



Experimental and modeling study of the pyrolysis and combustion of dimethoxymethane

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ABSTRACT

The pyrolysis and low- to intermediate temperature oxidation chemistry of dimethoxymethane (DMM), the simplest oxymethylene ether, is studied theoretically and experimentally in a JSR setup. The potential energy surfaces for peroxy species relevant during the low-temperature oxidation of dimethoxymethane are studied at the CBS-QB3 level of theory and the results are used to calculate thermodynamic properties of the main species as well as rate expressions for important reactions. An elementary step model for DMM pyrolysis and oxidation is built with the automatic kinetic model generation software Genesys. To describe the chemistry of small species not directly related to DMM, the AramcoMech 1.3 mechanism developed by Metcalfe et al. is used. If the more recently extended version of this mechanism, i.e. the propene oxidation mechanism published by Burke et al., was used as alternative base mechanism, large discrepancies for the mole fractions of CO₂, methyl formate and methanol during the pyrolysis of DMM were observed. The validation of the new DMM model is carried out with new experimental data that is acquired in an isothermal quartz jet-stirred reactor at low and intermediate temperatures. Different equivalence ratios, $\phi = 0.25$, $\phi = 1.0$, $\phi = 2.0$ and $\phi = \infty$, are studied in a temperature range from 500 K to 1100 K, at a pressure of 1.07 bar and with an inlet DMM mole fraction of 0.01. The experimental trends are well predicted by the model without any tuning of the model parameters although some improvements are possible to increase quantitative agreement. The largest discrepancies are observed at fuel lean conditions for the hydrocarbon mole fractions, and at low-temperatures as can be noticed by the over prediction of formaldehyde and methyl formate. The kinetic model is also validated against plug flow reactor, jet-stirred reactor and lean and rich premixed flames data from the literature. Rate of production analyses are performed to identify important pathways for low- and intermediate-temperature oxidation and pyrolysis.

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1. Introduction

Environmental issues like the urge to reduce the emission of greenhouse gases and particulate matter create concerns that encourage the research on alternative fuels or the use of additives. Diesel engines are known for their high fuel efficiency, but also for their higher emission of toxic exhaust gases like polycyclic aromatic hydrocarbons and NO_x. By blending diesel fuels with oxygenated additives emission levels can be reduced [1–4]. For example, blends of diesel with ethanol and biodiesel are worldwide used and their beneficial effect on emissions has frequently been demonstrated [5]. It is found that compared to conventional diesel,

emissions of carbon monoxide, unburned hydrocarbons and particulate matter are reduced, while NO_x emissions tend to increase [6].

Dimethyl ether (DME) is another potential clean fuel additive. The addition of DME to diesel reduces smoke emissions depending on the operating conditions and NO_x, carbon monoxide and unburned hydrocarbon emissions are lower for most operating conditions [7]. However, the increased vapor pressure, the lower viscosity and a limited solubility at lower temperatures prevent the use of diesel/DME mixtures in conventional diesel engines [7]. The oxidation chemistry of DME has been studied extensively as summarized by Rodriguez et al. [8]

The emission reduction of oxygenates is thought to be related to the C–O bonds found in these molecules. A polyether such as poly(oxymethylene) dimethyl ethers (also oxymethylene ethers, OMEs or CH₃–O–(CH₂–O)_n–CH₃ should be an even more efficient additive and the few available studies support this conclusion

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[9–15]. These oxygenates open a new route for enhancing diesel properties. Especially OMEs with a chain length of $n=3,4$ are attractive fuel additives, as they can be produced from the sole feedstock methane with gas-to-liquid technology. Their miscibility with diesel fuels allows these blends directly to be used in existing diesel engines without the need for technical modifications [12].

Studies on the oxidation chemistry of OMEs are scarce. Some attention has been paid to the oxidation of the simplest OME, dimethoxymethane (also methylal or DMM) with chain length $n=1$. Daly et al. [16] performed experiments in a jet-stirred reactor to study the oxidation of DMM at intermediate temperatures ranging from 800 to 1200 K, 5.07 bar and at various equivalence ratios. Daly et al. also developed a kinetic model, which relies mainly on kinetic parameters that are estimated by analogies to reactions of hydrocarbons, dimethyl ether and diethyl ether. Despite these approximations, their model predicts the observed product mole fractions reasonably well. Lean and rich DMM flames have been studied by Dias et al. [17–19] and a kinetic model was developed in order to simulate the DMM flame data. The kinetic parameters were taken from literature, mainly from the work of Daly et al. [16]. Recently, experiments in a plug flow reactor at atmospheric and high pressures were reported by Marrodán et al. [20,21]. Their experiments were performed for a large temperature range, 373 K–1073 K, and air excess ratios ranging from 0.7 to 20. A kinetic model was developed by combining in-house kinetic models for small hydrocarbons such as DME, ethanol, acetylene and methyl formate with the slightly modified kinetic model developed by Dias et al. for DMM [17–19]. The agreement between experimental data and model predictions is reasonable but not perfect, suggesting that the DMM chemistry is not yet fully understood.

In this work the pyrolysis and oxidation chemistry of DMM is studied in detail experimentally and through simulations using a newly developed kinetic model. This model distinguishes itself from prior models through the use of ab initio calculated thermodynamic properties for important species and rate expressions for crucial reactions. In this context, the potential energy surfaces relevant for the low-temperature oxidation are investigated in detail. A large part of the comprehensive kinetic model is constructed automatically with Genesys [22,23]. Experiments are performed in an isothermal quartz jet-stirred reactor for temperatures ranging from 500 to 1100 K, at a pressure of 1.07 bar, studying pyrolysis as well as three oxidizing conditions to validate the new kinetic model. Rate of production analyses are presented at 650 and 700 K to explain the low-temperature reactivity in oxidizing environments. Furthermore, rate of production analyses performed at 900 K for both oxidizing and pyrolysis conditions are used to identify chemistry differences between oxidation and pyrolysis conditions. Finally, sensitivity analyses are employed to identify reactions that may be responsible for discrepancies between observed and predicted mole fractions.

2. Experimental methods

The pyrolysis and oxidation of dimethoxymethane are studied in an isothermal quartz jet-stirred reactor. The main features of the experimental apparatus are summarized below. Details regarding the set-up can be found elsewhere [24].

Helium (Messer, 99.99%) and dimethoxymethane (Sigma-Aldrich, 99%) are passed through an evaporator and mixed. Downstream, oxygen (Messer, 99.999%) is added to the gaseous flow. The helium and oxygen flow rates are controlled by gas-mass-flow controllers (Bronkhorst IN-FLOW) and the liquid fuel mass flow rate is regulated by liquid-Coriolis-flow controllers (Bronkhorst M12).

The gaseous mixture passes through an annular preheating zone, where it is heated to the reactor temperature, and enters

the jet-stirred reactor through four nozzles. The nozzles and reactor are designed to limit as much as possible thermal and concentration gradients. Thermocoax resistance wires provide heating for the annular preheating zone and the reactor. A type K thermocouple measures the temperature in the center of the reactor (measured temperature gradients $< \pm 5$ K). The pressure is set with a needle valve downstream of the reactor.

The reactor outlet is connected to three gas chromatographs (GC) that allow online quantification of product species. The transfer lines to the GCs are kept at 433 K to avoid condensation. The first GC is used to detect O_2 , CO, CO_2 and CH_4 in case of oxidation and H_2 in case of pyrolysis. This GC is equipped with a Carbo-sphere packed column and a thermal conductivity detector. If H_2 needs to be detected at pyrolysis conditions, Ar is used as carrier gas, otherwise the carrier gas is He. The second GC contains a PLOT-Q capillary column and a flame ionization detector (FID) preceded by a methanizer. The methanizer enables the detection of species like CO, CO_2 and formaldehyde with the FID. The third GC has a HP-5 ms capillary column installed and is equipped with a FID. A GC connected to a mass spectrometer (GC-MS) is used for either online or offline product identification. The GC-MS is operated either with a PLOT-Q or with a HP-5 ms capillary column. The MS is a quadrupole mass spectrometer with a mass range of 10–400 m/z . Products are quantified by either injecting known amounts of pure samples into the GCs or by applying the effective carbon number method. The relative experimental error of the compound mole fraction determined by injecting a known amount of the pure substance is 5% based on experience. When the effective carbon number method is applied, the relative experimental error is estimated to be 10%.

The volume of the quartz reactor is 85 cm^3 . During experiments, the volumetric flow rate in the reactor, calculated with the total molar inlet flow rate and the temperature and pressure in the reactor, is set to $3.0 \times 10^{-5} m^3 s^{-1}$, which corresponds to an residence time of 2.83 s. The temperature ranges from 500 to 1100 K and the pressure is kept at 1.07 bar. The DMM inlet mole fraction equals 0.01 for all experiments. Four equivalence ratios, $\phi=0.25$, $\phi=1.0$, $\phi=2.0$ and $\phi=\infty$, are investigated. 21 species are identified and quantified with the online gas chromatographs. The carbon balances are closed within 5% at most conditions. Since the analysis section does not allow quantifying water and hydrogen peroxide, the hydrogen and oxygen elemental balances are not available. A spreadsheet of the experimental results is provided in the Supporting information.

3. Computational method

Electronic structure calculations are performed on the high-performance supercomputer at Ghent University at the CBS-QB3 level of theory [25] as implemented in Gaussian 09 [26]. The lowest energy conformers are determined manually by carrying out calculations for the most likely structures at the B3LYP/6-31G(d) level of theory, for most species and transition states. For more complex molecules and transition states, in which several hydrogen bonds are present, in-house developed algorithms are used to automatically search for the lowest energy conformer [27].

The CBS-QB3 results are used to calculate the heat capacities at different temperatures, the standard entropy and the standard enthalpy of formation. Internal modes are treated as harmonic oscillators except for modes that resemble rotations around single bonds. The latter are approximated by 1-dimensional hindered internal rotations (1D-HIR). All single bonds and bonds in the reactive moiety of the transition state are treated this way as long as the hindrance potential does not exceed 40 $kJ mol^{-1}$. The hindrance potentials are calculated at the B3LYP/6-31G(d) level of theory with relaxed surface scans in which all coordinates,

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