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1 Ozone-Assisted Oxidation of Ethylene in a Jet-Stirred
2 Reactor: an Experimental and Modeling Study

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33 **KEYWORDS**

34 Ozonolysis; Jet-stirred reactor; mass-spectrometry; gas chromatography; kinetic
35 model

36 **ABSTRACT**

37 Ozone addition is a promising method to achieve improvement and control of
38 combustion/ignition processes due to ozone-derived chemistry. However, the complexity
39 induced by ozonolysis reactions make investigations on O₃-assisted oxidation with alkenes still
40 scarce. In this work, the ozone-assisted oxidation of ethylene was studied in a jet-stirred
41 reactor from 300 to 1000 K. The main products were identified and quantified by mass
42 spectrometry/gas chromatography analysis. The mole fractions were then compared to those
43 computed with a kinetic model from the literature. This work provides data for the
44 development of detailed chemical kinetic models relevant to atmospheric and combustion
45 chemistry studies.

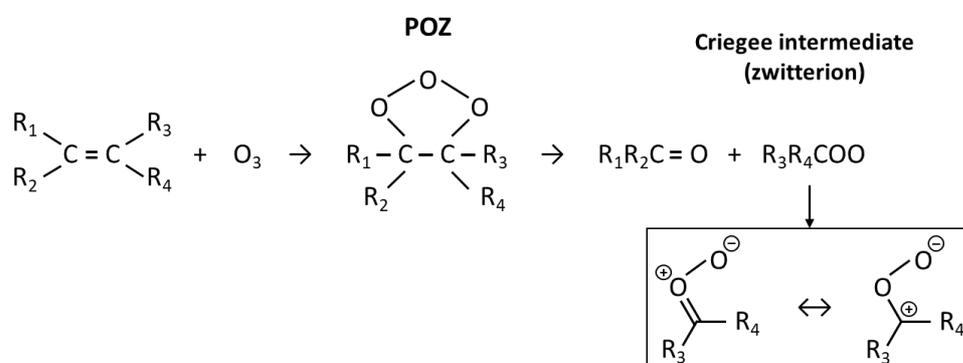
46
47 **INTRODUCTION**

48 The so-called ozonolysis process during the gas-phase oxidation of organic compounds
49 in presence of ozone (O₃) has been the subject of numerous studies for over a century in
50 different scientific fields. The exothermic 1,3-dipolar cycloaddition of O₃ reaction onto
51 unsaturated volatile organic compounds leads to the formation of reactive species called
52 Criegee intermediates through a three-step mechanism [1,2]. Criegee intermediates affect the
53 oxidative capacity of the atmosphere by being both a direct source of oxygenated compounds
54 and radicals and by reacting with other species to form low-volatility compounds leading to
55 the growth of aerosols and particles that impact the radiation balance and air quality (e.g., [3–
56 6]). O₃-assisted oxidation of hydrocarbons is also a subject of recent interest in low-
57 temperature combustion studies due to the recent rise of investigations into non-equilibrium
58 plasma-assisted combustion techniques and chemically controlled engine designs for
59 emission control and efficiency enhancement [7–11]. Efficiently generated by electric
60 discharge, O₃ is a low-temperature reaction promoter and an enhancer of combustion
61 processes through the formation of various reactive intermediates [12–14]. This enhancement
62 is related to O₃ chemistry, with the production of oxygen atoms from the thermal
63 decomposition of O₃ at elevated temperatures accelerating the overall chain-propagating
64 process, as well as the rapid exothermic ozonolysis reactions initiating direct reactions

65 between fuel and O₃ at low temperatures (even at room temperature). While the direct
 66 reaction between O₃ and saturated hydrocarbons is almost negligible, the nearly barrierless
 67 reaction with unsaturated species (a difference of several orders of magnitude [15]) is very
 68 fast. Although considerable studies have been conducted on O₃-assisted oxidation of alkanes
 69 [16–23], investigations on alkenes are scarce, partially due to the much higher chemical
 70 complexity induced by these ozonolysis reactions.

71 Most ozonolysis reactions involve the formation of a primary cyclic 1,2,3-trioxy
 72 ozonide (POZ) from the van der Waals O₃-alkene complex resulting from the addition of O₃
 73 onto the C=C bond. POZ then decomposes to form a carbonyl compound (R₁R₂C=O) and
 74 carbonyl oxide (R₃R₄COO), the famous Criegee intermediate (CI), via homolytic cleavage of C-
 75 C and C-O bonds (see FIGURE 1). After that, the quenching processes of the Criegee
 76 intermediate give access to many reaction pathways, such as the formation of 1,2,4-trioxy
 77 cyclic secondary ozonide (SOZ) [24–31]. A single O-O bond of the POZ can also break to give a
 78 POZ biradical, making the accessible kinetic networks even more complicated [32,33]. For
 79 recent reviews of CI's reaction pathways, readers may refer to Osborn & Taatjes [34] and
 80 Taatjes [35].

81



82

83 FIGURE 1. Formation of POZ and Criegee intermediate from ozonolysis reaction.

84

85 Due to the multiplicity of kinetic pathways involved in ozonolysis, grey areas remain
 86 even in the chemistry of the simplest O₃-alkene system. The chemical pathways following the
 87 reaction of O₃ with ethylene (CH₂=CH₂), despite being extensively studied for decades (see
 88 [36–41] for the most recent studies) are still not fully understood and significant
 89 disagreements remain between quantitative experiments and kinetic model predictions. The
 90 most recent quantitative investigation on the O₃-assisted oxidation of C₂H₄ was reported by

91 Rousso et al. [39]. The oxidation of C₂H₄ was carried out in a near atmospheric pressure (933
92 mbar) jet-stirred reactor (JSR) from 300 to 1000 K by adding 1000 ppm of O₃. The mole fraction
93 as a function of temperature of the oxidation products were obtained by electron-ionization
94 mass spectrometry analysis. Their data were compared to the predictions of a kinetic model
95 developed at Princeton [42–44], in which ozonolysis reactions were described using global
96 reactions based on IUPAC recommendations. They reported significant discrepancies between
97 the experimental data and the predictions, even for the consumption of C₂H₄ and O₃, from
98 low to intermediate temperatures (< 700 K) suggesting missing major reaction pathways in
99 the kinetic model. However, no mechanistic insight has been provided and many questions
100 remain regarding the formation pathways of intermediates in this system.

101 The aim of this work is to focus on the mostly unknown kinetic networks initiated by
102 ozonolysis reactions over a wide temperature range. While O atoms from the O₃ thermal
103 decomposition are of interest in lowering the fuel conversion temperature, ozonolysis can
104 initiate alkene-based fuel conversion at even lower temperatures and may have an impact on
105 auto-ignition [45]. In this work, new experimental data are generated over a wider range of
106 experimental conditions for the O₃-assisted oxidation of C₂H₄ to confront the predictions of
107 current kinetic models. Especially, due to a different experimental configuration, the newly
108 obtained data shows that a global ozonolysis mechanism can accurately simulate the mole
109 fractions of the main products as well as the consumption of C₂H₄ and O₃. The O₃-assisted
110 oxidation of C₂H₄ was carried out in a JSR between 300 K and 1000 K with varying the mole
111 fraction of O₃ from 1000 to 2000 ppm. The identification and the quantification of the main
112 products and stable intermediates were performed by gas chromatography with mass
113 spectrometry, thermal conductivity and flame ionization detections, and the obtained mole
114 fractions were recorded as a function of temperature. The experimental data were then
115 confronted to the predictions of the abovementioned kinetic model from the literature [42–
116 44] to provide mechanistic insights into the O₃-assisted oxidation of C₂H₄.

117

118 **EXPERIMENTAL SETUP**

119 The experimental setup used in this work has been extensively described in the past,
120 see for instance Bourgalais et al. [46], and only the essential information and modifications
121 for the current experiments are given here. Constant pressure, residence time, and
122 equivalence ratio of 1.067 bar, 2.5 s, and 0.5, respectively, were maintained for all the

123 experiments, with a continuous flowing gas mixture with mole fraction of 0.02 ethylene, 0.12
124 O₂, and 0.86 He in the JSR using calibrated Bronkhorst mass flow controllers (relative
125 uncertainty of 0.5%). He and O₂ are provided by Messer (both 99.999% pure) and C₂H₄ by Air
126 Liquide with a purity of 99.95%. A JSR temperature range from 300 to 1000 K was investigated
127 and the flow rates were adjusted to maintain a constant nominal residence time. A preheating
128 zone upstream of the JSR inlet ensured the temperature gradient inside the vessel to be
129 limited. The annular quartz tube has an approximate cross section of 0.25 cm² and a length of
130 12 cm. The tube, as well as the JSR, is heated using THERMOCOAX resistances. To provide
131 progressive preheating, its length is divided into two heating stages (6 cm long each) that are
132 set to two different temperatures. For experiments without O₃, the preheaters were set to
133 temperatures close to the desired temperature in the JSR. However, for O₃-assisted oxidation
134 experiments, this procedure was followed only below the JSR temperature of 425 K, which is
135 the threshold for the onset of O₃ thermal decomposition (as will be discussed later). From this
136 temperature, to prevent O₃ decomposition before entering the reactor, the first preheater
137 was set to 353 K and the second to 393 K, regardless of the JSR temperature. The reactor
138 temperature was measured with a K-type thermocouple positioned in a glass finger close to
139 the JSR center with an uncertainty of around 1%.

140 The C₂H₄ ozonolysis experiments were achieved adding an O₃ mole fraction of 1000
141 and 2000 ppm using an ozone generator (BMT 802N). Gas feeds of C₂H₄ and O₃ were mixed
142 just before entering the preheated zone of the JSR (see FIGURE 2 for a scheme of the
143 experimental setup). An ozone analyzer (BMT 965 ST) based on a dual-beam UV photometer
144 at 254 nm was used at the exit of the JSR to measure the O₃ mole fraction. The uncertainty of
145 15% for the measurement of the O₃ mole fraction was derived including accuracy and
146 repeatability error.

147

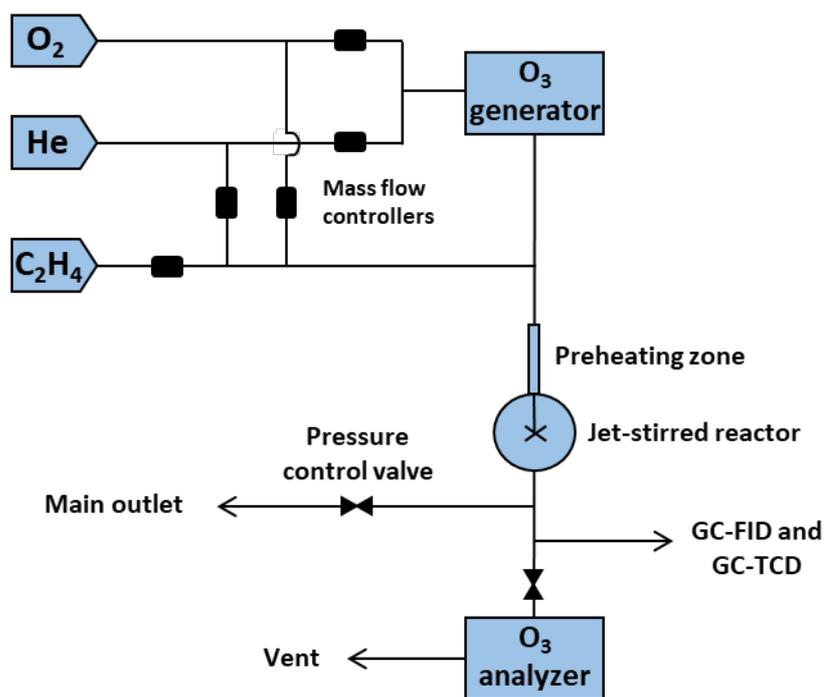


FIGURE 2. Scheme of the experimental setup.

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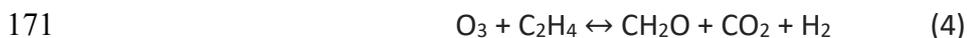
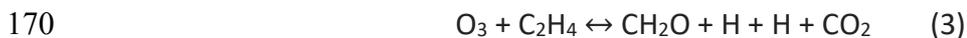
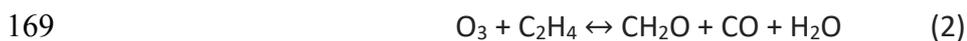
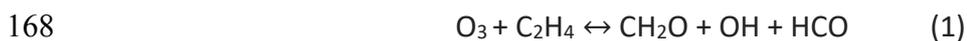
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151 C_2H_4 and its oxidation products were quantified using two gas chromatographs (GCs)
 152 connected to the exit of the JSR, one with a carbosphere-packed column and a thermal
 153 conductivity detector (TCD) to quantify lightweight and permanent gas species, the second
 154 with a Q-Bond capillary column and a flame ionization detector (FID) preceded by a
 155 methanizer for the quantification of organic compounds. For species identification, a GC
 156 equipped with a Q-Bond capillary column was coupled to a quadrupole mass spectrometer.
 157 Ions were generated via electron impact ionization at 70 eV. The mole fractions of species
 158 detected with the FID were calibrated using the effective carbon number (ECN) method. Their
 159 calibration factors were deduced from that of C_2H_4 by taking into account their effective
 160 carbon number. The relative uncertainties in their mole fractions were estimated to be $\pm 10\%$.
 161 The obtained carbon balance presented values from 87.8 to 107.0%, with an average of 99.6%

162

163 KINETIC MODEL

164 An up-to-date kinetic model developed at Princeton coupling an ethylene oxidation
 165 mechanism and an O_3 sub-mechanism was used to simulate the experimental data [42–44].
 166 Based on IUPAC recommendation (<https://iupac.org/>), the following direct reactions between
 167 O_3 and C_2H_4 were implemented to simulate global ozonolysis reactions:



172 Using the CHEMKINPro software [47], the oxidation of C_2H_4 without O_3 was modelled
173 considering a perfectly stirred reactor (see results in FIGURE S1 in Supplementary Material) as
174 it is usually the case when modelling JSR, since the residence time in the preheating zone is
175 only a few percent of that in the JSR [48]. In the O_3 -assisted oxidation case, two plug flow
176 reactors (PFR) were included ahead of the JSR to simulate the experimental preheating zone
177 composed of two heating stages. This strategy of including a PFR was also used by Rousso et
178 al. [39]. This was performed to account for the reactivity, especially the O_3 thermal
179 decomposition, before entering the JSR. The PFR simulations were based on the physical
180 dimensions of the quartz tube from the entrance of the preheating zone to the JSR and utilizes
181 the same temperature as used in the experiments. A numerical comparison between the
182 composition at the outlet of the second PFR and that of the outlet of the JSR during O_3 -assisted
183 oxidation, as well as simulations using both reactor configurations (with and without PFRs),
184 are presented in Supplementary Material. FIGURE S2 well demonstrates that a significant
185 amount of O_3 enters the JSR. As it can be seen in FIGURE S3, a slightly improved agreement
186 when PFRs were considered is observed. Flow rates used in each experiment were also
187 implemented in the model and were provided as inputs of the PFRs.

188

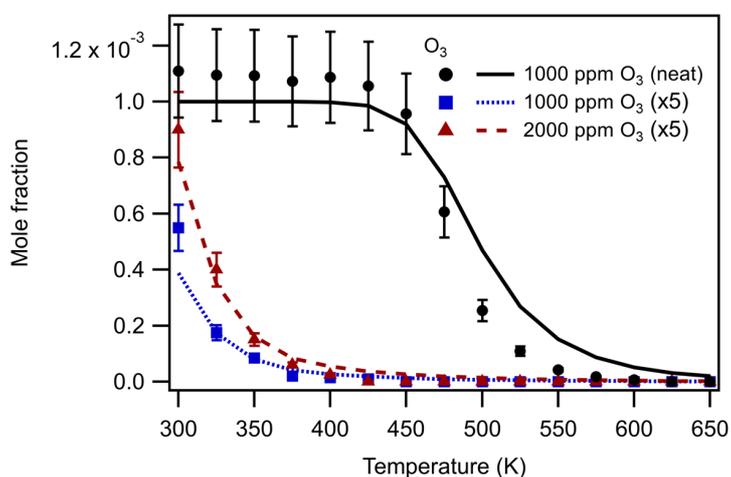
189 **RESULTS**

190 As a starting point, oxidation experiments without O_3 addition were first conducted
191 from 300 to 1000 K, as a reference for no low-temperature chemistry behavior. The evolution
192 of the mole fractions of C_2H_4 , O_2 , the intermediates (CH_2O , C_3H_6 , CH_3CHO , CH_4 , and oxirane
193 $\text{C}_2\text{H}_4\text{O}$), and the major products (CO and CO_2) as a function of temperature are given in FIGURE
194 S1. No decrease in the mole fraction of C_2H_4 and O_2 is observed below 800 K in the absence of
195 ozone. Note that H_2O is also predicted as a major product with a mole fraction comparable of
196 those of CO and CO_2 , but it remains difficult to quantify it accurately by GC analysis. Oxirane
197 was detected with a maximum mole fraction of 130 ppm at 850 K and mainly formed from
198 $\text{HO}_2 + \text{C}_2\text{H}_4$ by direct epoxidation. An overall good agreement between experimental data and
199 simulations is observed even if a slight overestimation of the predicted conversion of C_2H_4 is

200 noticed between 800 and 850 K. At these temperatures, the conversion of C_2H_4 is mainly
201 driven by addition of OH on C_2H_4 , as can be observed in the flow rate analysis of FIGURE S4,
202 at 900 K. The rate constants provided in the literature for this reaction and currently
203 implemented in the kinetic model correspond to the formation of all the three C_2H_5O isomers
204 (CH_2CH_2OH , OCH_2CH_3 , and $HOCHCH_3$) [49]. This might result in a slight overestimation of
205 CH_3CHO (see FIGURE S1). These results on the oxidation of neat C_2H_4 give confidence to the
206 experimental setup and the analysis procedure used in this work.

207 Thermal decomposition of O_3 was also measured before considering the O_3 -assisted
208 oxidation of C_2H_4 . O_3 mole fraction as a function of temperature was recorded at the same
209 residence time and pressure as in the ozonolysis case but without C_2H_4 , using as gas mole
210 fractions: 0.12 O_2 /0.001 O_3 /0.879 He. FIGURE 3 presents the O_3 mole fraction as a function of
211 temperature for neat O_3 thermal decomposition and for C_2H_4 oxidation with two O_3 mole
212 fractions (1000 and 2000 ppm). Consistent with previous data in the literature [39,44,50], the
213 thermal decomposition of O_3 starts ~ 450 K and $\sim 90\%$ of O_3 is consumed by 550 K. This result
214 indicates that above this temperature, fuel interactions with O-atoms can potentially compete
215 with ozonolysis reactions in the formation of intermediate species and products.

216



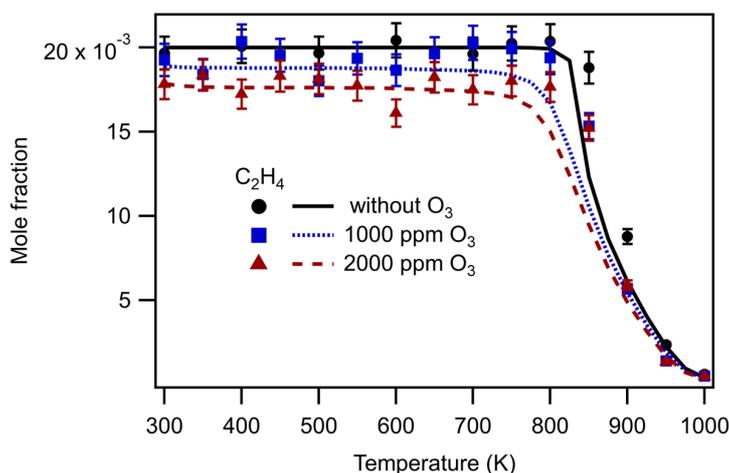
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218 FIGURE 3. O_3 mole fraction as a function of temperature. Data in black correspond to the
219 thermal decomposition of 1000 ppm of O_3 (without C_2H_4). Data in blue and red correspond
220 to C_2H_4 oxidation with 1000 ppm and 2000 ppm of O_3 , respectively. The markers refer to the
221 experimental data and the lines to simulations.

222

223 Compared to neat O_3 thermal decomposition, O_3 -assisted oxidation of C_2H_4 in FIGURE
224 3 shows that the addition of C_2H_4 induces a drastic shift of the O_3 consumption toward lower
225 temperatures, with a consumption of $\sim 90\%$ of O_3 at 300 K and $\sim 99\%$ at 350 K. The simulations
226 show a relatively good agreement for O_3 consumption for both mole fraction conditions.
227 Increasing by a factor of two the mole fraction of O_3 in presence of C_2H_4 does not change the
228 conversion yield of O_3 .

229 FIGURE 4 shows that with the addition of O_3 , the conversion of C_2H_4 starts since room
230 temperature. A decrease in the mole fraction of C_2H_4 , 4.5% and 9% respectively, compared to
231 the initial mole fraction is observed at 300 K. Multiplying the mole fraction of O_3 by two leads
232 to a twofold decrease of C_2H_4 at low temperatures. The C_2H_4 conversion is stable between 400
233 and 800 K, but decreases significantly from 850 K, indicating a transition to the high-
234 temperature kinetic regime. No temperature shift is observed compared to the O_3 -free
235 experiments, but the conversion is more important (a factor of 5 at 850 K) when O_3 is added.
236 This difference reduces as the temperature increases, until it becomes almost negligible at
237 about 950 K. A similar onset of the high-temperature reactivity under different O_3 -addition
238 levels suggests that the addition of O-atom from the thermal decomposition of O_3 hardly
239 alters the kinetics of the C_2H_4 oxidation above 800 K.

240



241
242 FIGURE 4. Consumption as a function of temperature of C_2H_4 diluted in a gas mixture made
243 of O_2 , O_3 , and He. Two inlet mole fractions of O_3 have been used: 1000 (blue squares) and
244 2000 ppm (red triangles).

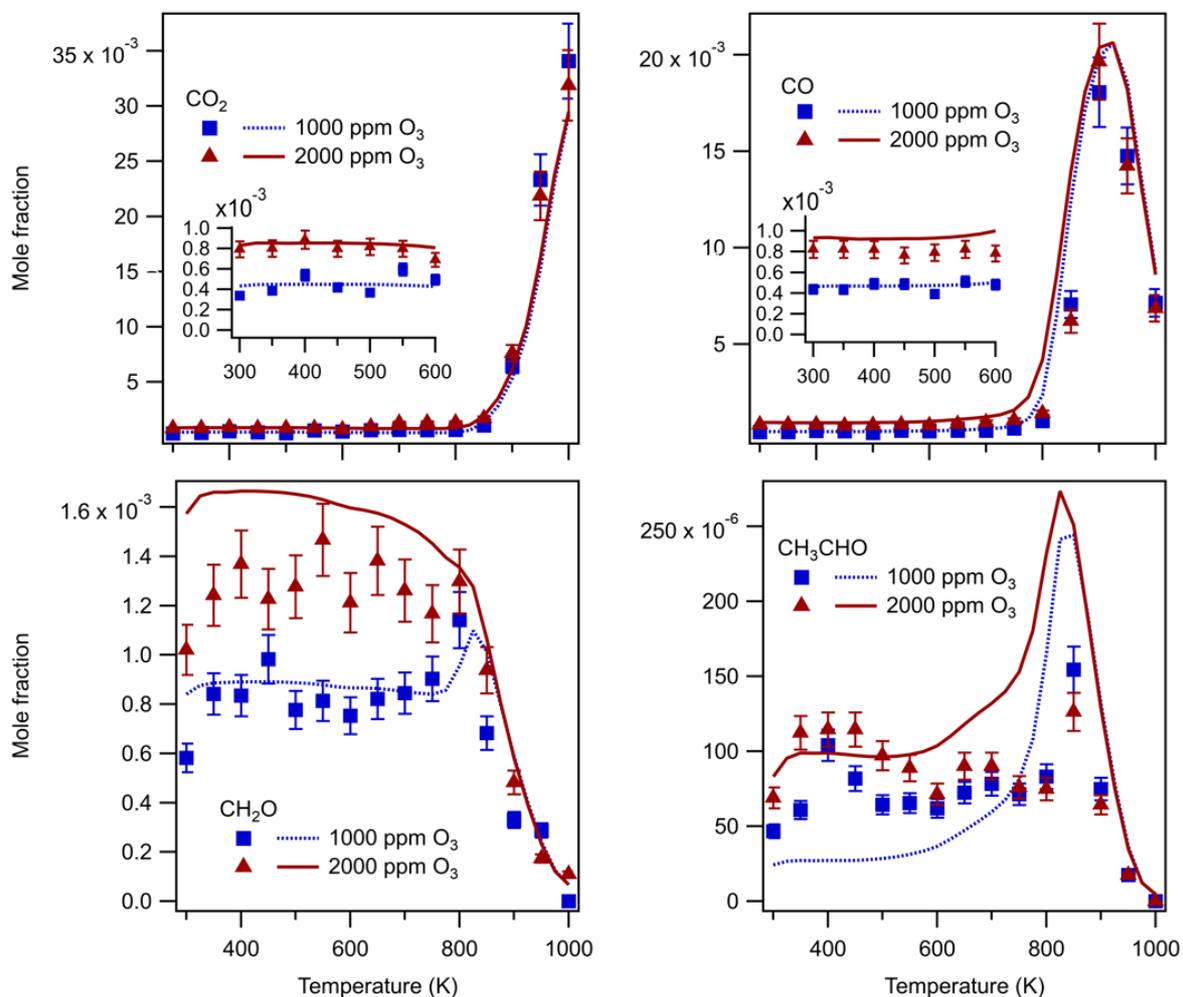
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269 The good agreement observed in this work between simulation and experiments for
270 the conversion of C_2H_4 deviates from the work of Rouso et al. [39], who showed a poor
271 agreement between experiments and simulation. Rouso et al. observed experimentally a
272 decrease of the C_2H_4 conversion as the temperature increased around 500 K. This increase of
273 the C_2H_4 mole fraction, however, does not seem to have any chemical explanation and might
274 be due to the thermal decomposition of O_3 in the injection line, as in their experimental setup
275 O_3 and C_2H_4 are injected through two separate heated lines into the JSR. The effect of the
276 thermal decomposition of O_3 is also reflected in Rouso et al. [39]'s profile of formaldehyde,
277 which is the major product at low temperatures, and whose mole fraction drops to 0 between
278 500 – 800 K in their study. Based on the global reactions implemented in the model to describe
279 the ozonolysis process, a 1:1 mole fraction of $CH_2O:C_2H_4(\text{consumed})$ is expected, but was not
280 observed from 500 K by Rouso et al. [39]. In the present work, all gas lines were mixed before
281 entering the preheating zone upstream of the reactor, in contrast to the separate injection of
282 O_3 and C_2H_4 in Rouso et al. [39]'s work. As shown in FIGURE 6, a similar agreement between
283 simulation and experiments as for C_2H_4 was found for CH_2O with a $CH_2O:C_2H_4(\text{consumed})$ mole
284 fraction ratio of 1:1. To be sure about the mentioned bias in the experiments of Rouso et al.
285 [39], additional experiments and simulations have been done using a similar injection
286 configuration. Similar profiles for C_2H_4 and CH_2O as those of Rouso et al. [39] have been found
287 (see FIGURE S7).

288 As is shown in FIGURE 6, a similar agreement between simulations and experiments as
289 for C_2H_4 can be observed for the mole fraction profile of the main products, CH_2O , CO , and
290 CO_2 . At the lowest temperatures, CH_2O is the main product formed by the ozonolysis of C_2H_4 .
291 At 350 K and in the case of 1000 ppm of O_3 , the mole fraction of CH_2O is about 800 ppm, which
292 is twice the mole fraction of CO and CO_2 . At 800 K, the mole fractions of CO and CH_2O are
293 equivalent (around 1000 ppm). CH_2O , CO , and CO_2 are formed through the global reactions
294 implemented in the kinetic model to describe ozonolysis (see FIGURE S8/equations 1 to 4).
295 Those reactions allow to fairly well reproduce the mole fraction profiles of the main products.
296 In the case of 2000 ppm of O_3 , however, CH_2O is overestimated by up to ~50%, indicating
297 needed refinements in the considered product formation pathways. Water is also one of the
298 major expected products at low temperatures, but as for the O_3 -free experiments, it could not
299 be quantified in this work. The predicted mole fraction of water is ~250 ppm (see FIGURE S9).

300 Note that a 2-fold increase in the mole fraction of O₃ leads to an approximately 2-fold increase
301 in the mole fraction of major products at low temperatures.

302



303
304 FIGURE 6. Comparison of experimental and predicted mole fractions as a function of
305 temperature of low-temperature products measured during the O₃-assisted oxidation of
306 C₂H₄. The symbols correspond to the experimental results and the lines to the predictions of
307 the kinetic model.

308

309 Two minor products were also detected, acetaldehyde (see FIGURE 6) and oxirane (see
310 FIGURE S10). Concerning CH₃CHO, discrepancies between experiments and simulations can
311 be observed with overestimation up to a factor of two above 600 K. For 2000 ppm of O₃, the
312 experimental data show a stable formation of CH₃CHO up to 800 K while the simulated mole
313 fraction profile starts increasing from 600 K. The flow rate analysis at 650 K (see FIGURE 5)
314 shows that the discrepancies at high temperature are still linked to the overestimation of the

315 reaction $C_2H_4 + OH$. The main fate of the CH_2CH_2OH radical coming from the addition reaction
316 $C_2H_4 + OH$ is an H-abstraction by O_2 leading to ethenol (CH_2CHOH). Note that according to the
317 literature, ethenol has never been observed so far in GC and thus was not observed in this
318 work either, probably due to a fast tautomerization into CH_3CHO . In the 1000 ppm O_3 case,
319 experiments display a local maximum mole fraction located at 400 K, which is not reproduced
320 by the model.

321 Concerning oxirane, simulation also underestimates the mole fraction at the lowest
322 temperatures. The simulated profile starts to increase only above 550 K, while the
323 experimental data show a stable formation of about 12 ppm from 400 K and 500 K for both
324 initial O_3 concentrations. The mole fraction of oxirane is fairly well reproduced at higher
325 temperatures.

326 The underestimation of the production of the two minor products at low temperature
327 shows missing reaction pathways in the kinetic model. The reaction mechanisms should
328 therefore be more detailed than the global ozonolysis reactions that are currently
329 implemented in the kinetic model. The formation of oxirane observed at low temperatures
330 can be explained by the 1,2,3-trioxy ozonide (POZ) biradical decomposition giving oxirane and
331 singlet oxygen as proposed in the literature but the exit channel with the formation of oxygen
332 atom is predicted to be minor due to a higher energy barrier. Alternatively, the reaction
333 between Cl and C_2H_4 can also be a source of oxirane with formaldehyde as co-product. The
334 measurement of the oxirane mole fraction profile in this work will provide a constraint for
335 future implementation of the kinetic parameters of the POZ biradical decomposition.
336 Moreover, a potential missing source for acetaldehyde could be the dissociation of the
337 hydroxymethyl formate ($HOCH_2OHCO$), coming from the isomerization of the POZ, through a
338 C-O bond rupture.

339 Methanol was also detected in smaller amounts than CH_2O , CO, and CO_2 since 300 K
340 in the 2000 ppm O_3 case but with a higher mole fraction than CH_3CHO and oxirane (see FIGURE
341 S10). In the 1000 ppm O_3 case, methanol only starts at 550 K. Above this temperature, both
342 profiles seem relatively similar. The mole fraction of methanol in both O_3 cases oscillates
343 between 30 and 70 ppm with a maximum around 700-750 K and is no longer detected above
344 850 - 900 K. The shape of the simulated mole fraction profile is relatively similar to the
345 experimental one at the highest temperatures, but with an order of magnitude lower and with
346 a ~ 90 K temperature shift. This temperature range fits with the formation of O-atoms (see

347 FIGURE S6). The flow rate analysis at 650 K (see FIGURE 5) shows that the main source of
348 methanol is the reaction $C_2H_4 + O$ leading to the formation of CH_3 with HCO. The main fate of
349 CH_3 is the addition of O_2 to form CH_3OO and then methyl hydroperoxide (CH_3OOH). The
350 formation of hydroperoxides following the reaction $C_2H_4 + O_3$ could not be addressed in this
351 work due to their decomposition during the GC analysis but have been observed in the
352 literature [39]. However, the formation of CH_3OH at low temperatures is not predicted by the
353 kinetic model and the temperature range does not fit with the formation of O-atoms. The
354 current formation of CH_3OH in the atmosphere is mainly due to the reactions of OH radical
355 with CH_3 and CH_3OO [51,52], which are currently implemented in the kinetic model. This result
356 shows that a reaction pathway is missing and that, as for CH_3CHO , CH_3OH would come from
357 secondary reactions after the ozonolysis of C_2H_4 .

358 Note that formic acid, HCOOH, has also been detected by GC-MS after condensation
359 of the gas phase using a liquid nitrogen trap, but cannot be quantified since FID is not sensitive
360 to formic acid. Its detection shows that it should be formed in notable amounts. As proposed
361 by Neeb et al. [53], the production of HCOOH can occur via a bimolecular reaction between
362 CIs and CH_2O , an important primary product at the lowest temperatures (see FIGURE 6).

363

364 CONCLUSION

365 The influence of the addition of O_3 on the oxidation of C_2H_4 was experimentally
366 investigated in a JSR coupled with GC analysis at temperatures from 300 to 1000 K under O_3
367 addition of 1000 and 2000 ppm. The evolution with temperatures of the mole fraction of eight
368 species was reported. The addition of O_3 enhanced the production of formaldehyde (CH_2O),
369 methanol (CH_3OH), acetaldehyde (CH_3CHO), oxirane (C_2H_4O), formic acid (HCOOH), CO, and
370 CO_2 . This work also demonstrates that the initial ozonolysis reaction shifts the temperature
371 window of the conversion of C_2H_4 and product formation to a lower temperature regime, in
372 which the traditional C_2H_4 oxidation cannot be initiated. However, the major role of the O_3
373 addition in the oxidation of C_2H_4 remains limited since the additional conversion of C_2H_4 is
374 below 10% with the initial mole fraction of O_3 used in this work and it does not change the
375 chemistry of the high temperature regime. Nonetheless CH_2O , which is an important
376 atmospheric pollutant, is the main product of the low-temperature ozonolysis reaction with a
377 significant mole fraction ~ 1000 ppm. This quantitative result is important to consider
378 especially for closed environments such as warehouses or fruit stores, where non-negligible

379 amounts of C₂H₄ can be present [54]. If these places use air purifiers, a phenomenon that is
380 growing lately because of COVID-19, then a significant amount of formaldehyde can be
381 expected, as many indoor appliances have been shown to generate significant amounts of O₃
382 [55]. More generally, the quantification of oxidation products and stable intermediates under
383 conditions relevant to atmospheric and combustion studies provides a database of
384 temperature-dependent products that can be used as a valuable guidance for future
385 validation and improvement of detailed chemical kinetic models.

386 It has been shown that the configuration of the experimental setup and especially the
387 mixing gas lines is important if one wants accurate quantitative ozonolysis experiments and
388 avoid any thermal degradation of O₃ before reacting with the fuel. The experimental data
389 were confronted to a kinetic model with an implemented ozone/ozonolysis submechanism
390 based on IUPAC recommendations. Overall, contrary to what was mentioned in the literature,
391 a kinetic model based on global reactions of the ethylene ozonolysis accurately reproduces
392 the conversion of C₂H₄, O₃, and main products over a wide temperature range from 300 K to
393 1000 K. The kinetic model is able to capture the trend of the mole fraction profile of the small
394 products above 800K, but below this temperature, disagreements between experiments and
395 simulations are noted. The disagreements are also slightly worse at 2000 ppm than at 1000
396 ppm of O₃. This demonstrates that the implementation of a higher level of detail is needed in
397 the kinetic model with further intermediate pathways to predict the entire product
398 distribution derived from the C₂H₄ ozonolysis chemistry. However, this is beyond the scope of
399 the current study because this would require a total remodeling of the current kinetic model
400 which is based on a global approach of the ozonolysis process. For this, it would be necessary
401 to have information on the kinetics and products of all the main and secondary reactions of
402 the CI network. For example, the formation of methanol is difficult to intuit because the
403 structure is different from the initial reactant. Due to its formation at low temperature, it is
404 likely to be formed from dissociation reactions following the formation of Cl. Rousso et al. [39]
405 also detected methanol and mentioned that its formation is difficult to address because it
406 could come from several pathways. The improvement of the knowledge of the C₂H₄ ozonolysis
407 reaction network would benefit first from a fine identification of the elusive intermediates,
408 which could not be detected in this work, to provide hints on the missing reaction pathways
409 using for instance advanced spectroscopic techniques, such as PEPICO coupled with tunable
410 photoionization sources.

411

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414

415 **REFERENCES**

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