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Experimental and modeling studies of $C_2H_4/O_2/Ar$, C_2H_4/methylal/O_2/Ar and C_2H_4/ethylal/O_2/Ar rich flames and the effect of oxygenated additives

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ABSTRACT

The addition of dimethoxymethane (DMM or methylal) and diethoxymethane (DEM or ethylal) to a rich ethylene/oxygen/argon flame has been investigated by measuring the depletion of soot precursors. Three rich premixed ethylene/oxygen/argon (with and without added methylal or ethylal) flat flames have been stabilized at low-pressure (50 mbar) on a Spalding–Botha type burner with the same equivalence ratio of 2.50. Identification and monitoring of signal intensity profiles of species within the flames have been carried out by using molecular beam mass spectrometry (M.B.M.S.). The replacement of some C_2H_4 by $C_3H_8O_2$ or $C_5H_{12}O_2$ is responsible for a decrease of the maximum mole fractions of the detected intermediate species. This phenomenon is noticeable for C_2–C_4 intermediates and becomes more effective for C_5–C_{10} species, mainly when $C_3H_8O_2$ added.

A new kinetic model has been elaborated and contains 546 reactions and 107 chemical species in order to simulate the three investigated flames: $C_2H_4/O_2/Ar$, $C_2H_4/DMM/O_2/Ar$ and $C_2H_4/DEM/O_2/Ar$. The reaction mechanism well reproduces experimental mole fraction profiles of major and intermediate species, and underlines the effect of methylal and ethylal addition on species concentration profiles for these flames.

1. Introduction

The effect of dimethoxymethane on soot emissions (DMM or methylal) has been mainly investigated in diesel engines. In those cases, it has been shown that the presence of such species reduces soot and the particulate matter formation. In a Caterpillar diesel engine, 20% methylal blend in diesel fuel showed a reduction of smoke opacity by about 50% at start up and high idle [1,2]. In the study of Sirman et al. [3], 15% methylal blend in ultra-low sulfur diesel was tested in a Daimler-Benz turbo-diesel engine. It emitted 52% lower particulate matter and 4% lower nitrogen oxides compared to a conventional diesel fuel. Vertin et al. [4] have demonstrated a substantial reduction of particulate matter emissions for 10–30% blends of methylal in diesel fuel. And, Cheng et al. [5] showed that the presence of methylal in diesel has reduced the total particle mass concentrations, as well as the particle number density and the mean particle diameter. Gerber et al. [6], studying diffusion flames, have shown a reduction of soot volume fractions when methylal is added to acetylene and ethylene flames. Using laser-induced incandescence, they showed that soot volume fraction increase with an admixture of up to 10–15% of methylal but fall more than proportional for higher percentages.

There are relatively little studies on the methylal kinetics reported in the literature. Molera et al. [7–9] investigated at moderate temperatures (491–685 K) gas-phase oxidation of methylal by molecular oxygen. They suggested a direct attack of DMM by O_2 at low temperatures but another process, which could be a decomposition one, becomes important at higher temperatures. Moreover, they concluded that hydroperoxides and peroxy radicals are produced at low temperatures. Fernandez Sanchez et al. [10] studying hydrogen abstraction reactions by methyl radicals forming $CH_3OCHOCH_3$ or $CH_2OCH_2OCH_3$ radicals, between a temperature range of 371 K and 573 K, suggested several decomposition pathways according to their molecular structure. Wallington et al. [11], Porter et al. [12] and Vovelle et al. [13] measured the overall rate coefficient of the reaction of hydroxyl radicals with methylal at room temperature, 3.2×10^{12}, 2.8×10^{12} and $2.6 \times 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$, respectively. In a comparative study, Porter et al. [12] showed that ethers and diethers with large molecular mass generally react faster than methylal. In 2001, Daly et al. [14] studied the oxidation of methylal in a jet-stirred reactor at 5.07 bar, from 800 K to 1200 K and for equivalence ratios varying from 0.44 to 1.78. A detailed kinetic model has been established and compared to experimental results. Recently, the kinetics of

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DMM has been investigated in order to understand soot precursors depletion, in a rich premixed ethylene flame doped with DMM [15,16] and also in neat DMM flames [17]. The experimental observations corroborate the impact of methylal blended diesel fuels on soot particulates abatement. The addition of DMM to a rich ethylene/oxygen/argon flame, keeping the equivalence ratio constant ($\phi = 2.50$), leads to lower concentrations of soot precursors. The lowering is already noticeable for C_2–C_4 intermediates (−10% to −30%), and more important for C_5–C_{10} species (−30% to −50%). A kinetic model was built in order to simulate ethylene flames with and without methylal addition [16]. The reaction mechanism provides more information on the chemical role played by methylal to deplete soot precursors.

Another diether, ethylal, has been tested in this research. Again, few informations are available about ethylal in the literature. In 1977, Molera et al. [18] have studied the slow gas-phase oxidation of ethylal with C-14 as a tracer at low temperatures by a static method. This work allowed to analyze products and to suggest a mechanism of ethylal oxidation. Porter et al. [12], Thüner et al. [19] and Vovelle et al. [13] have studied the reaction rate of OH + DEM at 298 K for the first two authors and between 293 and 617 K for the third one, respectively. In 1997, Herzler et al. [20] studied the decomposition of ethoxy compounds (tetraethyl orthocarbonate, diethyl carbonate and diethoxymethane) in a single-pulse shock tube experiments. For one DEM molecule destroyed, approximately 1.2 molecules of ethylene and 0.5 molecule of ethanol were produced. The ethylene and ethanol account for about 85% of the available ethoxy groups. Significant amounts of methane and ethane were also found and account for much of the missing mass. Three rate constants of ethylal decomposition are proposed by authors: $k(\mathrm{DEM} \rightarrow \mathrm{products}) = 10^{15.93\pm0.15} \exp(-36{,}179 \pm 403K/T)\ \mathrm{s}^{-1}$; $k(\mathrm{DEM} \rightarrow C_2H_4 + C_2H_5OCH_2OH) = 10^{15.07\pm0.45} \exp(-34{,}517 \pm 1090K/T)\ \mathrm{s}^{-1}$ and $k(\mathrm{DEM} \rightarrow C_2H_5 + OCH_2OC_2H_5) = 10^{16.32\pm0.45} \exp(-38{,}214 \pm 1160K/T)\ \mathrm{s}^{-1}$. Tajima et al. [21] investigated the decomposition of ethylal upon electro-impact by means of mass-analyzed ion kinetic energy spectrometry (MIKE). They obtained detailed spectra of ethylal fragmentation and of the formed ions. Recently, Zeng et al. [22] tested four diethers (1,2-dimethoxyethane, 2,2-dimethoxypropane, diethoxymethane and 1,1-diethoxyethane) for the production of biodiesel from vegetable oil and methanol by transesterification process. They investigated the optimal transesterification conditions: effect of diether type as co-solvent, molar ratio of diether in methanol/oil, the catalyst concentration and the reaction temperature to improve biodiesel production.

The first objective of this work is to compare the influence of methylal to that of ethylal addition on the structure of a slightly sooting premixed rich ethylene–oxygen–argon flame burning at 50 mbar and keeping constant the equivalence ratio ($\phi = 2.50$). The second is to elaborate a kinetic model which can be validated by comparison with the experimental structure of these three flames: $C_2H_4/O_2/Ar$, $C_2H_4/DMM/O_2/Ar$ and $C_2H_4/DEM/O_2/Ar$.

2. Experimental setup

Three rich flat premixed ethylene–oxygen–argon flames (with and without methylal or ethylal added), have been stabilized on a Spalding–Botha type burner. The setup consists of a combustion chamber where a flat flame is stabilized at low-pressure (50 mbar) on a movable flat burner of 8 cm in diameter. Facing the burner surface, a conical quartz probe with a 45° angle within 2 cm and with a small hole of 0.1 mm at the top allows the sampling in the flame. Behind this probe, three differentially pumped chambers leads to the formation of a molecular beam that is directed towards the electronic ionization source of a quadrupole mass spectrometer (Balzers QMG 511). The axis of the mass spectrometer is perpendicular to the molecular beam one. Such an arrangement allows the initial composition of the sampling to be "frozen" at the point where the mass spectrometer is reached and therefore reactive species can be detected and monitored. Moreover, the molecular beam is chopped at 30 Hz, allowing a phase detection of the signal coming from the electron multiplier which strongly enhances the signal-to-noise ratio. The experimental setup has been described elsewhere [23].

Table 1
Flames inlet compositions.

Flame	X C_2H_4	X O_2	X Ar	X C3H8O2	X $C_5H_{12}O_2$	φ	C/O
F2.50	0.330	0.400	0.270	–	–	2.50	0.83
F2.50E	0.272	0.400	0.303	–	0.025	2.50	0.79
F2.50M	0.273	0.400	0.284	0.043	–	2.50	0.76

With φ: equivalence ratio and C/O: Carbon/Oxygen rate.

For the three investigated flames, the initial flow velocity is 40.3 cm/s at 298 K and the total mass flux is 6.0 L/min. Initial molecular oxygen concentrations were kept constant and mole fractions of fuels (ethylene, methylal and ethylal) were adjusted to keep the equivalence ratio equals to 2.50 (Table 1). Taking into account the following reactions of complete combustion of C_2H_4, $C_3H_8O_2$ and $C_5H_{12}O_2$, an addition of α $C_3H_8O_2$ must be compensated by the suppression of 1.33α of C_2H_4 and an addition of β $C_5H_{12}O_2$ must be compensated by the suppression of 2.33β of C_2H_4:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{1}$$

$$C_3H_8O_2 + 4O_2 \rightarrow 3CO_2 + 4H_2O \tag{2}$$

$$C_5H_{12}O_2 + 7O_2 \rightarrow 5CO_2 + 6H_2O \tag{3}$$

Methylal (99.79% DMM, 0.203% water) and ethylal (99.85% DEM, 100 ppm butylated hydroxytoluene (BHT)) from Lambiotte and Cie are colorless liquids at 1 bar and room temperature (boiling point: 42 °C and 88 °C, respectively). They are vaporized at reduced pressure (172 mm Hg and 116 mm Hg), at 20 °C and 55 °C respectively, through a calibrated capillary to ensure a constant flow rate.

Identification and monitoring of signal intensity profiles of stable, atomic and radical species within the flames have been carried out by using molecular beam mass spectrometry (M.B.M.S). For every species, contributions either from fragmentation during the electron impact, or from overlapping of species with same mass have been kept low or taken into account. Conversion of signal intensities to mole fractions has been performed by using a calibrated mixture for stable compounds and by estimating ionization cross-sections for carbon-containing radicals and C_5–C_{10} species. Such estimation has been made by adding the individual ionization cross-sections of the constituting atoms ($Q_C = 1.8$, $Q_O = 1.3$, $Q_H = 0.65$). This method takes into account ionization potential of the chemical species and is reliable with experimental errors of the order of 10–20%.

Mole fraction profiles of the following species have been monitored in all investigated flames: H_2, CH_3 (methyl radical), CH_4 (methane), H_2O, C_2H_2 (acetylene), C_2H_4 (ethylene), CO (carbon monoxide), O_2, C_3H_3 (propargyl radical), C_3H_4 (allene + propyne), Ar, C_3H_5 (propenyl radical), C_3H_6 (propene), CO_2 (carbon dioxide), C_4H_2 (diacetylene), C_4H_4 (vinylacetylene), C_4H_6 (butadiene), C_4H_8 (butene), C_5H_6 (cyclopentadiene), C_6H_2 (triacetylene), C_6H_4 (benzyne + hexa 1,5-diyne 3-ene), C_6H_6 (benzene), C_7H_8 (toluene), C_6H_6O (phenol), C_8H_6 (phenylacetylene), C_8H_8 (styrene), C_9H_8 (indene), $C_{10}H_8$ (naphthalene).

Profiles of some supplementary oxygenated species have been recorded in flames with the additives (F2.50M and F2.50E):