121f - An Experimental and Modeling Study on Low- and High-Temperature Pyrolysis and Oxidation of Oxymethylene Ethers As a Sustainable Alternative Fuel

📅 Wednesday, November 17, 2021

🕑 9:30 PM - 9:55 PM

📍 *Virtual - Fuels and Petrochemicals Division (16)*

Abstract

Introduction

The present research focuses on the combined modeling and experimental work on the pyrolysis and oxidation of oxymethylene ethers (OMEs). OMEs are a family of molecules with alternating carbon and oxygen atoms in the backbone saturated with hydrogen atoms, represented with structural formula $CH_3O(CH_2O)_nCH_3$ (further indicated as OME-*n*). These molecules have interesting properties for applications as alternative fuel. OMEs are categorized as e-fuels since they can be produced in a carbon-neutral manner via carbon capture and utilization (CCU) starting from captured CO_2 and renewable energy. In addition, blending them with conventional diesel reduces toxic soot emissions, due to the absence of carbon-carbon bonds, while still being compatible with the current generation of diesel engines. OMEs could as such contribute to the development of a more sustainable transport sector within the near future, and a circular carbon economy in general. However, before being widely applicable, it is important to fully understand the pyrolysis and

oxidation chemistry of these compounds and their interactions with hydrocarbons. Therefore, a new microkinetic model is developed based on first principles that describes the low- and high-temperature decomposition pathways of oxymethylene ethers up to OME-5. This model enables predictive simulations for combustion applications.

Methodology

During the last decade, great progress has been made in the construction of reliable kinetic models for numerous technologically important radical chemistry processes. The resulting models typically contain hundreds of species, and several thousands of associated reactions. The generation of microkinetic models by hand is thereby a tedious, error-prone and often incomplete process. To facilitate this process, automatic kinetic model generation codes such as Genesys at the Laboratory for Chemical Technology have been developed to systematically generate kinetic models [1]. For this research, the thermodynamic and kinetic databases of Genesys are extended with more relevant data for C-O-C and O-C-O bonds, to enable construction of microkinetic models for oxymethylene ethers based on high-level quantum chemical data.

A prerequisite for the generation of detailed kinetic models is the availability of accurate thermodynamic and kinetic data for species and reactions, respectively. Ideally, these parameters are available from experiments or high-level quantum chemical calculations. Since these methods are expensive and time-consuming, Genesys instead often relies on approximation methods such as group additivity theory and rate rules. In this work, thermodynamic and kinetic parameters are obtained from quantum chemical calculations at the CBS-QB3 level of theory for important reaction pathways of both low- and high-temperature oxidation of OMEs. The lowest energy conformer is searched extensively by in-house developed tools. Non-harmonic normal modes are accounted for by performing one-dimensional hindered-rotor calculations. The generated data – thermodynamic properties for around 700 species and modified Arrhenius parameters for around 120 reactions – is extrapolated to become valid for longer chain OMEs by regression of new values for Benson's group additivity and rate rules.

Results

Within Genesys, the possible reactions are generally defined in terms of reaction families. Reaction families from earlier studies on smaller compounds with C-O-C bonds (i.e., dimethyl ether and dimethoxy methane/OME-1 [2]) with Genesys are extended with new unimolecular decomposition pathways. The latter were identified as

depicted on the potential energy surface for OME-2 in Figure 1. Roaming reactions are observed with the formation of products with a hydroxyl functionality and carbenes. These carbenes (except for methylene) can decompose with the formation of radicals. In addition, three other concerted reactions are found forming a carbonyl functionality in addition to a smaller ether. The reaction from OME-2 to OME-1 and formaldehyde can proceed via three different transition states since each carbon-oxygen bond can be eliminated. For the thermal decomposition of OMEs, these reactions are dominant pathways, because several of them have an electronic barrier that is significantly lower than the lowest bond dissociation energy, i.e., 348 kJ mol^{-1}. This clarifies the high reactivity already at low temperatures and indicates that radical chemistry is less dominant at these temperatures. Eventually, the outcome is a model containing the chemistry for OME-1 up to OME-5. To include detailed chemistry of smaller (oxygenated) hydrocarbons in the final model, the Genesys model is merged with the AramcoMech 1.3 base model [3]. In case of conflicting thermodynamic or kinetic properties, the input of the AramcoMech model is kept to maintain the integrity of this experimentally fitted model.

Various pyrolysis and oxidation experiments have been performed to validate both the primary and secondary chemistry of the generated model. Low-temperature pyrolysis experiments are performed for OME-2, OME-3, OME-4 and OME-5 in the micropyrolysis set-up at the Laboratory for Chemical Technology (LCT). Small amounts of fuel are vaporized, diluted, and brought in a tubular reactor where the decomposition products are measured over the broad temperature range of 373 K to 873 K at a pressure of 3.4 bara. The main products are shorter ethers, formaldehyde, methane, methanol and at higher temperatures hydrogen, carbon monoxide and carbon dioxide due to secondary decomposition reactions. Preliminary results indicate significant decomposition of OME-2 starting at around 450 K, as depicted in Figure 2. Similarly, high-temperature pyrolysis experiments are performed for OME-2 and OME-3 in the bench-scale steam cracker setup at LCT over a range of temperatures 723 K to 1073 K at 1.5 bara. A similar product spectrum is identified accompanied by minor amounts of OME-derived species with carbonyl and hydroxyl functionalities, e.g., formic acid, methyl formate, methoxymethanol and methoxymethyl formate. The number of products with carbon-carbon bonds detected and the associated quantities are low.

Ignition delay times have been measured via rapid compression experiments at 5 bara for and for OME-2 and OME-3 to validate the low-temperature oxidation section of the model. Samples were taken during compression to identify the most important reactants and

products. These include, in the case of OME-3, methyl formate, methoxymethyl formate and methoxymethoxymethyl formate. From quantum chemical calculations, it follows that the formation of cyclic ethers plays an important role which is confirmed qualitatively from the measured products. Cyclic ethers derived from OMEs tend to decompose quickly by formation of carbonyl functionalities, similar to a reverse Diels-Alder reaction.

Finally, flat flame burner experiments have been performed with OME-3 for validation of the high-temperature combustion chemistry. The flame experiments are performed at 0.0533 bara and with a fuel composition of 20 mol% OME_3 and 80 mol% CH_4. Concentration profiles are constructed as function of height above burner. The main compounds detected are OME-3, formaldehyde, methanol, hydrogen, carbon dioxide and carbon monoxide. While ethane, ethylene, dimethyl ether, methyl formate, dimethoxy methane and methoxymethyl formate are observed in minor amounts. Preliminary simulation results indicate good agreement between the model and experimental observations for major and minor species without fitting of model parameters.

Conclusions

The thermodynamic and kinetic databases of Genesys are extended to enable the construction of microkinetic models for oxymethylene ethers. A microkinetic model has been constructed with Genesys for pyrolysis and both low- and high-temperature oxidation of oxymethylene ethers up to OME-5 based on first principles. The model is validated with several series of experiments including pyrolysis in tubular reactors, ignition delay time measurements in a rapid compression machine and flat flame burner experiments.

Acknowledgments

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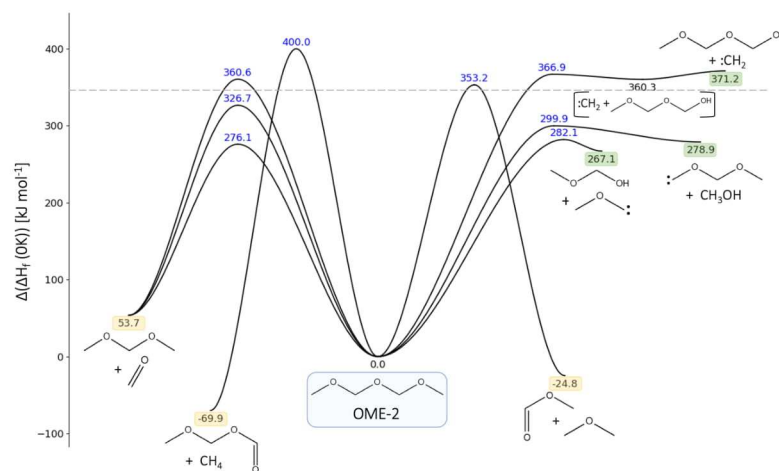
Figure 1: Potential energy surface at 0 K for OME-2 at the CBS-QB3 level of theory. Energies are relative to OME-2. The dashed line indicates the lowest bond dissociation energy of 348 kJ/mol. Products between brackets indicate the formation of a van der Waals-well. Energies within a green box correspond with roaming reactions, energies in a yellow box correspond with carbonyl functionality formation.
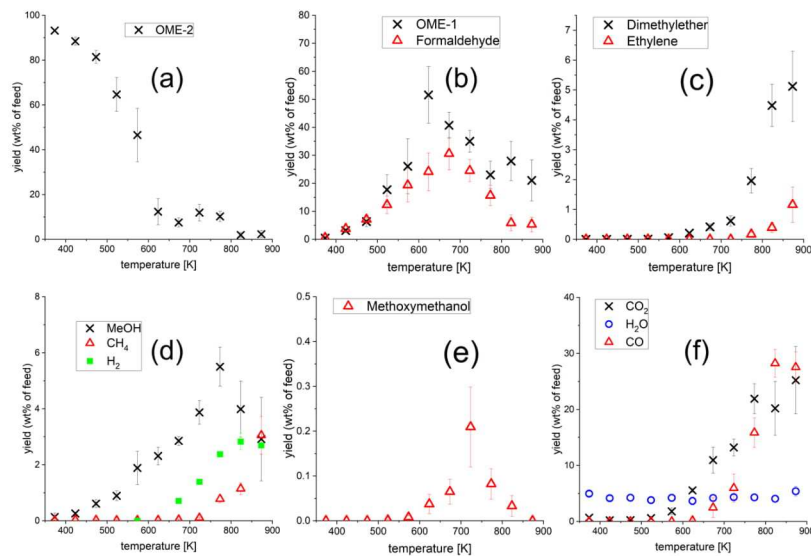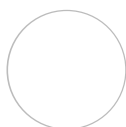

Figure 2: Preliminary results of the decomposition products of OME-2 obtained from pyrolysis of OME-2 diluted with helium in the temperature range 373 to 873 K at a pressure of 3.4 bara.
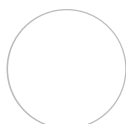
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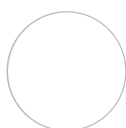V Robin Varghese
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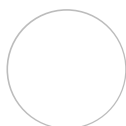T Luc-Sy Tran
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