Effect of Hydroxyl Radical Precursors Addition on LTC-affected Detonation in DME-O_2-CO_2 Mixtures

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1 Introduction

Although it is generally accepted that detonations propagating in hydrocarbon-based mixtures are driven only by high-temperature chemistry (HTC), it was recently pointed out [1] that low-temperature chemistry (LTC) could play an important role for detonation propagating in highly CO_2-diluted mixtures. Liang et al. [1] estimated the dynamic parameters of LTC-affected detonation for n-heptane-O_2-CO_2 using various empirical and semi-empirical models. They indicated that for such mixtures, an induction zone length on the order of 10 cm is obtained, resulting in an estimated cell size of several meters. This characteristic length-scale is beyond the capability of any existing experimental facility which precludes observation of LTC-affected detonation for large alkanes such as n-heptane. It was latter shown by Mevel et al. [2] that for mixtures of dimethyl-ether (DME) highly diluted with CO_2, the induction zone length could be reduced to the order of 1 cm. However, the induction length is still too large to enable experimental observation. In order to implement a further reduction of the induction zone length and enable experimental observation or multi-dimensional numerical simulation of LTC-affected detonation, a number of additives could be evaluated.

The objective of the present work was to assess the effect of some hydroxyl radical precursors on the characteristic length-scales of LTC-affected detonation propagating in DME-O_2-CO_2 mixtures. For this purpose, Zeldovich-von Neumann-Doering (ZND) calculations have been performed for mixtures with hydrogen peroxide (H_2O_2) or tert-butyl hydroperoxide (TBHP) addition. The effect of these two additives on the energy release rate dynamics and chemical kinetics have been studied in details.

2 Modeling approach

The chemical mechanism adopted to simulate DME kinetics came from Bhagatwala et al. [3], which consists of 39 species and 175 reactions containing both low- and high-temperature chemical pathways. The chemical pathways for H_2O_2 chemistry are included in the base DME model. To account for the reactions of TBHP, the sub-mechanism from [4] was integrated to the base DME model. It includes 6 additional species and 5 reactions.

A numerical version of the ZND model implemented in Chemkin II, see Shepherd [5] for ZND model description, was employed to perform all the calculations. Given standard utilities for chemical kinetics analysis are not implemented in our ZND code, the Senkin code [6] was used 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 corresponding pressure profiles obtained from the ZND model were constrained in the Senkin calculations.

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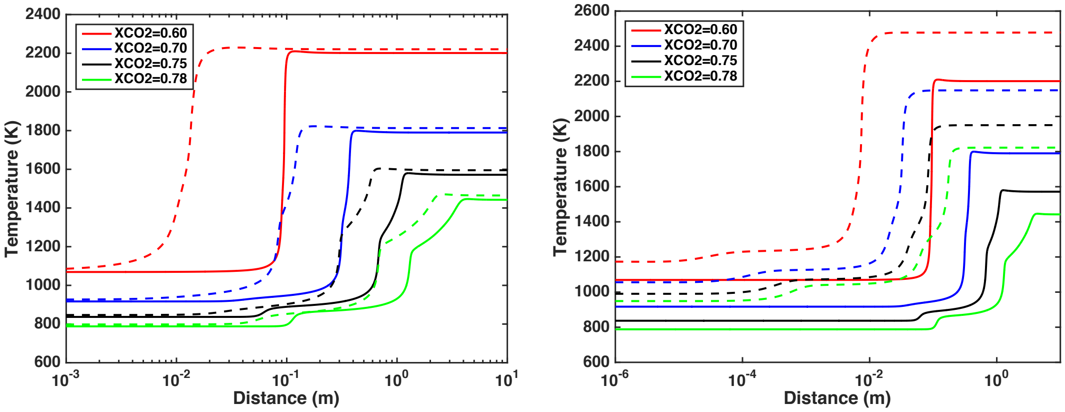
All the calculations were carried out for a lean DME-O_2 mixture with equivalence ratio of Φ=0.5, initial conditions of T_1=300 K and P_1=100 kPa, and CO_2 content ranging from 60 to 80%. These conditions were selected since they favor the occurrence of a LTC-driven multi-stage ignition process. In order to evaluate the effect of H_2O_2 and TBHP addition, 10 to 10000 ppm of CO_2 were replaced by the additive. Significant impact was observed mostly for 1% addition and consequently, only the results for such a content of additive are discussed in the present work.

3 Results and discussion

3.1 Effect of OH precursors addition on the characteristic scales

Figure 1 and Figure 2 show the effect of H_2O_2 and TBHP addition on the temperature and thermicity profiles at different dilution conditions, respectively. A further characterization of the effect of OH precursors addition as a function of CO_2 content is depicted in Figure 3. Regardless of the number of peaks present in the thermicity profile, the peak caused by the LTC is regarded as ”the first peak”, even if it is absent under some given conditions.



a) 1% H_2O_2 addition

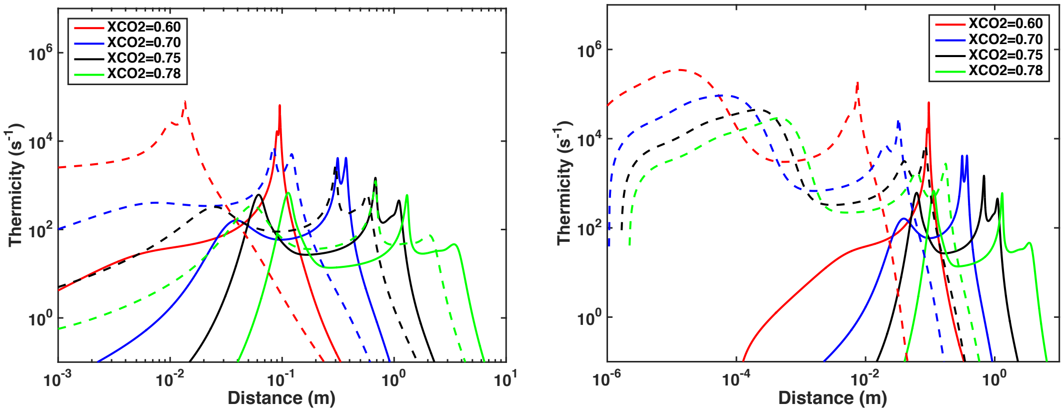
b) 1% TBHP addition

Figure 1: ZND temperature profiles of DME-O_2-CO_2 mixtures with (dashed lines) and without (solid lines) OH precursors addition. Conditions: Φ=0.5; P_1=100 kPa; T_1=300 K.

A two-step energy release is observed when the CO_2 content is below 70%, and a three-step energy release is observed when the CO_2 content is above 70% for mixtures with and without H_2O_2 addition. This tends to imply that H_2O_2 addition does not modify the main chemical pathways of the DME-O_2-CO_2 mixture. Nevertheless, the addition of H_2O_2 leads to a decrease, by 2 to 9 times, of the induction zone length for the three oxidation steps. The addition of H_2O_2 strengthen the energy release rate during the second step but induces a decrease of the two other peaks of thermicity except for the first peak at X_{CO2}=0.69-0.72. The addition of H_2O_2 extends the range of conditions for which the LTC is activated to 65%-80%.

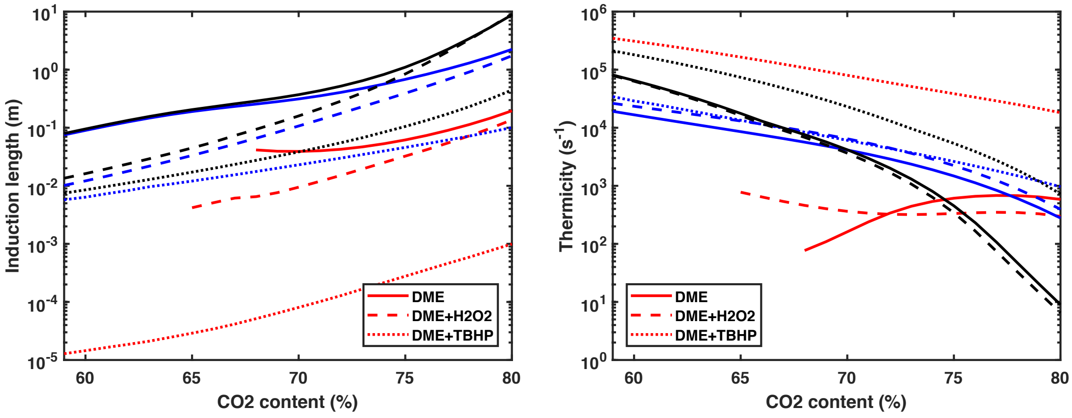
Compared to H_2O_2 addition, the addition of TBHP demonstrates a distinct impact on the temperature and energy release. Because TBHP contains more carbon and hydrogen atoms than oxygen atoms, the addition of 1% of TBHP significantly modifies the effective equivalence ratio, defined as $\Phi_{eff} = (2X_C + 0.5X_H)/X_O$ in the reactive fraction of the mixture, which increases from 0.5 for the neat mixture and 0.53 for the mixture with

H_2O_2 to 0.78 for the DME-O_2-TBHP-CO_2 mixture. At higher equivalence ratio, the detonation Mach number is higher, 4.6 against 4.0 for the neat mixture, which results in a higher von Neumann temperature as seen in Figure 1 b). For a CO_2 content below 70%, a three-step energy release is still observed for the mixtures with TBHP. This indicates that the addition of TBHP extends the range of conditions for which the LTC is activated to 59%-80%. The addition of TBHP shortens the induction zone length for the three oxidation steps. The most remarkable reduction is for the first induction length with a factor ranging between 250 and 540 depending on the CO_2 content. The decrease ranges from 15 to 30 times for the second and the third induction length. Concerning the energy release rate maximum, it is increased by 40-570, 2-4 and 3-130 times for the first, second and third steps, respectively. The increase in the peak thermicity height is higher for higher CO_2 content.



a) 1% H_2O_2 addition b) 1% TBHP addition

Figure 2: ZND thermicity profiles of DME-O_2-CO_2 mixtures with (dashed lines) and without (solid lines) OH precursors addition. Conditions: Φ=0.5; P_1=100 kPa; T_1=300 K.



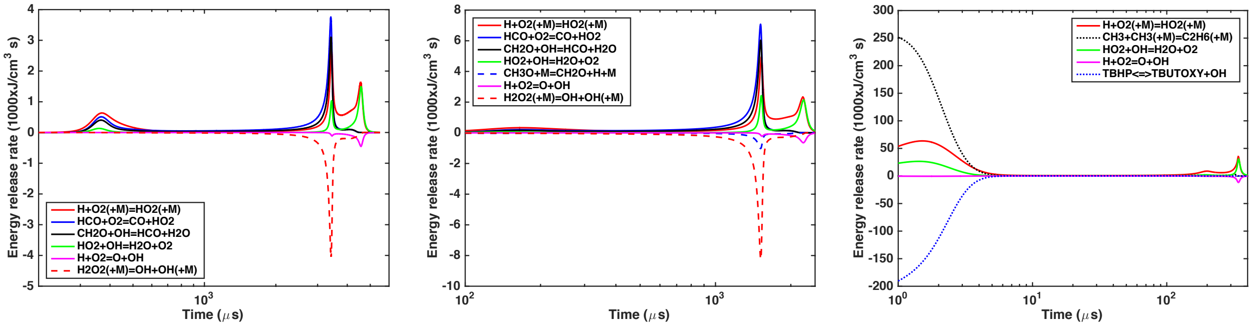
a) Induction length b) Thermicity peak

Figure 3: Effect of H_2O_2 and TBHP addition on the ZND induction zone lengths and thermicity peak heights of DME-O_2-CO_2 mixtures with and without OH precursors addition. Conditions: Φ=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.

3.2 Effect of OH precursors addition on the thermo-chemical dynamics

To perform the analysis of the thermo-chemical dynamics, the mixtures with 74-75% CO_2 dilution were chosen because they demonstrate three steps of energy release with and without OH precursors addition. Figure 4, 5, and 6 respectively display the ERR profiles, the normalized ROP of OH and HO_2, and the normalized sensitivity coefficients on temperature.

Regarding the ERR, the first and second peaks are attributed to R_1: $H+O_2(+M)=HO_2(+M)$, R_2: $HCO+O_2=CO+HO_2$, and R_3: $CH_2O+O_2=HCO+H_2O$ for the neat DME mixtures, while the third peak is attributed to only R_1 and R_4: $HO_2+OH=H_2O+O_2$. For the mixture with H_2O_2 addition, the reactions that are responsible for the three peaks remain the same but the energy release rate values decrease during the first step of ER and increase during the second step. For the mixtures with TBHP, the recombination reaction R_5: $CH_3+CH_3(+M)=C_2H_6(+M)$ overwhelmingly dominates the first step of ER and the contributions of R_2 and R_3 are suppressed during both the first and second steps. In terms of energy consumption, the H_2O_2 decomposition reaction R_6: $H_2O_2(+M)=2OH(+M)$ is the most important reaction during the second stage, and the chain branching reaction R_7: $H+O_2=OH+O$ exhibits a weak contribution during the third stage. The addition of H_2O_2 amplifies the contributions of R_6 and simultaneously brings in a new contribution of R_8:$CH_3O(+M)=CH_2O+H(+M)$ during the second stage. The addition of TBHP leads to a prominent contribution of TBHP decomposition reaction R_9: TBHP=TBUTOXY+OH during the first stage and suppresses the contribution of R_6 substantially during the second stage of ERR.

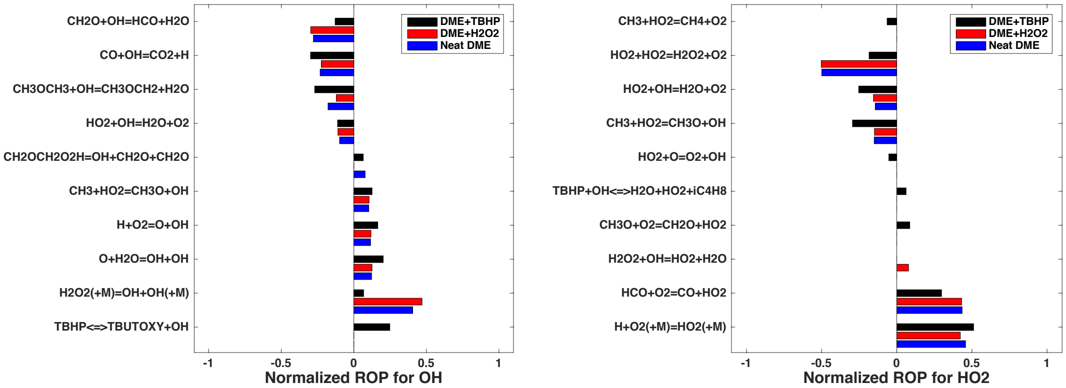


a) Neat DME b) DME+H_2O_2 c) DME+TBHP

Figure 4: Effect of 1% H_2O_2 or 1% TBHP addition on the energy release rate profile for ZND detonation propagating in DME-O_2-CO_2 mixtures. Conditions: Φ=0.5; X_{CO2}=0.74-0.75; P_1=100 kPa; T_1=300 K.

The ROP analysis of OH radical, as shown in Figure 5 a), indicates that the production is dominated by H_2O_2 decomposition (R_6) whereas the chain branching reaction R_7 has a weak contribution. The consumption of OH radicals is mainly due to the H-abstraction reactions on CH_2O (R_{10}: $CH_2O+OH=HCO+H_2O$) and DME (R_{11}: $DME+OH=CH_3OCH_2+H_2O$), and to the reaction with CO (R_{12}: $CO+OH=CO_2+H$) for neat DME mixtures. The addition of H_2O_2 enhances the contribution of H_2O_2 decomposition (R_6) to OH formation and suppresses the contribution of R_{11} to OH consumption. The addition of TBHP exerts a more significant influence on OH radical pathways. The TBHP decomposition reaction R_9 dominates the OH formation together with R_7 and R_{13}: $O+H_2O=OH+OH$, and the contribution of R_6 is weakened dramatically. The reaction R_{11} and R_{12} dominate the consumption of OH radical instead of R_{10}.

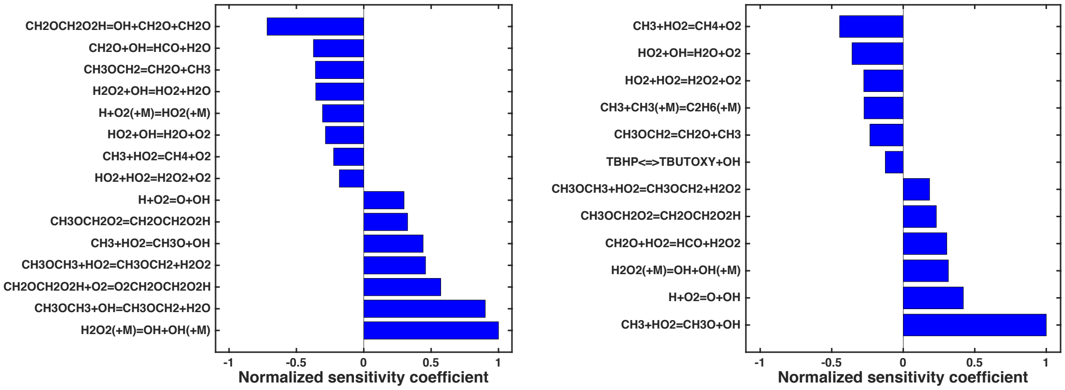
Concerning the ROP of HO_2 radical, displayed in Figure 5 b), for the neat DME mixture, the production is dominated by R_1 and R_2, and the consumption by R_{14}: $HO_2+HO_2=H_2O_2+O_2$. The addition of H_2O_2 does not modify the contribution of the main reactions to both the formation and consumption of HO_2. The addition of TBHP strengthens the contribution of R_1 and weakens that of R_2 to HO_2 formation. It also enhances the contributions of R_4 and R_{15}: $CH_3+HO_2=CH_3O+OH$ to HO_2 consumption whereas the contribution of R_{14} is significantly decreased.



a) ROP for OH

b) ROP for HO_2

Figure 5: Effect of 1% H_2O_2 or 1% TBHP addition on the OH and HO_2 ROP for ZND detonation propagating in DME-O_2-CO_2 mixtures. Conditions: Φ=0.5; X_{CO2}=0.74-0.75; P_1=100 kPa; T_1=300 K.



a) DME+H_2O_2

c) DME+TBHP

Figure 6: Effect of 1% H_2O_2 or 1% TBHP addition on the sensitivity coefficient on temperature for ZND detonation propagating in DME-O_2-CO_2 mixtures. Conditions: Φ=0.5; X_{CO2}=0.74; P_1=100 kPa; T_1=300 K.

The addition of H_2O_2 or TBHP has an important impact on the sensitivity coefficients on temperature (shown in 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_{16}: $DME+O_2=CH_3OCH_2+HO_2$ is sensitive. For mixtures with H_2O_2 addition, the sensitive reactions are those which involve HO_2 radical and DME-related compounds, such as R_{11}, R_{17}: $CH_2OCH_2O_2H+O_2=O_2CH_2OCH_2O_2H$, R_{18}: $DME+HO_2=CH_3OCH_2+H_2O_2$ and R_{19}: $CH_2OCH_2O_2H=OH+CH_2O+CH_2O$. Among these reactions, the H_2O_2 decomposition reaction (R_6) which produces OH radical and the H abstraction reaction by OH radical (R_{11}) demonstrate the highest positive sensitivity coefficient. For the mixture with TBHP addition, 8 of the 12 most sensitivity reactions correspond to reactions which involve HO_2 and CH_3 radical, such as R_4, R_5, R_{14}, R_{15}, R_{18}, R_{20}: $CH_2O+HO_2=HCO+H_2O_2$, and R_{21}: CH_3+HO_2=CH_4+O_2. Particularly, among these reactions the normalized sensitivity coefficient of R_{15}: CH_3+HO_2=CH_3O+OH is more than twice higher than the coefficient of any other reactions.

The analyses based on Figure 4 to 6 enable to draw the following conclusions:
(i) The effect of H_2O_2 addition reduces the three induction lengths by approximately a factor of 2. At the initial stage of LTC, a small amount of H_2O_2 (R_6) decomposes to two OH radicals, directly providing OH radical for the H-abstraction reaction on DME (R_{11}). The initial oxidation of DME is advanced since the reaction rate of R_{11} is much faster than that of R_{16}. In addition, the larger amount of H_2O_2 present during the intermediate-temperature stage advances both the second and the third steps. Overall, the main chemical pathways are not modified by H_2O_2 addition, except the initiation step.
(ii) The effect of TBHP addition is the most significant in reducing the first induction length by 300 times against 20 times for the other two induction lengths. With addition of TBHP, the von Neumann temperature is increased due to the modification of the effective equivalence ratio, and TBHP is more active than H_2O_2 to accelerate the LTC stage. During the LTC stage, the decomposition of TBHP provides not only OH radical but also a large amount of CH_3 radical which recombination releases a large amount of energy. In addition, the reaction between CH_3 and HO_2 (R_{15}) is strengthened which diminishes the formation of H_2O_2 from HO_2 by R_{14} and directly produces more reactive OH radicals without the need for the temperature to be high enough to trigger the decomposition of H_2O_2. Then the endothermic sequence R_8 and R_1 is also enhanced, regenerating HO_2 radical, which can further enhance R_{15} producing additional OH radical. This “LTC chain propagation loop” is responsible for the substantial decrease of the successive steps of energy release which remain, however, separated from each other.

4 Conclusion

In the present study, the effect of 1% H_2O_2 or TBHP addition on the LTC-affected detonation propagating in DME-O_2-CO_2 mixtures has been investigated. The H_2O_2 addition demonstrates an approximately ”parallel shift effect” reducing the induction zone length, as well as increasing the energy release rate. The addition of TBHP induces both a thermal and a chemical effect. Thermally, since the effective equivalence ratios of the mixtures are higher, higher Mach numbers and higher von Neumann temperatures are achieved. Chemically, there is a“LTC chain propagation loop” which leads to a significant decrease of the induction zone length along with a substantial increase of the energy release rate, especially for the first peaks. Hence, TBHP appears as a promising additive for experimentally observing LTC-affected detonation with multi-stage energy release.

References

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