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The impact of EGR components on ozone decomposition under engine relevant conditions in a Rapid Compression Machine

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10 Abstract

11 In this work, with the addition of 90 ppm ozone, the influence of the main EGR components, namely 12 nitrogen, carbon dioxide, steam, and methane, along with the gasoline surrogate iso-octane, on ozone oxidation were investigated at 30 bar, 800 K using a rapid compression machine (RCM). Taking the case 13 14 diluted with nitrogen as a reference, it was found that the chemical effects of CO_2 on ozone decomposition 15 accelerated with the increase in the carbon dioxide concentration. The promoting effect of steam on ozone 16 decomposition remained constant regardless of the steam mole fraction added. The mutual effect of methane 17 and ozone was detectable, but the enhancement of ozone decomposition was lower than when iso-octane was 18 added. A comprehensive detailed kinetic model was employed to interpret the experimental data. The model 19 performance was improved by replacing the rate coefficients of O₃+O=2O₂. Analysis of the rate of 20 production showed that the $IC_8H_{18}+O=CC_8H_{17}+OH$ reaction predominated over the chain terminating 21 reaction $O_3+O=2O_2$, which can explain the significant promoting effect in the presence of iso-octane. When 22 steam is added, two OH radicals are derived from the chain branching reaction $H_2O+O=2OH$. When methane 23 is added, only one OH radical, originating from the O radical attacking methane, is formed. Consequently, 24 the promoting effect of methane addition is the lowest.

25 **Keywords**: Ozone decomposition; EGR components; rapid compression machine.

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27 **1. Introduction**

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Ozone (O_3) is a popular plasma oxidizer which has attracted widespread attention during the last 29 30 decade. When applied to the combustion field, it exhibits significant advantages in terms of ignition promotion especially in the ultra-lean combustion mode, which can provide better efficiency and attenuate 31 32 pump losses [1]. The byproducts of ozone decomposition are oxygen atoms (O) and molecular oxygen (O_2) , which are very environmentally friendly. The use of ozone-assisted combustion would therefore 33 simultaneously fulfill the two requirements of high efficiency and low emissions. In particular, it could solve 34 the issues associated with on-load vehicle auto-ignition in Homogeneous Charge Compression Ignition 35 36 (HCCI) engines. Given the fact that commercial ozone generators are compact and economical, ozone-37 assisted combustion could serve as an alternative method to deal with the ignition process [2].

38 Reports associated with ozone-assisted combustion can be found in engine studies [1-8], jet-stirred 39 reactors [9-10], flow reactors [11], shock tubes [12-15], and flame studies [16-17]. Among engine studies, 40 the impact of ozone on various kinds of fuels has been investigated, ranging from light alkane (natural gas) 41 [5] to primary reference fuel blends [6], with an extension to alcohol [7]. In general, ozone addition was found to have a promoting effect on fuel activity, apart from one case [8] in which ozone and NO were 42 43 injected simultaneously, where it delayed iso-octane combustion when the ozone concentration was less than 44 half of the nitric oxide concentration seeded. This is attributed to the reaction between ozone and nitric oxide, yielding nitric dioxide and oxygen. Recently, in our group, Seignour et al. [18] experimentally investigated 45 46 the effect of different gas compositions, namely exhaust gas recirculation (EGR) components, on ozone 47 decomposition in a diesel engine, since EGR is considered a promising method to overcome emission mitigation issues. However, as temperature stratification may exist inside the engine, a better controlled 48 49 experimental apparatus relevant to engine studies is necessary to obtain more precise experimental results.

A rapid compression machine (RCM), which operates at low-intermediate temperatures and intermediate-high pressures, is a well-suited for engine relevant studies. Equipped with a well-designed crevice in the piston, an RCM can guarantee temperature homogeneity in the core region since the effect of the boundary layer is negligible. In a recent study on ozone-enhanced compressed ignition in an RCM [19], it was found that ozone decomposition accelerated when the charge temperature was increased, oxygen concentration was reduced, or fuel was added. In the unfueled condition, the temporal prediction of O_3 decomposition was generally retarded too much by the model adopted. It appears that the impact of the diluent on ozone decomposition is still unclear.

From the modelling point of view, Sun [20] reviewed the kinetic models in terms of O₃ oxidation. 58 Several elementary reactions included in the O₃ sub-mechanism were highlighted. Various kinetic models 59 associated with O₃ oxidation have been put forward to predict the experimental results. In terms of ozone 60 61 decomposition reactions, early in the 1960s, Benson and Axworthy [21] studied the O₃+M=O₂+O+M reaction, which is an initial step for ozone reactions. This was followed by numerical studies devoted to this 62 63 elementary reaction [22-25]. In 2013, Peukert et al. [26] experimentally and numerically measured and 64 validated the rate of $O_3+M=O_2+O+M$ with the reflected shock tube technique using O-atom atomic resonance absorption spectrometry (ARAS) detection. Temperature and pressure dependent rate coefficients 65 66 were proposed in this work, but the third-body role of triatomic molecules such as CO₂ and H₂O was not 67 addressed. On the other hand, the rate constants of the $O_3+O=2O_2$ reaction remain more uncertain; the most common rate constants adopted in the O_3 mechanism are derived from the evaluation by Atkinson et al. [27]. 68 Hence, a validation of the current O₃ kinetic model is needed. 69

The purpose of this study was to extend previous work [18-19] to an experimental and modelling study aiming to determine the impact of different EGR intermediate species on ozone decomposition with the aid of an RCM setup. A modified comprehensive kinetic model was used to interpret the experimental data. A rate of production (ROP) analysis was also conducted to study the chemical effects of the various additives on ozone decomposition.

75 2. Experimental setup

The experimental apparatus used in this work was a classical single piston RCM, developed and built by the University of Orléans. A detailed description of this setup can be found in [28]; here, only a brief description is given. Firstly, homogeneity inside the combustion chamber of the RCM is guaranteed thanks to the crevice design, which allows strong absorption of boundary layers. It was therefore assumed that compression in the core area of the chamber was isentropic. With the aid of a mass flow controller, the gases (CH₄, O₂, N₂ and CO₂) from the individual cylinders supplied by Messer (purities of 99.99%) passed through the manifold and entered the mixture tank (volume of 4.08 L) directly. Liquid iso-octane and deionized water were injected into the tank by the syringe with the desired value. Apart from the gas supply system, the main part of the RCM was equipped with several kinds of temperature and pressure sensors. A type K thermocouple with an accuracy of ± 1 K was used to measure the intake temperature.

An Anseros COM-AD-01 corona-discharge ozone generator was used to generate ozone in the RCM chamber. With the intake bypass connected to the compressed air, the ozone was generated at the outlet of the generator. An ozone analyzer (Anseros Ozomat MP6060) with a range of 0-200 ppm ozone was used to measure and monitor the desired ozone mole fraction.

Two opposed Suprasil windows were mounted on the sides of the RCM chamber head to provide
optical access. UV light was produced by an Ocean Optics Deuterium Lamp, and collimated by a lens into a
Thorlab integrating sphere. A Hamamatsu photomultiplier tube (254 nm) was employed to collect the signals
through the port. A schematic of the setup is shown in Fig.1.



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Fig.1. Schematic of optical setup of the RCM. PM: photomultiplier

The signal was recorded and analyzed over 20 shots by the RCM. Two independent samples were measured during each experiment. One is a "reference" sample in which no ozone was injected into the system to account for the light attenuation from the optical setup, and the other is a "target" sample with ozone seeded. The ozone mole fraction was calculated with the Beer-Lambert Law:

100
$$X_{O3} = \ln\left(\frac{I_{ref}}{I}\right) \frac{K_b T}{P B \sigma_{O3}}$$

101 where I_{ref} is the reference sample absorption rate, I is the target sample absorption rate, K_b is the Boltzmann 102 constant, B is the bore diameter, σ_{03} denotes the absorption cross section at 254 nm as a function of 103 temperature [29], T and P are the in-cylinder temperature and pressure, respectively. In-cylinder temperature 104 was deduced from the in-cylinder pressure trace.

105 **3. Kinetic Model**

The mechanism adopted in this work consists mainly of the recent comprehensive kinetic model used in [8], in which the ozone decomposition reactions were updated. A modification to the $O_3+M=O_2+O$ reaction was made [30], which turns out to predict the experimental data better. The third body coefficient of triatomic molecules (CO₂ and H₂O) was adopted following the modularity principle behind [21]. The current complete mechanism (1037 species and 4250 reactions) is provided in the supplementary material (SM) in CHEMKIN format, along with thermodynamic properties.

112 **4. Results and discussion**

Ozone decomposition measurements were conducted in the presence of various amounts of N_2 , CO_2 , H₂O, CH₄ and the gasoline surrogate iso-octane in the 313-800 K temperature range and at a pressure of 30 bar. The experimental conditions investigated in this study are presented in Table 1. The initial experimental conditions selected are relevant to engine conditions. Numerical calculations were performed with CHEMKIN-PRO software [31]. A closed homogenous reactor solver with variable volume profiles (see SM), which was derived from the aforementioned non-reactive pressure profiles by adopting the calculation methods proposed in [32], was employed for ozone quantification.

120 4.1 Experimental results and comparison with simulations

121 The ozone conversions as a function of time under various conditions are presented in this section. 122 Simulation results are also shown to compare with the experimental data. Experimental results are 123 represented by solid lines, and simulations by different types of dashed lines in all the figures depicted in this 124 part.

4.1.1 Ozone decomposition diluted in nitrogen

126	Fig.2 shows the ozone (90 ppm) decomposition diluted in nitrogen as a function of time, along with
127	the corresponding temperature and pressure profiles. A small ozone consumption can be observed between
128	t= -5 ms to t=-2 ms, followed by a steep ozone consumption until complete depletion is achieved. Note that
129	the initial oscillation arises from the uncertainty and the vibrations caused by the UV technology and RCM
130	apparatus, respectively.

Table 1 Experimental conditions (Inlet composition volume basis; ozone mole fraction: 90 ppm; End of compression pressure $P_c = 30$ bar).

Exp.	$T_{in}\left[K ight]$	X_{N2}	X_{O2}	X _{CO2}	$X_{\rm H2O}$	X _{CH4} [ppm]	X _{IC8H18} [ppm]
1	313	0.79	0.20991	-	-	-	-
2	313	0.395	0.20991	0.395	-	-	-
3	313	0.5925	0.20991	0.1975	-	-	-
4	313	0.69125	0.20991	0.9875	-	-	-
5	333	0.395	0.20991	0.395	-	-	-
6	353	0.5925	0.20991	0.1975	-	-	-
7	393	0.69125	0.20991	0.9875	-	-	-
8	313	0.69	0.20991	-	0.1	-	-
9	313	0.74	0.20991	-	0.05	-	-
10	313	0.765	0.20991	-	0.025	-	-
11	313	0.7895	0.20991	-	-	500	-
12	313	0.78975	0.20991	-	-	250	-
13	313	0.7895	0.20991	-	-	-	500
14	313	0.78975	0.20991	-	-	-	250

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Two simulations were compared in this work. First, with the previous model (Model-1) used in [18], a retarding effect was detected compared to the experimental trend. On replacing the rate coefficient of $O_3+O=2O_2$ [30], the prediction improved as the sharp consumption timing was better captured by the updated model (Model-2), although the model still failed to predict the initial slow ozone consumption zone (t= -5 to -2 ms). Overall, good agreement between the steep ozone oxidation experimental data and model
output was observed. A possible explanation for the slow ozone consumption might be the surface effect
when the temperature is above 550 K.





Fig.2 Ozone decomposition as a function of time during the compression stroke. Solid lines denote the
experimental results and dashed lines represent the simulation. Temperature and pressure profiles are also provided as a
reference.

145 4.1.2 The impact of carbon dioxide

146 Fig. 3 shows the ozone decomposition profile with different amounts of carbon dioxide (0, 9.875%, 147 19.75%, 39.5%) as a function of time. In these cases, the initial temperatures were kept the same (313 K). 148 The end pressures (P_c) was approximately 30 bar, which is consistent with the cases shown in Fig.2. As for 149 the following cases (steam, methane and iso-octane added), the P_c were all kept at 30 bar. The corresponding 150 temperature profiles are given in Fig.4. Overall, CO₂ addition retarded the initiation of ozone decomposition. 151 In the presence of CO_2 , the inhibiting effect increased with the increase in the CO_2 mole fraction. In particular, in the case of 39.5% CO₂ addition, 30% of ozone still remained in the system compared to the 152 nearly completed consumption case without CO_2 addition at a time of 9 ms. Due to the high thermal capacity 153 of CO₂, the temperature profiles with CO₂ addition were generally below that without CO₂, as shown in Fig.4. 154 155 In this case, the retarding effect might be ascribed to the thermal effect of CO₂, which deteriorates the whole 156 system.

157 The model predicted the experimental data well in the case of 9.875% and 19.75% CO₂ addition, but 158 a deviation between the experimental data and simulation was found with 39.5% CO2 addition. While it 159 might be assumed that the main role of CO₂ in ozone decomposition is participating in the O₃+M=O₂+O+M 160 reaction as a third body, the introduction of the third body coefficient did not in fact impact the model behavior significantly. It could be ascribed to the predominantly thermal role of CO₂ in this temperature 161 162 range.



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Fig.3. Ozone decomposition in the presence of CO₂ as a function of time during the compression stroke. Solid 165 lines denote the experimental results and dashed lines represent the simulation.



In order to decouple the CO₂ thermal effect, another set of experiments was conducted in which the 168 initial temperature was increased to 60, 80, and 120 °C for the three carbon dioxide conditions (9.875%, 169 170 19.75%, 39.5%), respectively, to ensure a similar end of compression temperature (T_c). Fig.5 shows the 171 ozone decomposition profile with different amounts of carbon dioxide (0, 9.875%, 19.75%, 39.5%) at a similar end of compression temperature as a function of time. With a similar T_c, the ozone decomposition 172 173 behavior is dramatically different from those shown in Fig.3. In the case of 9.875% CO₂ addition, ozone 174 decomposition shows a similar trend compared to the one without CO_2 addition, while in the presence of 175 19.75% CO₂, a slight promoting effect can be observed. As CO₂ is further increased to 39.7%, the 176 accelerating effect becomes significant. Although the temperature profiles for the aforementioned cases are 177 not exactly the same as the one without CO₂ addition as shown in Fig.6, the temperature is consistent among 178 the 0, 9.875%, and 19.75% CO₂ addition cases at t=3 ms. When taking a close look at Fig.5 again at t= 3 ms, one may note that the ozone is consumed more in the presence of CO_2 than without CO_2 addition. This 179 180 implies that the chemical effect of CO₂ should not be neglected even at 800 K, 30 bar, under engine relevant 181 conditions.





Fig.5. Ozone decomposition in the presence of CO₂ as a function of time during the compression stroke with a
 similar T_c. Solid lines denote the experimental results and dashed lines represent the simulation.



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Fig.6. The temperature profiles corresponding to the conditions shown in Fig.5

The model reproduced the cases with different amounts of carbon dioxide (9.875% and 19.75%) reasonably well, but the deviation between the experimental and simulated results became larger when further increasing the carbon dioxide mole fraction to 39.5%. The reason for this poor model performance in the case of a relatively high amount of carbon dioxide is still unclear.

191 4.1.2 The impact of steam

192 Fig.7 shows the ozone decomposition profile with different amounts of steam (0, 2.5%, 5%, 10%) as 193 a function of time. It is interesting to note that different amounts of steam exhibit a very similar promoting 194 trend compared to the one without steam addition, which is also observed in engine work [18]. In addition, at around t= 0.4 ms, a short plateau (1 ms) was observed, after which it continued to decompose. The "plateau" 195 phenomenon could be explained by the potential formation of H_2O_2 or HO_2 , which also show characteristic 196 197 absorption at this wavelength [33]. In general, Fig.7 shows that ozone initiation advances by 2 ms in the presence of steam. In this case, the temperature profiles (Fig.8) are almost the same among all the 198 investigated conditions, except the one with 10% steam addition, whose temperature is 10 K lower. Hence 199 200 the promoting effects can be attributed to the chemical effect of steam.



Fig.7. Ozone decomposition in the presence of H₂O as a function of time during the compression stroke. Solidlines denote the experimental results and dashed lines represent the simulation.



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Fig.8. The temperature profiles corresponding to the conditions shown in Fig.7

While the model was able to capture the promoting trend, a retarded model performance was observed compared to the experimental data. A possible explanation for the deviation between the experimental results and numerical calculations could be the inaccuracy of the elementary reaction $O_3+H_2O=H_2O_2+O_2$. Its reaction rate was adopted from the early experimental work by [34]. By implementing this rate constant, the contribution of $O_3+H_2O=H_2O_2+O_2$ is minor as shown in the following analysis (Fig.9).

212	The rate of production (ROP) analysis (Fig.9 and 10) showed that the main consumption channel for
213	ozone is $O_3+M=O_2+O+M$, following $O_3+O=2O_2$. The ROP of the reaction $O_3+H_2O=H_2O_2+O_2$ was
214	negligible. For steam, H ₂ O+O=2OH is the main consumption channel; the formation channels are
215	$HO_2+OH=H_2O+O_2$ and $H_2O_2+OH=H_2O+HO_2$. Once ozone has decomposed, the O atoms can react with
216	either ozone or steam. Steam can serve as a promoter since the products of O radicals and steam are
217	hydroxide radicals. On the other hand, $O_3+O=2O_2$ is a chain terminating reaction due to the stable oxygen
218	products. In this case, the participation of steam in the system competes with the chain terminating reaction
219	and yields two OH radicals, which may accelerate ozone decomposition. This could explain the advance of
220	the experimental and model results in the presence of steam shown in Fig.7.



Fig.9. The main rate of production (ROP) involved in ozone as a function of time in the presence of steam



Fig.10. The main rate of production (ROP) involved in steam as a function of time in the presence of steam

225 It is worth mentioning that different amounts of steam have a very similar promoting trend compared 226 to the case without steam. In [18], the effect of steam was attributed to the low activated energy required by 227 O₃+H₂O=O₂+O+H₂O. However, the similar promoting effect in the presence of different amounts of steam 228 was not clarified. In the present work, the ROP involved in steam evolves as shown in Fig.10. The main 229 consumption channel of steam is $H_2O+O=2OH$. The function of this elementary reaction can be twofold: on 230 the one hand, it competes with the chain terminating reaction $O_3+O=2O_2$; on the other hand, the two OH 231 radicals are reactive radicals, which is beneficial to the whole system. It is reported in the review paper [20] 232 that the highly oxidative hydroxy radical attaching ozone is of importance. The main steam formation 233 reactions are OH radical consuming ones, along with the yield of stable products. Note that the ROP of 234 $O_3+H_2O=O_2+O+H_2O$ increases with the increase of steam; accordingly, the ROP of the chain terminating 235 reactions HO₂+OH= H_2O+O_2 and $H_2O_2+OH=H_2O+HO_2$ also increase. In sum, the balance of the consumption 236 and formation channels of steam results in the similar influence of various amounts of steam addition on 237 ozone decomposition.

238 4.1.3 The impact of methane and iso-octane

With methane addition, surprisingly, the accelerating effect was also observed. In [20], it was argued that the interaction between methane and ozone is very limited at room temperature. In contradiction with [20], a promoting effect of methane addition was found here, demonstrating the mutual effect between methane and ozone under engine relevant conditions as shown in Fig.11. In the presence of methane, the acceleration of ozone decomposition was observed after the time (t= 0 ms). Fig.12 shows that the temperature profile was similar with and without methane addition. So the chemical effect of methane is noticeable during the ozone decomposition process.



Fig.11. Ozone decomposition in the presence of CH_4 as a function of time during the compression stroke. Solid lines denote the experimental results and dashed lines represent the simulation.



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Fig.12. The temperature profiles corresponding to the conditions shown in Fig.11

The agreement between the experimental data and simulation results was generally acceptable although a slight deviation was observed. The promoting effect of methane was also illustrated by ROP analysis. At the beginning of ozone decomposition as shown in Fig.13, $O_3+M=O_2+O+M$ is the main contributing reaction. The chain terminating reaction $O_3+O=2O_2$ also shows a significant effect on ozone decomposition. With regard to methane oxidation (Fig.14), $CH_4+O=CH_3+OH$ exhibits a similar production rate to the $O_3+O=2O_2$ reaction. Only one OH radical is released by the $CH_4+O=CH_3+OH$ reaction. This could explain the relatively small promoting effect compared to the case with steam since two OH radicals are formed via $H_2O+O=2OH$. On the other hand, $CH_4+OH=CH_3+H_2O$ is the main consumption channel of methane. When comparing the different cases (250 and 500 ppm addition), as shown in Fig.14, it can be seen that the initiation timing of $CH_4+O=CH_3+OH$ with 500 ppm methane addition is advanced compared to the one with 250 ppm addition. Moreover, the more methane is added, the higher the rate of production, which explains the more promoting effect with 500 ppm methane addition.





Fig.13. The main rate of production (ROP) involved in ozone as a function of time in the presence of methane





Fig.14. The main rate of production (ROP) involved in methane as a function of time in the presence of methane The effect of iso-octane addition on ozone decomposition at 30 bar is shown in Fig.15. Two different iso-octane mole fractions (250 and 500 ppm) were tested. As expected, ozone consumption started at early timing, indicating that the presence of iso-octane promotes ozone oxidation. In this case, at around

t=1.4 ms, a small plateau also occurred. However, with the decrease in the iso-octane mole fraction, this
plateau vanished. Note that the temperature profile (Fig.16) shows a similar trend when the timing is below 2
ms. This is the timing range of ozone decomposition in the iso-octane addition cases.

274 The model captured the experimental results well regardless of the prediction failure for the "plateau" characteristic since it is the absorption signal of the HO₂ or H₂O₂ species. The ROP analysis (Fig.17 and 18) 275 showed that the main ozone consumption channel is O₃+M=O₂+O+M, while other channels exhibited a 276 277 minor effect in terms of ozone oxidation. On the other hand, upon the initial iso-octane oxidation, $IC_8H_{18}+O=CC_8H_{17}+OH$ and $IC_8H_{18}+OH=AC_8H_{17}+H_2O$ played a similar role, while the other channels 278 279 involving IC_8H_{18} +OH exhibited a minor effect compared to that of IC_8H_{18} +OH=AC₈H₁₇+H₂O. Note that the 280 yield of O atoms serves as a reactant in the branching reaction $IC_8H_{18}+O=CC_8H_{17}+OH$, as shown in the inset 281 of Fig.18. This reaction plays a dominant role compared to the chain terminating reaction $O_3+O=2O_2$, which 282 shows a small effect on ozone decomposition, as depicted in Fig.17. This is the reason why the promoting 283 effect of iso-octane on ozone decomposition is greater than that of methane. The influence of different amounts of iso-octane on ozone decomposition exhibits the same trend as in the presence of methane. 284



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Fig.15. Ozone decomposition in the presence of iso-octane as a function of time during the compression stroke.Solid lines denote the experimental results and dashed lines represent the simulation.



Fig.16. The temperature profiles corresponding to the conditions shown in Fig.15





Fig.17. The main rate of production (ROP) involved in ozone as a function of time in the presence of iso-octane



293

Fig.18. The main rate of production (ROP) involved in iso-octane as a function of time in the presence of iso-octane.
The insets present the ROP profile of the IC₈H₁₈+O reaction.

297 **5. Conclusions**

In this work, in the presence of 90 ppm ozone, the impact of the main EGR components, i.e. nitrogen, carbon 298 299 dioxide, steam, and methane along with the gasoline surrogate iso-octane, on ozone oxidation were studied at 300 30 bar, 800 K with the aid of an RCM. Results reveal that the chemical effect of CO₂ on ozone 301 decomposition increases with the increase in the carbon dioxide mole fraction, whereas the promoting effect 302 of steam on ozone decomposition remains constant regardless of the steam concentration added. The 303 enhancement of ozone decomposition is less in the presence of methane compared to that of iso-octane. A 304 comprehensive detailed kinetic model with rate modification of $O_3+O=2O_2$ was employed to interpret the 305 experimental data. It is found that the reaction $IC_8H_{18}+O=CC_8H_{17}+OH$ strongly dominates the chain 306 terminating reaction $O_3+O=2O_2$ in the presence of iso-octane. As for steam additives, the chain branching 307 reaction $H_2O+O=2OH$ shows a high production rate and is of particular importance since it competes with 308 the chain terminating reaction $O_3+O=2O_2$ and two OH radicals are formed. The ROP of CH₄+O=CH₃+OH is 309 similar to that of $O_3+O=2O_2$, and only one OH radical is released in the presence of methane.

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