

Low Temperature Autoignition of Dimethylether

K. HadjAli, G. Vanhove, M. Ribaucour, V. Carré, R. Minetti

Physico-Chimie des Processus de Combustion et de l'Atmosphère, UMR CNRS 8522
Université des Sciences et Technologies de Lille, Bâtiment C11, 59655 Villeneuve d'Ascq, Cedex, France

1 Context

Early interest in the use of dimethylether (DME) for homogeneous charge compression ignition (HCCI) engines in lean operation with stable autoignition and combustion have emphasised that the engine operating region is narrowly limited due to knocking or misfire. Chemical reactions govern the autoignition and the process is complicated by the low-temperature oxidation taking place in the first stage of ignition. The resulting cool flame only produces a small fraction of the total heat release but change the temperature and composition of the compressed gas mixture, greatly affecting the final ignition timing. Many fundamentals studies have been devoted to the low-temperature oxidation and autoignition of hydrocarbons but much less to ethers. However, autoignition delay times of DME have been measured by the shock tube technique, showing a complex behaviour [1,2]. The understanding of the behaviour of DME would be much easier with the help of a realistic thermokinetic mechanism. Many mechanisms of the oxidation and autoignition of DME have already been published but their validity should be compared in the conditions of the rapid compression machine. Those are close to the conditions of HCCI autoignition. The present study is focused on the autoignition delay times of the cool flame, the final ignition, and the intermediate oxidation species in the of low-temperature regime. The rapid compression machine at Lille was used for stoichiometric and lean conditions at different initial charges to fully examine the phenomenology of low-temperature autoignition. The stable intermediate species were identified and their evolutions were followed in the relatively steady state of the gas mixture between the cool flame delay time and the final ignition delay time. An extensive experimental database of low-temperature autoignition of DME has been built and the ability of existing models to reproduce the recorded observations examined.

2 Results

Dimethylether/"air" mixtures showed a very high reactivity under rapid compression. Even at the lowest initial charge suitable to the rapid compression machine ($P_0 = 0.13$ bar) autoignition delay times of DME were shorter than the delay times of the primary reference fuel n-heptane. Between $T_1 = 600$ and 700 K, the autoignition occurred in two stages with a nearly steady-state pressure "plateau" after top dead centre and after the cool flame. The limit under which autoignition by compression did not take place was $T_1 = 610$ K at $P_1 = 1.73$ bar. Figure 1 shows the dependence of the cool flame and total delay times on the core gas temperature T_1 and pressure P_0 . The cool flame ignition times were relatively insensitive to the gas pressure and the total ignition delay times had a marked negative temperature dependence between $T_1 = 670$ and 700 K. Above $T_1 = 700$ K, the first stage of ignition occurred always during the last three seconds of the compression stroke.

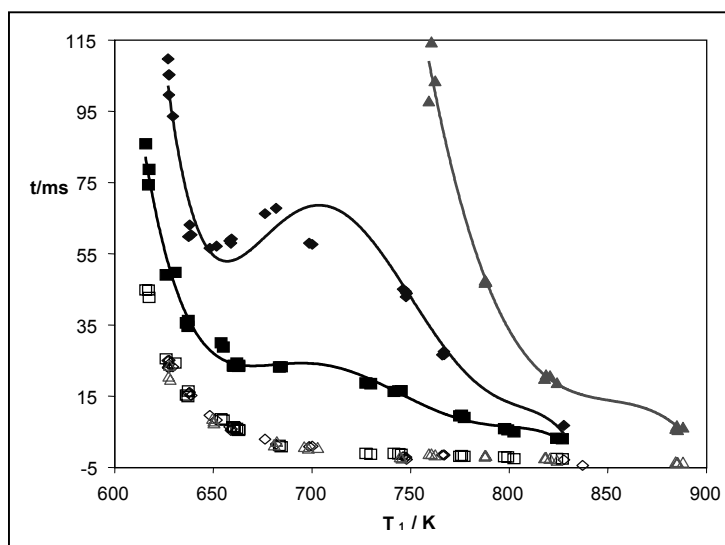


Fig. 1. Total (black symbols) and cool flame (open symbols) delay times of stoichiometric DME/ "air" mixtures. $P_0 = 0.26$ bar (triangles), $P_0 = 0.34$ bar (diamonds), $P_0 = 0.47$ bar (squares). The pressure at top dead centre P_1 varied between 3.59 and 8.67 bar, according to the initial pressure and composition of the inert gas.

All attempts to prevent an early cool flame event by changing dilution, or equivalence ratio, or initial pressure, failed. No attempt was made to prevent an early cool flame by changing the compression time because previous studies have shown that the rate of compression has no visible influence on the onset of the cool flame. Therefore the adiabatic core gas temperatures above $T_1 = 700$ K are overestimated by ca. 10 K and the autoignition delay times underestimated by a few milliseconds.

Leaner mixtures have a higher autoignition limit: $T_1 = 620$ K at $P_1 = 3.57$ bar and $\Phi = 0.5$. Higher total pressures up to $P_1 = 8.27$ bar were reached when oxygen was diluted to $\alpha = 0.85$ instead of 0.76 as in air and the negative temperature coefficient was less perceptible. Formaldehyde, methylformate, methane, carbon monoxide, water, carbon dioxide, and traces of methanol were detected and determined by the chemical analyses of the reacting gas mixture between the cool flame event and the final ignition.

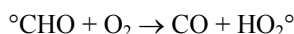
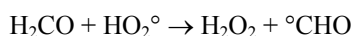
3 Discussion

A comparison of the reactivities of structurally related fuels clearly shows that dimethylether, a potential substitution biofuel, is more reactive than any other related structure. It was recognised early that ethers have a high reactivity with oxygen and a strong tendency to built hydroperoxides. Nor the ether function, nor the molecular structure can account alone for such a high reactivity.

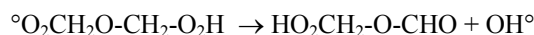
The phenomenology of autoignition of DME/"air" mixtures in the rapid compression machine presents the same general features as the phenomenology of the long chain alkanes. Autoignition of alkanes also occurs in a two-stage process with a cool flame and a negative temperature dependence of the ignition delay times between 600 and 750 K. In a typical two-stage autoignition of alkanes by rapid compression, the pressure remains relatively constant between the end of compression and the cool flame explosion and between the cool flame

explosion and the final ignition. The same general phenomenology was observed for DME/"air" mixtures. It is generally believed that the system remains nearly isothermal during the two pressure "plateaus" and that a delicate balance between the sources and sinks of the chain carriers control the overall reaction rate. The delayed chain branching processes increase the chain carrier pool via the thermal decomposition of branching agents, whereas the termination processes between radicals decrease the chain carrier pool. The branching agents are supposed to be various compounds containing a O-O bond weakened by the repulsion of non bonding electrons. Thermal dissociation of the weak bond generates radical chain carriers. It is believed that the ketohydroperoxides are the branching agents responsible for the cool flame explosion of alkanes and hydrogen peroxide the branching agent for the final explosion.

The pathways generally admitted for the low-temperature oxidation of alkanes can be applied to DME with caution. The set of low-temperature reactions is certainly restricted, as the molecule DME possesses one type of C-H bond only. This is a distinctive feature common to neo-pentane, which also has an early cool flame ignition [3]. The initiation reactions occur through H-transfers to O₂ followed by oxygen addition. Isomerization of the resulting methoxymethylperoxyl RO₂[°] has been considered theoretically. The species corresponding to QO in the oxidation of alkane should be dioxetane, but it has not been detected. The first intermediate species detected after the cool flame were formaldehyde and methylformate. Formaldehyde can be formed by the decomposition of the hypothetical dioxetane or by a direct reaction between the methoxymethyl radical (CH₃-O-CH₂[°]) and molecular oxygen. DME has another distinctive feature common to neo-pentane: there cannot be competition between (1) R[°] + O₂ → RO₂[°] → branching and (2) R[°] + O₂ → alkene + HO₂[°] because the second reaction is impossible. Hydrogen abstraction from methoxymethyl radical by oxygen would lead to oxirane. This compound or its isomer acetaldehyde has not been detected in spite of their known stability. The building up of hydrogen peroxide must follow another channel. For example, H₂O₂ can be formed from formaldehyde by a chain process carried by HO₂[°] and [°]CHO:



Another important difference with the accepted hydrocarbon oxidation scheme is the nature of the first branching agent. Applied to DME, the double peroxidation scheme of alkanes leads to hydroperoxymethylformate instead of ketohydroperoxides. This is a well-characterised compound called HPMF, but its kinetic properties are not well known. However, it can be surmised that its formation is fast because it occurs through the internal hydrogen transfer of hydrogen bound to a carbon bearing two oxygens:



Another low-temperature branching agent could well be the methoxymethylhydroperoxide detected by [4].

4 Modelling

At least eight detailed mechanisms have been published for the oxidation of DME. Mechanisms [5] and [6] were tested against experimental values in a the large range 550 - 1300 K and 1 - 40 bar. Mechanism [5] has 80 species in 351 reactions and mechanism [6] 53 species in 289 reactions. Mechanism [5] uses HPMF as a low-temperature degenerate branching agent for the first stage and mechanism [6] uses HPMF and methoxymethylperoxide. Two versions of mechanism [6] have been developed, one at P = 1 bar and one at P = 10 bar. The models have been improved either by a better evaluation of some key rate coefficient and/or by adding new reactions important in the negative temperature coefficient region.

References

- [1] Dagaut P. Daly C. Simmie JM. Cathonnet M. (1998). Proceed. Combust. Instit. 27:361
- [2] Pfahl U. Fieweger K. Adomeit G. (1996). Proceed. Combust. Instit. 26:781
- [3] Ribaucour M. et al. (2000). Proceed. Combust. Instit. 28 :1701
- [4] Sehested J. et al. (1996). J. Phys. Chem. 100:17218
- [5] Curran HJ. Fischer SL. Dryer FL. (2000). Int. J. Chem. Kin. 32:741
- [6] Dagaut P. Luche J. Cathonnet M. (2001). Comb. Sci. Technol. 165:61