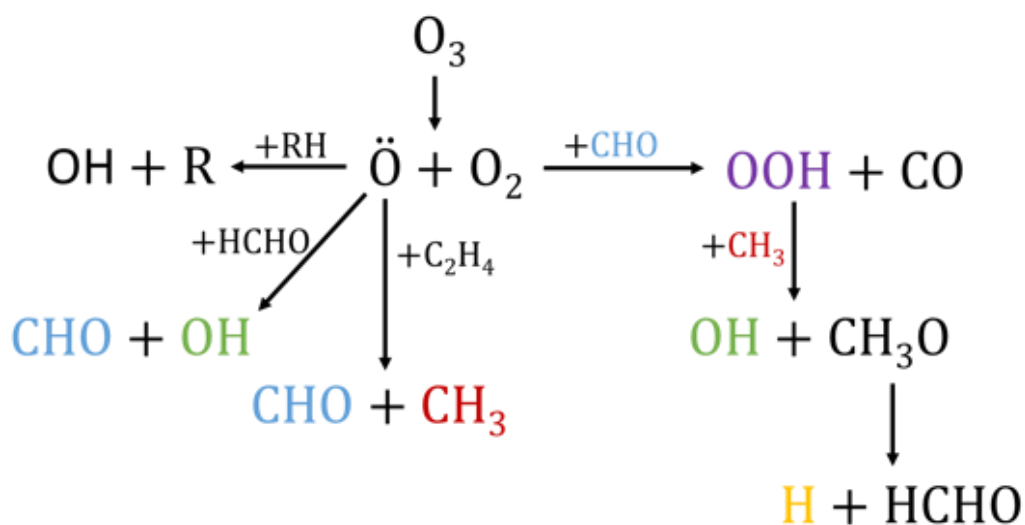
341 *The impact of O-atoms*

342 The flow rate analysis in Fig. 8 shows that the thermal decomposition of O₃ into O+O₂ initiates
343 radical reactions promoting fuel conversion. Predominantly, 48.5% of O-atoms react with the fuel
344 by H-abstraction, which results in the formation of OH radicals along with mainly allylic radicals.
345 However, O + RH = OH + R represents only less than 1% of both the fuel consumption and the
346 OH formation. Most of the fuel consumption by H-abstraction is achieved via reactions with H
347 and OH radicals (see Fig. S8).

348 The flow rate analysis in Fig. 8 shows that the thermal decomposition of O₃ into O+O₂ initiates
349 radical reactions promoting the fuel conversion. Predominantly, 48.5% of O-atoms react with the
350 fuel by H-abstraction, which results in the formation of OH radicals along with mainly C₆ allylic
351 radicals. However, O + RH = OH + R represents only less than 1% of both the fuel consumption
352 and the OH formation. Most of the fuel consumption by H-abstraction is achieved via reactions

353 with OH (45 %) and OOH (2.9%) radicals, as well as H-atoms (4.3%), as it is shown in the last
 354 flow rate analysis for 1-hexene consumption made at 750 K and displayed in Fig. S8.

355 The remaining O-atoms engage in reactions with formaldehyde HCHO (11.7%) and C₂H₄ (6.3%),
 356 producing CHO + OH and CH₃ + CHO, respectively. The CHO radicals primarily react with O₂,
 357 leading to the formation of OOH + CO, which accounts for the rise in the OOH radical mole
 358 fraction, as observed in Fig. S8. This process is also the predominant consumption route for O₂.



359

360 *Figure 8. The important reactions initiated by the thermal decomposition of O₃ at 750 K.*

361

362 While a significant portion of OOH (44%) recombines to yield H₂O₂+O₂, a notable amount of
 363 OOH (7.1%) also reacts with CH₃ radical, producing OH + CH₃O. This accounts as one of the
 364 main sources of OH: 6% at 750 K. It is interesting to compare this value to that coming from the
 365 decomposition of H₂O₂ into OH+OH, which accounts for 4.5% of OH formation at 750 K. The
 366 interaction of OOH with CH₃ intensifies when O₃ is introduced, primarily because O-atoms react
 367 by addition on C₂H₄, generating CHO and CH₃ radicals. The major formation of H-atoms (45%)
 368 occurs through the decomposition of CH₃O radicals, which results in H + HCHO. This elucidates

369 the gradual increase in H + fuel reactions observed from 650 K to 750 K in both flow rate and
370 sensitivity analyses.

371 In summary, the observed decrease of the NTC behavior in this study does not predominantly stem
372 from the conventional H-abstraction from RH by the O-atoms produced by O₃ decomposition. As
373 an additional channel, O-atoms, when reacting with C₂H₄ and HCHO boost the formation of H-
374 atoms and, OH and OOH radicals.

375

376 **CONCLUSION**

377 This work shows that O₃ triggers fuel conversion under conditions that typically inhibit oxidation,
378 ranging from room temperature to higher temperatures. This process effectively diminishes the
379 NTC behavior and continues until reaching a high-temperature phase (> 800 K) where all the fuel
380 is consumed. The inclusion of O₃ fosters a significant production of aldehydes and pentanoic acid
381 from 400 K, consistent with the ozonolysis mechanism. A significant concentration of KHPs is
382 also formed between 400 – 500 K.

383 The model predictions align reasonably with the observed mole fraction profiles of major species
384 considering that the O₃-related chemistry has been described in the kinetic model using global
385 ozonolysis reactions due to a lack of kinetic information in the literature. However, more thorough
386 theoretical kinetic studies on ozonolysis-related reactions would be required to implement more
387 accurate mechanisms and improve the predictions. We hope these experimental data will stimulate
388 future theoretical studies for the validation of kinetic parameters. In addition to the O-atom
389 production by O₃ decomposition, we discerned that the observed diminution of NTC behavior is

390 mainly attributed to the O-atoms interacting with C₂H₄ and formaldehyde leading to a boost of the
391 population of H and OH radicals.

392 The results suggest that the inclusion of O₃ can enable efficient molecule conversion across a wide
393 temperature range, overcoming efficiently the usual reactivity barriers seen with NTC behavior.

394 This demonstrates even more the interest of using O₃ as an oxidant to improve fuel combustion
395 efficiency. This knowledge could influence fuel blend optimization, the development of novel
396 combustion techniques working at extremely low temperature, and better pollution control in
397 combustion systems.

398

399 **SUPPLEMENTARY INFORMATION**

400 Experimental data under tabulated format, reaction mechanism and thermochemical data files
401 under CHEMKIN format, additional description of experimental data and simulation results.

402

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406

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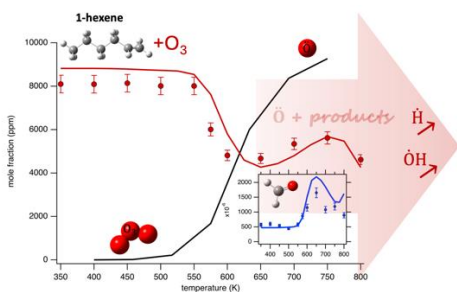
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