

# Effect of Oxygen Atom Precursors Addition on LTC-affected Detonation in DME-O<sub>2</sub>-CO<sub>2</sub> Mixtures

Rémy Mével<sup>1,2</sup> and Yizhuo He<sup>1,2</sup>

<sup>1</sup> Center for Combustion Energy, Tsinghua University, Beijing, China

<sup>2</sup> Department of Automotive Engineering, Tsinghua University, Beijing, China

## 1 Introduction

While detonations propagating in hydrocarbon-based mixtures have always been considered as a process driven only by high-temperature chemistry (HTC), it was recently shown by Liang et al. [1] that low-temperature chemistry (LTC) could be activated for mixtures highly diluted with CO<sub>2</sub>. Liang et al. estimated the dynamic detonation parameters of LTC-affected detonation for n-heptane-O<sub>2</sub>-CO<sub>2</sub>. It is noted that for such mixtures, an induction zone length on the order of 10 cm was calculated, which leads to an estimated cell size of several meters. Such a large characteristic length-scale prevents any experimental observation of LTC-affected detonation for large alkanes like n-heptane. It was latter shown by Mevel et al. [2] that for mixtures of dimethyl ether (DME) highly diluted with CO<sub>2</sub>, the induction zone length could be reduced to few cm. Nevertheless, the induction length is still very large to enable experimental observation. In order to further reduce the induction zone length and enable experimental observation or multi-dimensional numerical simulation of LTC-affected detonation, a number of additives could be considered.

The goal of the present study was to evaluate the impact of some oxygen atom precursors on the characteristic scales of LTC-affected detonation in DME-O<sub>2</sub>-CO<sub>2</sub> mixtures. To this end, Zeldovich-von Neumann-Doering (ZND) calculations were performed for mixtures with ozone (O<sub>3</sub>) or nitrogen dioxide (NO<sub>2</sub>) addition. The effect of these additives on the energy release rate dynamics and chemical kinetics were studied in details.

## 2 Modeling approach

The chemical mechanism employed to describe DME kinetics was that of Bhagatwala et al. [3]. It is composed of 39 species and 175 reactions and include both low- and high-temperature chemical pathways. In order to account for the reactions of ozone, the sub-model from Zhao et al. [4] was added to the base DME model. It includes 3 additional species and 11 reactions. The reaction model of Mevel et al. [5, 6] was employed to describe the NO<sub>x</sub> chemistry. It includes 45 additional species and 293 reactions.

The calculations were performed using a numerical version of the ZND model, as described by Shepherd [7], implemented in Chemkin II. Because standard utilities for chemical kinetics analysis are not implemented in our ZND code, the Senkin code [8] was employed to perform the analysis of (i) the energy release per reaction (ERR); (ii) the rate of production (ROP); and (iii) the sensitivity coefficient. For these analyses, the pressure profile was constrained to match the one obtained from the ZND calculation.

All the calculations were performed for a lean DME-O<sub>2</sub> mixture with equivalence ratio of  $\Phi=0.5$  and initial conditions of  $T_1=300$  K and  $P_1=100$  kPa. The CO<sub>2</sub> content was varied between 60 and 80%. These conditions were chosen because they favor the occurrence of a LTC-driven two-stage ignition process. To test the effect of O<sub>3</sub> and NO<sub>2</sub> addition, amounts of 10, 100, 1000 and 10000 ppm of CO<sub>2</sub> were replaced by the additive. Significant impact was observed mostly for 1% addition and consequently, only the results for such an amount of additive are reported in the present manuscript.

### 3 Results and discussion

#### 3.1 Effect of O precursors addition on the characteristic scales

The effect of O<sub>3</sub> and NO<sub>2</sub> addition on the temperature and thermicity profiles are shown in Figure 1 and Figure 2, respectively. A quantitative assessment of the effect of the O precursors addition on the ZND characteristic scales is shown in Figure 3. It is noted that regardless of the number of peaks present in the thermicity profile, the peak generated by the LTC is referred to as “the first peak”, even if it is not present under given conditions.

For a CO<sub>2</sub> content lower than 70%, a two-step energy release is observed for mixtures without ozone which indicates that the LTC is not activated under these conditions. For a CO<sub>2</sub> content higher than 70%, a three-step energy release is observed for mixtures with and without ozone. The addition of ozone extends the range of conditions for which a multi-step energy release process is observed since for the neat DME mixture diluted with 60 and 68% of CO<sub>2</sub>, monotonous temperature profile is predicted whereas the mixtures containing ozone demonstrate a two-step energy release profile. The addition of 1% of ozone induces a decrease of the induction zone length for the three steps of oxidation. The decrease is the most important for the induction length associated with the first step with a reduction by 45 to 87 times depending on the CO<sub>2</sub> content. The second induction length is reduced by 11 to 15 times whereas the third induction length is reduced by 2 to 10 times. In addition, the mixtures containing O<sub>3</sub> exhibit higher peaks of energy release rate. For the first step of energy release, the increase ranges between 30 and 400 times whereas for the two other steps of energy release, the increase is between 20 and 80%.

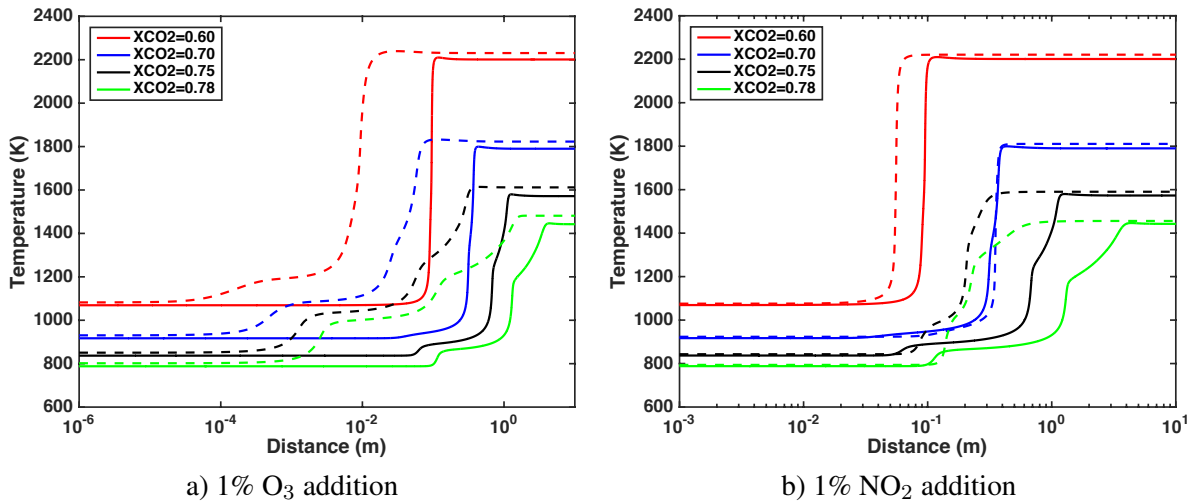


Figure 1: ZND temperature profiles of DME-O<sub>2</sub>-CO<sub>2</sub> mixtures with (dashed lines) and without (solid lines) O precursors addition. Conditions:  $\Phi=0.5$ ;  $P_1=100$  kPa;  $T_1=300$  K.

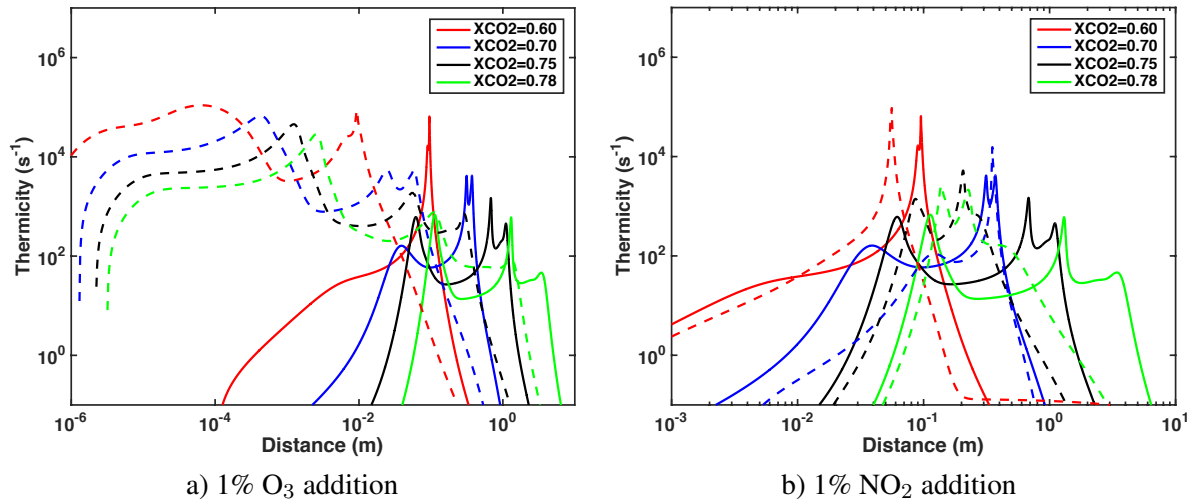


Figure 2: ZND thermicity profiles of DME-O<sub>2</sub>-CO<sub>2</sub> mixtures with (dashed lines) and without (solid lines) O precursors addition. Conditions:  $\Phi=0.5$ ;  $P_1=100$  kPa;  $T_1=300$  K.

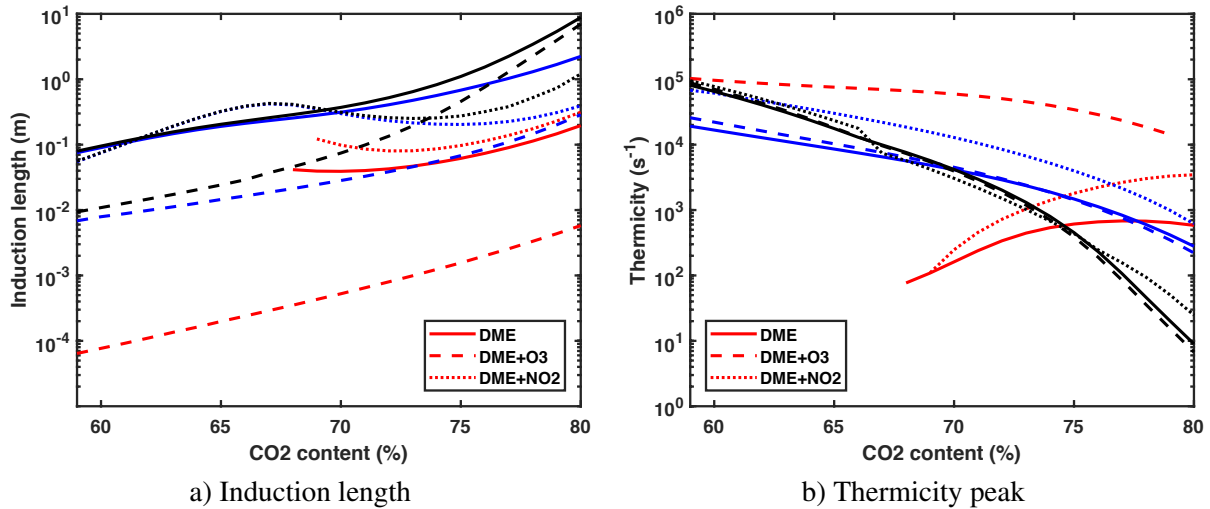


Figure 3: Effect of 1% O<sub>3</sub> or 1% NO<sub>2</sub> addition on the ZND induction zone lengths and thermicity peak heights of DME-O<sub>2</sub>-CO<sub>2</sub> mixtures. Conditions:  $\Phi=0.5$ ;  $P_1=100$  kPa;  $T_1=300$  K. Red lines: first step of energy release (ER); Blue lines: second step of ER; Black lines: third step of ER

The addition of NO<sub>2</sub> has a very different impact on the temperature and thermicity profiles as compared to that of ozone. The range of CO<sub>2</sub> content for which the LTC is activated is slightly reduced to 69-80% whereas it extends down to 68% for the neat DME mixtures. Within the range 74-79% of CO<sub>2</sub> the first induction length is increase by 20 to 40% whereas the peak height is increased by 2 to 6 times. Within the range 59-79% of CO<sub>2</sub>, the second induction length for the mixtures with NO<sub>2</sub> demonstrates a non-monotonous evolution with an increase up to 69% of CO<sub>2</sub>, followed by a decrease up to 74% of CO<sub>2</sub>, and finally another increase up to 80% of CO<sub>2</sub>. The second peak of thermicity is increased by approximately 4 times. The third step of energy release also demonstrates a non-monotonous evolution and the peak of thermicity associated with this oxidation step is

on the same order of magnitude than the one observed for the neat DME mixtures with a maximum increase of 75%.

### 3.2 Effect of O precursors addition on the thermo-chemical dynamics

To perform the analysis of the thermo-chemical dynamics, the mixtures with 74-75%  $\text{CO}_2$  dilution have been selected because the three steps of energy release were observed both with and without O precursors addition. Figure 4, 5, and 6 respectively show the ERR profiles, the OH and  $\text{HO}_2$  normalized ROP, and the normalized sensitivity coefficients on temperature.

Concerning the ERR, the first and second peaks are due to  $\text{R}_1$ :  $\text{H}+\text{O}_2(+\text{M})=\text{HO}_2(+\text{M})$ ,  $\text{R}_2$ :  $\text{HCO}+\text{O}_2=\text{CO}+\text{HO}_2$ , and  $\text{R}_3$ :  $\text{CH}_2\text{O}+\text{O}_2=\text{HCO}+\text{H}_2\text{O}$  for the three mixtures. For the mixture with  $\text{O}_3$ , the reaction  $\text{R}_4$ :  $\text{CH}_3\text{OCH}_2+\text{O}_2=\text{CH}_3\text{OCH}_2\text{O}_2$  also contributes to the first peak whereas for the mixture with  $\text{NO}_2$ , the reaction  $\text{R}_5$ :  $\text{NO}_2+\text{H}=\text{NO}+\text{OH}$  is important for the first and second peaks. For the neat DME mixture, the third peak is due to  $\text{R}_1$  and  $\text{R}_6$ :  $\text{HO}_2+\text{OH}=\text{H}_2\text{O}+\text{O}_2$ . Both the addition of  $\text{O}_3$  and  $\text{NO}_2$  suppress the contribution of  $\text{R}_6$  to the third peak of ERR. In addition, for the mixture with  $\text{NO}_2$ , the high-temperature reaction  $\text{R}_7$ :  $\text{CO}+\text{OH}=\text{CO}_2+\text{OH}$  significantly contributes to the third stage of ERR. In terms of energy consumption, the  $\text{H}_2\text{O}_2$  decomposition reaction  $\text{R}_8$ :  $\text{H}_2\text{O}_2(+\text{M})=2\text{OH}(+\text{M})$  is the most important reaction during the second stage and the branching reaction  $\text{R}_9$ :  $\text{H}+\text{O}_2=\text{OH}+\text{O}$  has a weak contribution during the third stage of ERR. The addition of  $\text{O}_3$  induce an increased contribution of the ozone decomposition reaction  $\text{R}_{10}$ :  $\text{O}_3(+\text{M})=\text{O}_2+\text{O}(+\text{M})$  and of the isomerization reaction  $\text{R}_{11}$ :  $\text{CH}_3\text{OCH}_2\text{O}_2=\text{CH}_2\text{OCH}_2\text{O}_2\text{H}$  during the first stage of ERR; as well as a decreased contribution of  $\text{R}_9$  during the third stage of ERR. The addition of  $\text{NO}_2$  reduces the contribution of  $\text{R}_8$  and increases the contribution of  $\text{HCO}$  and  $\text{CH}_3\text{O}$  decomposition reactions,  $\text{R}_{12}$ :  $\text{HCO}+\text{M}=\text{H}+\text{CO}+\text{M}$  and  $\text{R}_{13}$ :  $\text{CH}_3\text{O}+\text{M}=\text{CH}_2\text{O}+\text{H}+\text{M}$ , during the second stage of ERR.

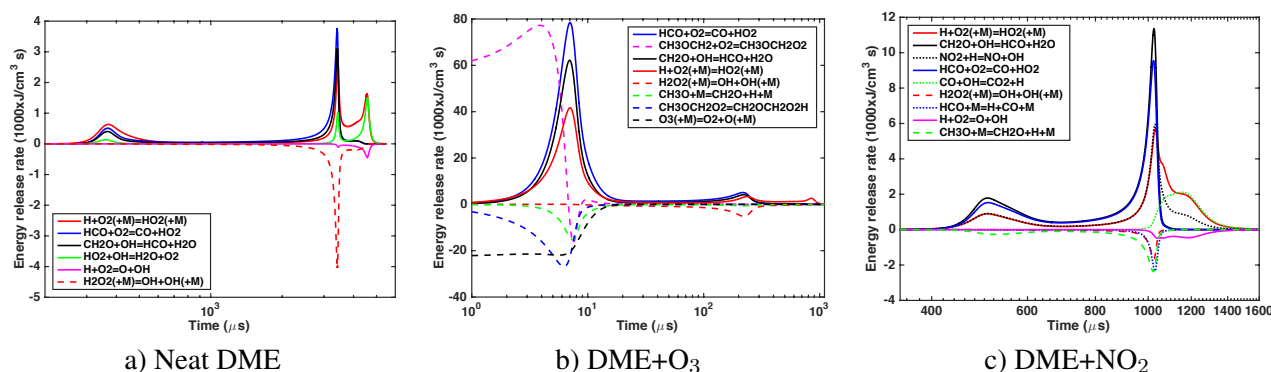


Figure 4: Effect of 1%  $\text{O}_3$  or 1%  $\text{NO}_2$  addition on the energy release rate profile for ZND detonation propagating in DME- $\text{O}_2$ - $\text{CO}_2$  mixtures. Conditions:  $\Phi=0.5$ ;  $X_{\text{CO}_2}=0.74-0.75$ ;  $P_1=100$  kPa;  $T_1=300$  K.

The analysis of the ROP for OH radical (see Figure 5 a)) shows that for the neat DME mixture, the production is dominated by  $\text{H}_2\text{O}_2$  decomposition ( $\text{R}_8$ ) whereas the branching reaction  $\text{R}_9$  has a weak contribution. The consumption of OH radicals is due to the H abstraction reactions on  $\text{CH}_2\text{O}$  ( $\text{R}_{14}$ :  $\text{CH}_2\text{O}+\text{OH}=\text{HCO}+\text{H}_2\text{O}$ ) and DME ( $\text{R}_{15}$ :  $\text{DME}+\text{OH}=\text{CH}_3\text{OCH}_2+\text{H}_2\text{O}$ ), and to the reaction with CO ( $\text{R}_7$ ). The addition of  $\text{O}_3$  weakens the contribution of  $\text{R}_8$  to the formation of OH which is mainly due to  $\text{R}_{16}$ :  $\text{CHOCH}_2\text{O}_2\text{H}=\text{OH}+2\text{CH}_2\text{O}$ ,  $\text{R}_{17}$ :  $\text{DME}+\text{O}=\text{CH}_3\text{OCH}_2+\text{OH}$ , and  $\text{R}_{18}$ :  $\text{CH}_3+\text{HO}_2=\text{CH}_3\text{O}+\text{OH}$ . The consumption of OH is mainly due to  $\text{R}_{14}$  and  $\text{R}_{15}$ , and the contribution of  $\text{R}_7$  is much lower. The addition of  $\text{NO}_2$  has a more dramatic impact on the formation

pathways of OH radicals since the two main contributors are two reactions which involve nitrogenated species,  $R_5$  and  $R_{19}$ :  $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$ . The consumption pathways of OH are not much modified by  $\text{NO}_2$  addition.

Concerning the ROP for  $\text{HO}_2$  (see Figure 5 b)), it is noted that the two additives do not modify the main production pathways which are  $R_1$  and  $R_2$ . The addition of  $\text{O}_3$  only induces an increase of the contribution of  $R_2$  and a decrease of that of  $R_1$ . For the neat DME mixture and the mixture with added  $\text{O}_3$ , the consumption of  $\text{HO}_2$  is through  $R_6$ ,  $R_{18}$ , and  $R_{20}$ :  $\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$ . The addition of  $\text{NO}_2$  completely suppresses the contribution of  $R_{18}$  and  $R_{20}$  to the consumption of  $\text{HO}_2$  which is essentially due to  $R_{19}$ .

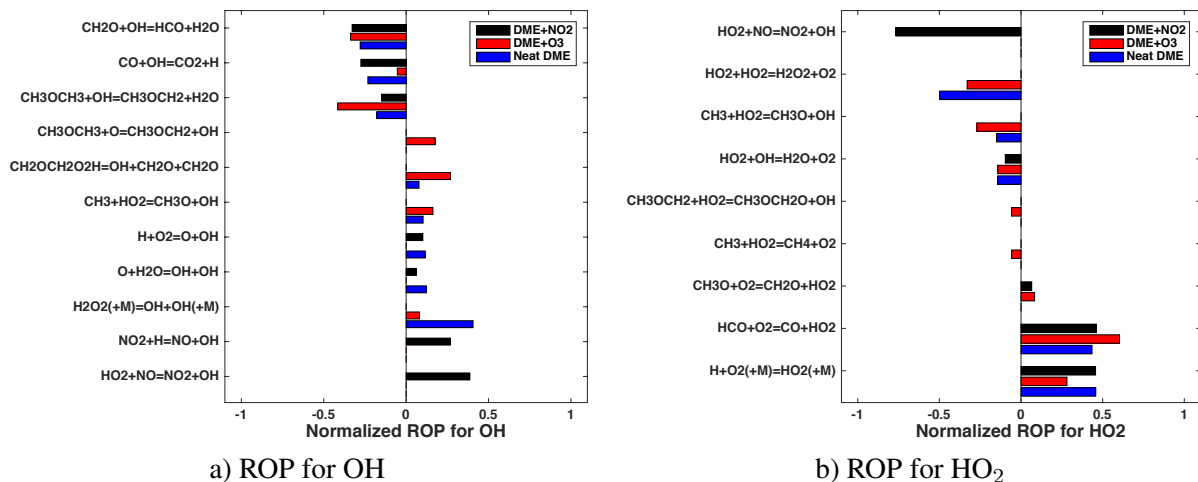


Figure 5: Effect of 1%  $\text{O}_3$  or 1%  $\text{NO}_2$  addition on the OH and  $\text{HO}_2$  ROP for ZND detonation propagating in DME- $\text{O}_2$ - $\text{CO}_2$  mixtures. Conditions:  $\Phi=0.5$ ;  $X_{\text{CO}_2}=0.74$ - $0.75$ ;  $P_1=100$  kPa;  $T_1=300$  K.

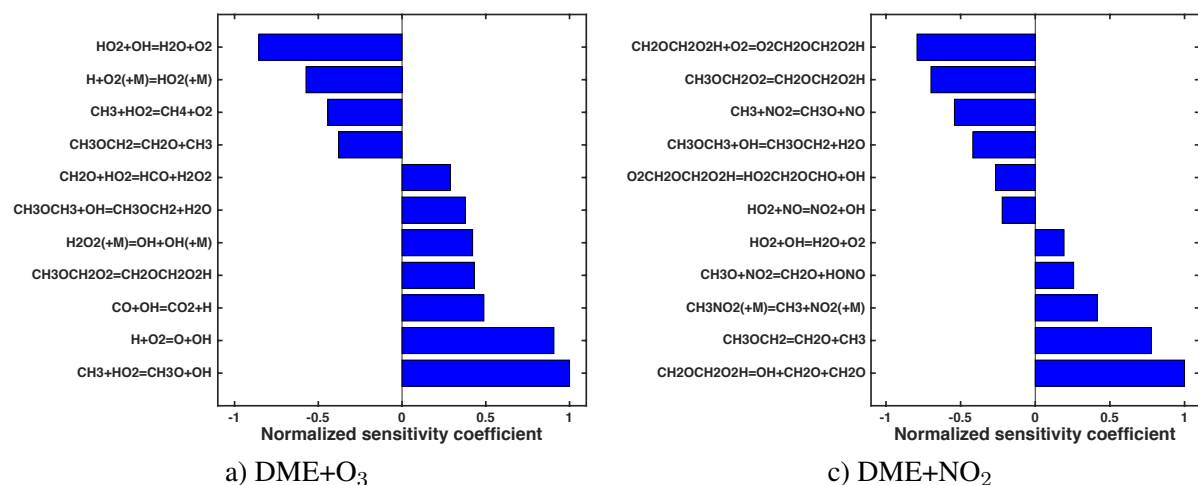


Figure 6: Effect of 1%  $\text{O}_3$  or 1%  $\text{NO}_2$  addition on the sensitivity coefficient on temperature for ZND detonation propagating in DME- $\text{O}_2$ - $\text{CO}_2$  mixtures. Conditions:  $\Phi=0.5$ ;  $X_{\text{CO}_2}=0.74$ ;  $P_1=100$  kPa;  $T_1=300$  K.

The addition of  $\text{O}_3$  or  $\text{NO}_2$  has an important impact on the sensitivity coefficients on temperature (see Figure 6) since for the mixtures with additive, many reactions exhibit large sensitivity coefficients whereas for the

neat DME mixture, only the initiation reaction  $R_{21}$ :  $\text{DME} + \text{O}_2 = \text{CH}_3\text{OCH}_2 + \text{HO}_2$  is sensitive. For the mixture containing  $\text{O}_3$ , the sensitive reactions are those which involve  $\text{HO}_2$ , such as  $R_1$ ,  $R_6$ , and  $R_{18}$ , and those which involve DME-related compounds, such as  $R_{11}$ ,  $R_{15}$ , and  $R_{22}$ :  $\text{CH}_3\text{OCH}_2 = \text{CH}_2\text{O} + \text{CH}_3$ . The high-temperature reactions  $R_7$  and  $R_9$  also demonstrate large positive coefficients. For the mixture containing  $\text{NO}_2$ , 6 of the 11 most sensitive reactions corresponds to reactions which involve DME-related compounds. The most sensitive ones are  $R_{11}$ ,  $R_{16}$ ,  $R_{22}$ , and  $R_{23}$ :  $\text{CH}_2\text{OCH}_2\text{O}_2\text{H} + \text{O}_2 = \text{O}_2\text{CH}_2\text{OCH}_2\text{O}_2\text{H}$ . The other most sensitive reactions involve  $\text{NO}$  and  $\text{NO}_2$ :  $R_{19}$ ,  $R_{24}$ :  $\text{CH}_3 + \text{NO}_2 = \text{CH}_3\text{O} + \text{NO}$ ,  $R_{25}$ :  $\text{CH}_3\text{O} + \text{NO}_2 = \text{CH}_2\text{O} + \text{HONO}$ , and  $R_{26}$ :  $\text{CH}_3\text{NO}_2(+\text{M}) = \text{CH}_3 + \text{NO}_2(+\text{M})$ . Reactions  $R_7$  and  $R_9$  are not within the most sensitive reactions.

The analyses shown in Figure 4 to 6 enable to draw the following conclusions:

- (i) The effect of the ozone addition is essentially to speed up the LTC. Because of the fast decomposition of  $\text{O}_3$  ( $R_{10}$ ), the main initiation reaction becomes  $R_{17}$ , which is faster than  $R_{21}$  and produces a much more reactive radical,  $\text{OH}$  instead of  $\text{HO}_2$ . This sequence is responsible for the important decrease of the successive steps of energy release which stay, however, separated from each other.
- (ii) The effect of  $\text{NO}_2$  addition is essentially to provide chemical pathways which induce a by-pass of the intermediate-temperature chemistry. The consumption of  $\text{HO}_2$  by  $R_{19}$  prevents the formation of  $\text{H}_2\text{O}_2$  by  $R_{20}$  and directly forms  $\text{OH}$  radicals without the need for the temperature to further rise for the decomposition of  $\text{H}_2\text{O}_2$  ( $R_8$ ) to become fast. Because of this additional pathway made available by the addition of  $\text{NO}_2$ , the second step of energy release is much closer to the first one than for the neat DME and the DME- $\text{O}_3$  mixtures.

## 4 Conclusion

In the present study, the effect of 1% ozone or nitrogen dioxide addition on the LTC-affected detonation propagating in DME- $\text{O}_2$ - $\text{CO}_2$  mixtures has been investigated. Ozone strengthens the LTC which induces a decrease of the induction zone length along with an increase of the energy release rate. The addition of  $\text{NO}_2$  provides chemical pathways which induce a by-pass of the intermediate-temperature chemistry and a decrease of the separation distance between the first and the second steps of energy release. An increase of the ERR is also observed for the two first peaks. Ozone appears as a promising additive to experimentally observe LTC-affected detonation with multi-stage energy release.

## References

- [1] Liang et al. (2018). *Combustion and Flame*, 193:463.
- [2] Mével et al. (2017). *Proceedings of the Asia-Pacific Conference on Combustion*, 11.
- [3] Bhagatwala et al. (2015). *Proceedings of the Combustion Institute*, 35:1157.
- [4] Zhao et al. (2016). *Combustion and Flame*. 173:187.
- [5] Mével et al. (2009). *Proceedings of the Combustion Institute*, 32:359.
- [6] Mével and Shepherd (2015). *Shock Waves*, 25:217.
- [7] Shepherd (1986). *Progress in Astronautics and Aeronautics*, 106:263.
- [8] Lutz et al. (1992). Technical report: Sand87-8248.