Direct Detonation Initiation in Dimethyl Ether-Oxygen-Nitrogen-Carbon Dioxide Mixtures: Effect of Low-Temperature Chemistry and Ozone Addition

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1 Introduction

Detonation can be initiated through two processes: (i) deflagration to detonation transition; and (ii) direct detonation initiation. For direct detonation initiation, a point energy source is employed to generate a strong blast wave, which initially propagates at a velocity much higher than the Chapman-Jouguet velocity (D_{CJ}). Three possible outcomes can take place following the formation of the strong blast wave: (i) if the energy of the source (E_S) is higher than the critical initiation energy (E_c), the over-driven detonation relaxes to a CJ detonation; (ii) if the energy is equal to E_c, the shock front and the reaction zone first decouples as the wave velocity reaches sub-D_{CJ} values. Then, a re-initiation process is taking place and eventually leads to the formation of a CJ detonation; (iii) if the energy is below E_c, the shock velocity continuously drops until the shock becomes an acoustic wave. According to the numerical and theoretical study of Eckett et al. [1], the direct detonation initiation is controlled by the competition between chemical heat release and volumetric expansion behind a decaying shock wave. This relatively simple physical situation enables to study direct initiation using a zero-dimensional reactor with time-dependent specific volume as was previously done by several authors [3, 4]. More generally, shock-ignition in expanding flow has been studied by Vazquez-Espi and Linan [2] and Radulescu and Maxwell using a 1-step chemical model [4], and by Mevel et al. using a detailed reaction model for H_2-air mixtures [5]. Recently, Tan et al. [6] performed a comprehensive review of this phenomenon.
Despite all these studies, the effect of low-temperature chemistry (LTC) on direct detonation initiation or on shock-ignition in an expanding medium has never been studied. Therefore, the goal of our study was to investigate the effect of LTC on the direct detonation initiation for dimethyl ether-oxygen-nitrogen-carbon dioxide mixtures with and without ozone addition using a simple zero-dimensional reactor with time-dependent specific volume.

2 Modeling approach

In the absence of heat transfer, body forces, and diffusion, the governing equations of a one-dimensional, inviscid reactive flow in a fixed reference frame correspond to the Euler equations given by [1]

$$\frac{D\rho}{Dt} + \rho\frac{\partial u}{\partial r} + \frac{j\rho u}{r} = 0;\ \frac{Du}{Dt} + \frac{1}{\rho}\frac{\partial P}{\partial r} = 0;\ \frac{DP}{Dt} = c^2\frac{D\rho}{Dt} + \rho c^2\dot{\sigma};\ \frac{Dy_k}{Dt} = \Omega_k; \tag{1}$$

where D/Dt represents the Lagrangian derivative; t is the time; ρ is the density; u is the flow velocity; j=0, 1, 2 for linear, cylindrical, and spherical geometry, is the geometrical factor; r is the distance from the coordinate origin; P is the pressure; c is the speed of sound; $\dot{\sigma}$ is the thermicity; y_k is the mass

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fraction of the k^{th} species; and Ω_k is the source term of the k^{th} species. Note that in Equation 1, the energy equation has been replaced by the adiabatic change equation [1]. In the strong shock limit, the variation of the specific volume, v, behind an unsteady curved shock wave is given as

$$\underbrace{\frac{1}{v}\frac{Dv}{Dt}}_{\text{Total}} = \underbrace{\frac{2\gamma\dot{\sigma}}{\gamma+1}}_{\text{Heat release}} \underbrace{-\frac{2j}{R}\frac{\gamma-1}{(\gamma+1)^2}U_S}_{\text{Curvature}} \underbrace{-\frac{6}{\gamma+1}\frac{dU_S}{U_S dt}}_{\text{Unsteadiness}}, \tag{2}$$

where γ is the isentropic coefficient; R and U_S are the position and velocity of the shock. To describe the evolution of the specific volume along the path of a Lagrangian particle and to link this evolution to the direct detonation initiation phenomenon, the Taylor-Sedov equations were used, leading to

$$\frac{1}{v}\frac{Dv}{Dt} = \frac{2\gamma\dot{\sigma}}{\gamma+1} + \left(\frac{6}{\gamma+1}\frac{j+1}{j+3} - \frac{4j}{j+3}\frac{\gamma-1}{(\gamma+1)^2}\right)t^{-1}. \tag{3}$$

The initial thermodynamic state for the simulation with variable specific volume was taken behind a shock wave propagating at D_{CJ}. The rate of change of the specific volume was described using Equation 3 in which t was related to E_S using the velocity evolution predicted by the Taylor-Sedov relationship and the condition U_S=D_{CJ}. Taking the expansion and curvature terms constant to their initial values for a given fluid element crossing the shock was previously justified [1].

Similar to our previous studies on LTC-affected detonation in lean dimethyl ether (DME) based mixtures [7, 8], the reaction model was taken from Bhagatwala et al. [9]. It includes 39 species and 175 reactions and considers both low- and high-temperature chemical pathways. The mixtures considered were DME-O_2-N_2(-CO_2) with a stoichiometric ratio of Φ=0.5 and a diluent mole fraction of $X_{N2} + X_{CO2}$=0.7632. The mole fractions of N_2 and CO_2 were varied between 0 and 0.7632 to progressively activate and strengthen the LTC pathways at the von Neumann state. To examine the effect of LTC, the relevant pathways were deactivated by removing the reaction CH_3OCH_2+O_2=$CH_3OCH_2O_2$ from the reaction model. To study the effect of ozone addition, 1,0000 ppm of nitrogen were replaced by O_3. The chemistry of O_3 was taken from Zhao et al. [10].

3 Properties of steady detonation

Before studying the response of the ignition process of DME-O_2-N_2-CO_2(-O_3) mixtures to expansion, we examined the ZND structure of detonation propagating in these mixtures for various CO_2 contents. Figure 1 shows the temperature and thermicity profiles for selected X_{CO2}, as well as the evolution of the distances to thermicity peaks with X_{CO2}. For the results shown in the top row, LTC is activated but no ozone is added to the mixture. As N_2 is gradually replaced by CO_2, the ZND structure becomes more and more complex. For moderate CO_2 contents such as X_{CO2}=0.30, a two-step thermicity profile appears clearly. For higher CO_2 contents such as X_{CO2}=0.50, three peaks of thermicity are observed corresponding to low-, intermediate-, and high-temperature chemistry (LTC, ITC, HTC). For high CO_2 contents, $X_{CO2} \geq 0.50$; the thermicity peak induced by the ITC becomes higher than the peak induced by HTC. Removing the LTC pathways, see middle row of Figure 1, the temperature profiles appear less complex, and only two thermicity peaks, associated to the ITC and HTC, are observed. The height of the ITC thermicity peak overcomes that of the HTC peak only for a CO_2 content above 65%. The addition of O_3, see bottom row of Figure 1, strongly strengthen the LTC pathways, which results in the existence of the LTC thermicity peak even without CO_2. For a CO_2 content up to 38%, the highest thermicity peak is the one generated by HTC. Above this limit, the LTC peak becomes the highest, whereas the thermicity peak associated with ITC is never the highest, regardless of the CO_2 content.

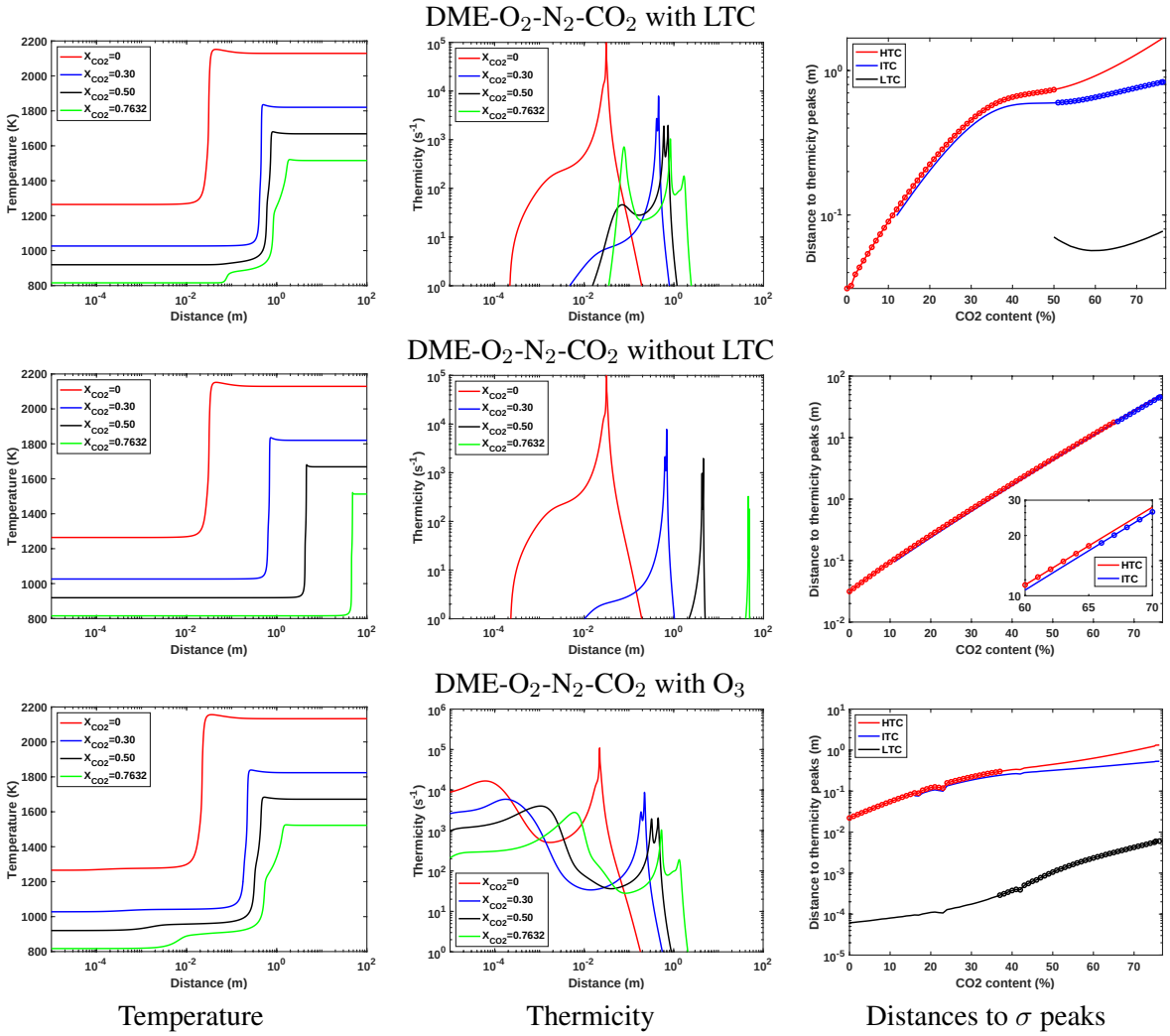
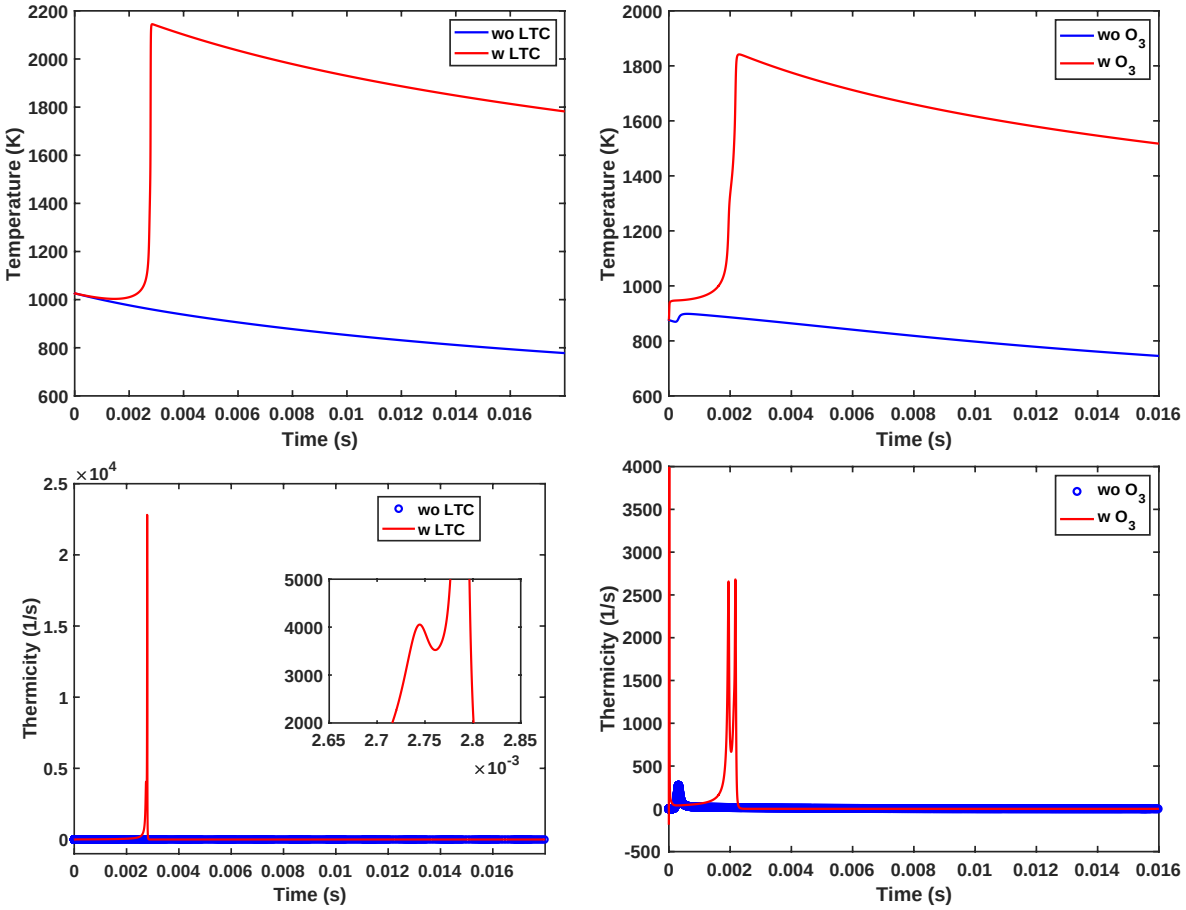


Figure 1: Left: Temperature profiles, Center: thermicity profiles, and Right: distance to thermicity peaks for ZND detonations in DME-O_2-N_2-CO_2 mixtures without O_3 (top and middle), and with O_3 (bottom). In the right figures, the symbols indicates the distance to the absolute maximum thermicity. Φ=0.5; X_{N2}; X_{CO2} ϵ [0-0.7632] with X_{N2}+X_{CO2}=0.7632; P_1=100 kPa; T_1=300 K. For mixtures with O_3, 1,000 ppm of N_2 were replaced by O_3.

4 Ignition in expanding flow

Figure 2 a) and b) show the effects of LTC and ozone addition on ignition of DME-O_2-N_2-CO_2(-O_3) mixtures undergoing volumetric expansion. As shown in Figure 2 a), for X_{CO2}=0.30 and E_S=8.00$\times 10^{11}$ J, ignition is taking place when the full reaction mechanism is employed. Consistent with the ZND structure, the thermicity profile demonstrates two peaks of thermicity, respectively associated with the ITC and HTC pathways. In contrast, quenching occurs when the reaction CH_3OCH_2+O_2=$CH_3OCH_2O_2$ is deactivated, and the thermicity profile is essentially flat, indicating that chemical activity has been dramatically slowed down by the expansion. Figure 2 b) illustrates the effect of O_3 addition for a CO_2 content of 60% and E_S=1.50$\times 10^{11}$ J. For the mixture with O_3, ignition is taking place. The temperature undergoes two main steps of increase. The first increase is taking place at a very early stage and is of 75 K. The second increase occurs around 2 ms and leads to a peak of temperature around 1800 K. Three peaks of thermicity are effectively present, indicating that LTC, ITC, and HTC all contribute to the heat

release. Consistent with the ZND profile, the highest thermicity peak is produced by the LTC, despite the moderate temperature increase. Without ozone, ignition does not occur. The temperature increases by a maximum of about 30 K, and only one peak of thermicity can be observed, with a maximum value below 300 1/s, i.e., more than 10 times lower than the LTC peak value when O_3 is added.



a) Effect of LTC b) Effect of O_3 addition

Figure 2: Temperature and thermicity profiles for DME-O_2-N_2-CO_2(-O_3) mixtures under volumetric expansion conditions. Φ=0.5; P_1=100 kPa; T_1=300 K. In a): X_{N2}=0.4632, X_{CO2}=0.3, E_S=8.00×10^{11} J. In b): X_{N2}=0.1622 or 0.1632, X_{CO2}=0.6, E_S=1.50×10^{11} J. For the mixture with O_3 addition, X_{O3}=1,000 ppm.

For carbon dioxide mole fraction within the range 0-0.7632, we have determined the minimum E_S for which the expected number of thermicity peaks in the ZND solution, i.e., one to three depending on X_{CO2}, could be observed within the computational time. This minimum E_S is referred to as critical energy (E_c) and its evolution as a function of X_{CO2} is shown in Figure 3. For the DME-O_2-N_2-CO_2 mixtures with and without LTC, the evolution of E_c seems consistent with the evolution of the distance to the maximum thermicity shown in Figure 1. Even if the LTC is activated, no pronounced negative temperature coefficient (NTC) behavior is observed and E_c essentially plateaus for X_{CO2} above 0.35-0.40. When LTC is deactivated, E_c continuously increases as the amount of CO_2 increases. As O_3 is added, the evolution of E_c closely follows the behavior of the mixture without ozone, but the curve is shifted to values 5 to 15 times lower.

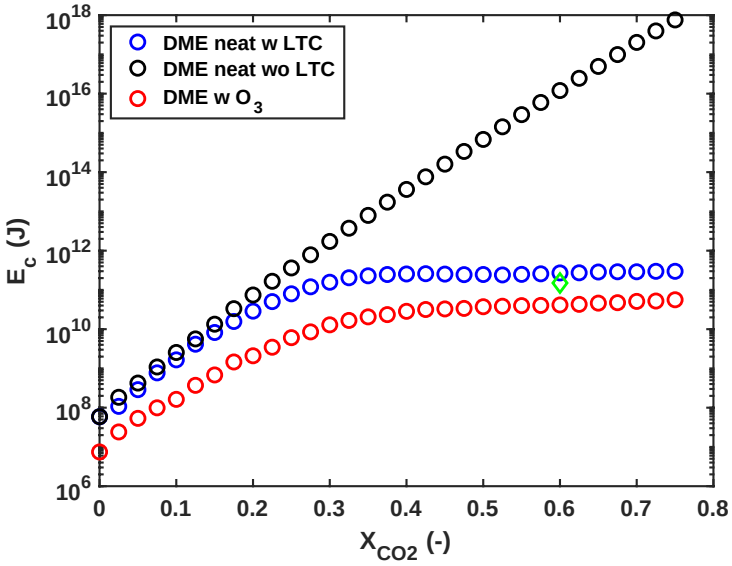
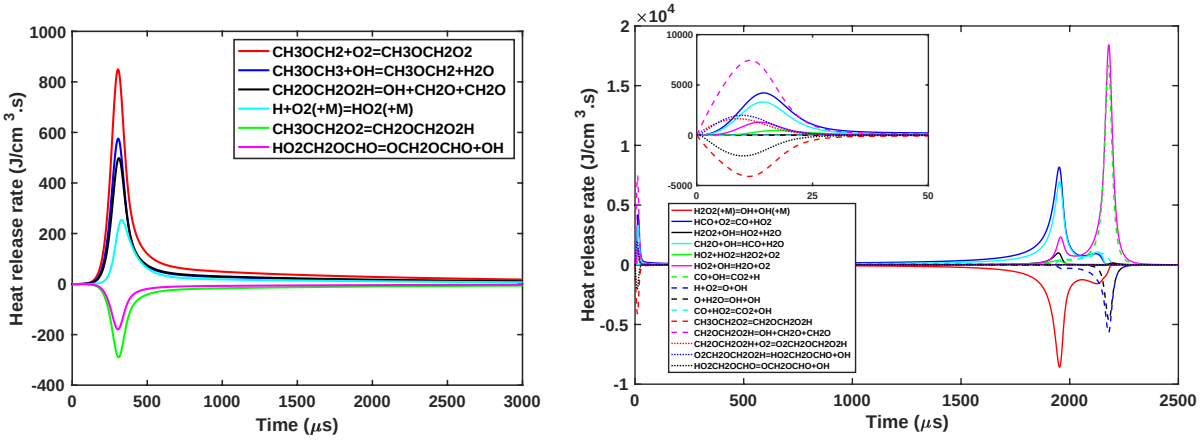


Figure 3: Critical energy for DME-O_2-N_2-CO_2(-O_3) mixtures undergoing volumetric expansion. Φ=0.5; P_1=100 kPa; T_1=300 K. X_{N2} and X_{CO2} ϵ [0-0.7632] with X_{N2}+X_{CO2}=0.7632. For mixtures with O_3 addition, X_{O3}=1,000 ppm. The green symbol indicates the reference conditions selected to perform thermo-chemical analyses. E_S=8.00×10^{11} J.

5 Thermo-chemical analyses

To gain further insight into the effect of ozone addition on E_c, we performed a number of thermo-chemical analyses. We calculated the energy release rate per reaction (ERR), and the sensitivity coefficients on temperature (C_s) for a mixture with X_{CO2}=0.60, while E_S=1.50×10^{11} J. The corresponding temperature and thermicity profiles are shown in Figure 2 b), whereas the position of the selected E_S with respect to the E_c curves obtained with and without O_3 is illustrated in Figure 3.



a) Without ozone b) With 1,000 ppm of ozone

Figure 4: Energy release rate in DME-O_2-N_2-CO_2(-O_3) mixtures undergoing volumetric expansion. Φ=0.5; P_1=100 kPa; T_1=300 K; X_{N2}=0.1622-0.1632; X_{CO2}=0.60. E_S=1.50×10^{11} J.

Figure 4 a) and b) show the ERR per reaction for mixtures without and with ozone addition, respectively. Without ozone addition, only one peak of thermicity is present. It is mainly due to LTC pathways, with

the main exothermic reactions being $CH_3OCH_2+O_2=CH_3OCH_2O_2$, $CH_3OCH_3+OH= CH_3OCH_2+H_2O$, and $CH_2OCH_2O_2H=OH+CH_2O+CH_2O$. The reaction forming HO_2 also contributes significantly to exothermicity. The heat release by these reactions is partially balanced by the endothermic isomerization of $CH_3OCH_2O_2$ into $CH_2OCH_2O_2H$ and the decomposition of HO_2CH_2OCHO into OCH_2OCHO and OH. The situation is much more complex when ozone is added, because of the presence of three distinct peaks of thermicity. The first peak is mainly due to the reactions $CH_2OCH_2O_2H= OH+CH_2O+CH_2O$, $CH_2OCH_2O_2H+O_2=O_2CH_2OCH_2O_2H$, and $O_2CH_2OCH_2O_2H=HO_2CH_2OCHO+ OH$, as well as the sequence $CH_2O+OH=HCO+H_2O$ followed by $HCO+O_2=CO+HO_2$. Two main endothermic pathways are $CH_3OCH_2O_2=CH_2OCH_2O_2H$ and $HO_2CH_2OCHO=OCH_2OCHO+OH$. After a delay of more than 1 ms, the sequence $CH_2O+OH=HCO+H_2O$, $HCO+O_2=CO+HO_2$ leads to a peak of heat release and is the main contributor to the ITC thermicity peak. During this phase, the dominant endothermic pathway corresponds to the decomposition of H_2O_2 into two OH radicals. The peak of thermicity associated to HTC is driven by two reactions involving OH: $HO_2+OH=H_2O+O_2$ and $CO+OH=CO_2+H$, while the endothermicity is due to the reactions forming these radicals: $H+O_2=O+OH$ and $O+H_2O=OH+OH$.

Figure 5 shows the C_S for ignition and quenching events, respectively obtained for mixtures with and without ozone addition, both containing 60% of CO_2. For the mixture with O_3, the two most sensitive reactions are $H_2O_2(+M)=OH+OH(+M)$ and $CH_3OCH_2=CH_2O+CH_3$, which respectively demonstrate a positive and negative C_S. Two LTC related reactions, $CH_3OCH_2O_2=CH_2OCH_2O_2H$ and $CH_2OCH_2O_2H$ $+O_2=O_2CH_2OCH_2O_2H$, exhibit strong positive coefficients. In contrast, the decomposition reaction of $CH_2OCH_2O_2H$ into OH and 2 CH_2O has an important negative coefficient. The reactions leading to the conversion of HO_2 into OH or H_2O_2, such as $CH_3+HO_2=CH_3O+OH$ and $CH_2O+HO_2=HCO+H_2O_2$, favor ignition, while the H-abstraction reactions by OH, CH_3, and HO_2 inhibit temperature increase by converting HO_2 into O_2. For the mixture without ozone, no change of sign of C_S is observed for any reactions. The main differences are: (i) the drastic decrease of the absolute values of the sensitivity coefficients for the reactions $H_2O_2(+M)=OH+OH(+M)$ and $CH_3OCH_2=CH_2O+CH_3$; and (ii) the important increase of the absolute values of the sensitivity coefficients for the reactions $CH_2OCH_2O_2H=OH+CH_2O$ $+CH_2O$ and $CH_2OCH_2O_2H+O_2=O_2CH_2OCH_2O_2H$.

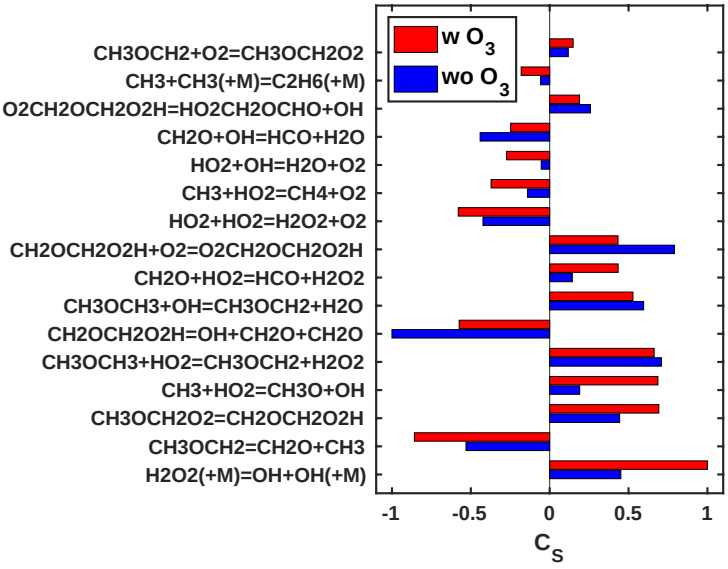


Figure 5: C_S for DME-O_2-N_2-CO_2(-O_3) mixtures undergoing volumetric expansion. Φ=0.5; P_1=100 kPa; T_1=300 K; X_{N2}=0.1622-0.1632 and X_{CO2}=0.60. X_{O3}=0 or 1,000 ppm. E_S=1.50×10^{11} J.

6 Conclusion

The effects of LTC and O_3 addition on the ignition of DME-O_2-N_2-CO_2 mixtures subjected to volumetric expansion has been studied through the determination of E_c and thermo-chemical analyses. The heat release due to LTC reactions promotes ignition and leads to a plateauing of the critical initiation energy for a CO_2 content above 30%. Deactivating the LTC pathways results in a dramatically higher E_c, which continuously increases with X_{CO2}. The O_3 addition strengthens the heat release due to LTC reactions, which decreases E_c by 5 to 15 times, while maintaining the plateauing feature.

References

[1] Eckett CA, Quirk JJ, Shepherd JE (2000). The role of unsteadiness in direct initiation of gaseous detonations. J. Fluid Mech. 421:147.

[2] Vazquez-Espi C, Linan A (2001). Fast, non-diffusive ignition of a gaseous reacting mixture subject to a point energy source. Combust. Theory Model. 5:485.

[3] He Y, Liu Y, Mevel R (2020). Effect of volumetric expansion on shock-induced ignition of H_2-NO_2/N_2O_4 mixtures. Combust. Flame 215:425.

[4] Radulescu M, Maxwell B (2010). Critical ignition in rapidly expanding self-similar flows. Phys. Fluids 22:066101.

[5] Mevel R, Melguizo-Gavilanes J, Davidenko D (2019). Ignition of hydrogen-air mixtures under volumetric expansion. Proc. Comb. Inst. 37:3503.

[6] Tan Y, Mével R, Liu Y (2023). A review on ignition in expanding gaseous media. Process. Saf. Environ. Prot. 179:241.

[7] Mevel R, He Y (2020). Effect of oxygen atom precursors addition on LTC-affected detonation in DME-O_2-CO_2 mixtures. Shock Waves 30:799.

[8] He Y, Mevel R (2020). Effect of hydroxyl radical precursors addition on LTC-affected detonation in DME-O_2-CO_2 mixtures. Shock Waves 30:789.

[9] Bhagatwala A., Luo Z., Shen H., Sutton J.A., Lu T., Chen J.H. (2015). Numerical and experimental investigation of turbulent DME jet flames. Proc. Combust. Inst. 35:1157.

[10] Zhao H, Yang X, Ju Y (2016). inetic studies of ozone assisted low temperature oxidation of dimethyl ether in a flow reactor using molecular-beam mass spectrometry. Combust. Flame 173:187.