Flame structure of dimethyl ether/O₂/Ar mixture at 1 atm

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Abstract. For diesel engines, dimethyl ether (DME) is widely used in the world, it is a perspective candidate to replace traditional diesel in the future. The consumption of DME as a motor fuel is constantly increasing. DME has a very low propensity to soot formation during combustion, which allows not only to reduce harmful emissions into the atmosphere, but also to improve the completeness of combustion. To validate available chemical kinetic models for DME combustion, in this work we report our experimental data on the chemical structure of a laminar premixed stoichiometric DME/O₂/Ar flame stabilized at 1 atm on a flat burner. Flame sampling molecular beam-mass spectrometry is used to obtain spatial distribution of mole fractions of many species in the flame. The experimental data are compared with the calculation results obtained using PREMIX code and two detailed chemical kinetic mechanisms available from literature for DME combustion.

1. Introduction

Dimethyl ether (DME: CH₃-O-CH₃) is a promising alternative for replacing conventional diesel fuel for most compression-ignition engines. DME has a high cetane number (55-60), during combustion it produces a much smaller amount of soot, polyaromatic compounds and other pollutants than as compared to traditional diesel fuel. Although dimethyl ether has lower energy value than diesel fuel (the lower heat of combustion of DME is 28.9 MJ / kg, and the traditional diesel fuel has 42.5 MJ/kg), lower viscosity and lubricity, it has lower boiling and ignition temperature (−25 °C and 235 °C, respectively), which makes this fuel very useful especially for the Arctic region.

The combustion of DME was investigated quite extensively. Processes of self-ignition of DME were investigated [2,3, 5-14] and chemical kinetic mechanisms for its oxidation were developed [3,5-6]. Low-temperature oxidation of DME was investigated in [11-13]. Measurement and numerical simulation of the chemical structure of flames stabilized on a flat burner represents one of the most effective approaches for studying high-temperature oxidation of DME and for developing detailed chemical kinetic mechanisms. Cool et al [3] measured the structure of fuel-rich DME flames at a pressure of ~20 torr. Mole fractions of 21 compounds, including H and O atoms, OH and CH₃ radicals, C₂-hydrocarbons, methanol, acetaldehyde, and ketene were measured. The measurement results of the mole fractions of the main components and some stable components (H₂, H₂CO, CH₄, C₂H₂,) and radicals (OH, CH₃) for fuel-lean and fuel-rich flames at a pressure of 30 torr are presented elsewhere [2]. Kaiser et al [4] carried out experiments for fuel-lean and fuel-rich flames at atmospheric pressure, they measured the mole fractions of stable components, such as formic acid, formaldehyde, propane. Kaiser et al. [4] used a microprobe for the flame sampling and analyzed the sample by gas...
chromatography and/or FTIR spectroscopy, whereas molecular beam-beam mass spectrometry (MBMS) was used in [1-3].

Despite the efforts undertaken to study the structure of DME flames, the reliable experimental data on the structure of DME flames at atmospheric pressure are needed for community to deeper understand the combustion chemistry of DME. In this work we report our new experimental data on the chemical structure of the DME-fuelled flame at atmospheric pressure. Our goal is to validate the detailed chemical kinetic mechanisms for DME oxidation available in the literature and to provide recommendations on improving the mechanisms.

2. Experimental and Modeling details
The flame of a stoichiometric DME/O2/Ar (0.0648/0.1852/0.75 in mole basis) mixture stabilized at 1 atm on a flat burner was studied in this work. The burner with a perforated matrix 16 mm in diameter was used in the experiments. Its temperature was kept at 368 K by thermostated water. The burner design was described in our previous works, see, e.g., [19]. The gases were supplied into the burner using mass flow controllers produced by MKS Instruments. The total velocity of the fresh mixture at the burner exit was 12.4 cm/s (at room temperature).

Flame sampling molecular beam mass spectrometric setup with soft ionization by electron impact was used to measure spatial variations of intensities of mass peaks corresponding to various flame species. The MBMS setup has been described in detail in our previous works, see, e.g., [19]. A quartz sampling probe with the opening angle of 40° and the orifice of 50 μm was used in the experiments.

The ionization energies were set individually for each species measured. They were selected according to the following rules. For a particular species, it must be, on the one hand, higher than the ionization energy of the species and, on the other hand, not too high to prevent the contribution to the measured mass peak of the fragment ions from other compounds. The mass peak signal intensities were converted to mole fractions using a procedure described earlier [19, 22]. The following methods of calibration were used: direct calibration (methane, acetylene, ethylene, ethane, O2, argon, propane, H2O2, DME), a method based on solution of O-, C-, and H-balance equations (H2, CO, CO2, H2O), and the relative ionization cross-section (RICS) method (H, CH3, OH, formaldehyde, HO2). The RICS-method is described in details in [22]. The uncertainties in determining the mole fractions were as follows: ±15% for DME, O2, CO2, H2, H2O; ±20% for species calibrated directly, like C2H2, C2H4, CO, H2, and for other species the mole fractions were determined to within a factor of about 2. The temperature profile in the flame was measured using a Pt-Pt + 10%Rh thermocouple made of wire 20 μm in diameter. During the measurements, the junction of the thermocouple was located at 0.2 mm from the tip of the sampling probe.

Numerical simulations of the DME/O2/Ar flame were also carried out. The PREMIX program from the CHEMKIN package [15] was used. The calculations were performed with the measured temperature profiles as input data using the TGIV keyword. The numerical simulations were performed using two detailed kinetic mechanism: Wang et al [20] (56 species, 301 reactions) and Tran et al [21] (378 species, 2385 reactions). Furthermore, the kinetic analysis was carried out based on the Wang et al mechanism.

![Figure 1](image-url). Temperature profile and mole fraction profiles of the main species. Symbols are experimental data, lines are simulation results. Solid lines: Wang et al model [20]; dashed lines: Tran model [21].
3. Results and Discussion

Figure 1 shows mole fraction profiles of the main species (DME, O2, H2O, CO2, CO) and temperature profile in the flame. As is seen, numerical results obtained using both mechanisms are in good agreement with the experimental data. Each mechanism predicts the profiles of the mole fractions of these species quite accurately.

Figure 2 shows the profiles of the mole fractions of some intermediates (H2, CH2O, CH4, C2H2, C2H4, C2H6, CH2CO, C3H8). There is a good agreement between the measured and calculated mole fractions of H2 and CH4. Formaldehyde mole fraction profile is also predicted quite satisfactorily.

All the mechanisms used in the calculations predict very similarly the mole fractions of the stable intermediates of DME combustion mentioned above. Although, the data on ethane indicate an unsatisfactory agreement between the results of modeling and experiment. As shown by our experiments, the products of incomplete combustion of DME are compounds containing 3 carbon atoms, in particular propane. The kinetic mechanism of Wang et al does not include C3 hydrocarbons, therefore in Figure 2 comparison of our measurement data for propane with the calculations using only Tran et al model [21] are shown.

Figure 3 shows the mole fraction profiles of major flame radicals and hydrogen peroxide. Both the mechanisms predict practically the same distribution of concentrations of these radicals. The mole fraction of peroxy species (HO2 and H2O2) is much lower than that of H and OH radicals. The agreement between the experimental data and the simulation results for these species can be considered as satisfactory, taking into account the fact that these species were measured with fairly high uncertainty.

We also detected and measured spatial variation of the signal of the mass peak with m/z=60 in the flame at the energy of ionizing electrons of 12.3 eV. Cool at al. [3] measured photoionization efficiency curve for this mass peak in low pressure flame of DME and they identified this species as ethyl methyl ether (C2H5-O-CH3) by its photoionization potential, which is equal to ~9.7 eV. Therefore we also assume that in our experimental conditions this peak also can be associated with ethyl methyl ether. We estimated its calibration coefficient to be nearly equal to the calibration coefficient for DME (due to very close molecular structure of these species their ionization cross section can not differ too much) and evaluated its mole fraction distribution in the flame. The resultant

![Figure 2. Mole fraction profiles of intermediates. Symbols are experimental data, lines are simulation results. Solid lines: Wang et al model [20]; dashed lines: Tran et al model [21].](image-url)
mole fraction profile is shown in Fig. 4. As is seen its peak mole fraction reaches \( \sim 8 \times 10^{-5} \) in the flame. Both mechanisms do not involve this species therefore no comparison with calculation data is presented in this figure.

![Graph showing mole fraction profiles of various species in the flame](image)

**Figure 3.** Mole fraction profiles of \( \text{H}_2\text{O}_2 \) and flame radicals. Symbols are experimental data, lines are simulation results. Solid lines: Wang et al model [20]; dashed lines: Tran model [21].

**Figure 4.** Measured mole fraction profile of ethyl methyl ether (mass peak \( m/z=60 \) was measured at 12.3 eV).

### 4. Conclusions
The profiles of mole fractions of reactants, major products and intermediates (formaldehyde, methane, ethane, ethylene, acetylene, propane, ketene, hydrogen, hydrogen peroxide) and radicals (\( \text{H}, \text{OH}, \text{CH}_3, \text{HO}_2 \)) are measured in the premixed stoichiometric flame of DME/O2/Ar mixture at atmospheric pressure. Computer simulations were carried out using two detailed kinetic mechanisms. The results obtained experimentally and by calculations are in general in good agreement. According to experiments and calculations, formaldehyde is one of the most abundant intermediates in the DME flame. Although Tran et al. mechanism was developed to describe combustion of diethyl ether, it reproduces adequately mole fraction profiles of most intermediate products in the DME flame. Both kinetic models underestimate the peak mole fractions of ethane. A fairly strong signal from the mass peak with \( m/z=60 \) in the flame, associated tentatively with ethyl methyl ether, indicates that both models should be reexamined to reproduce chemistry of formation of this intermediate in the DME.
flame. The observed inconsistencies indicate the need to further improve the kinetic models for DME combustion.

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