

# Automatic mechanism generation for auto-ignition of the promising e-fuels oxymethylene ethers (OMEn, n = 2-4)

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## Introduction

Polyoxymethylene dimethyl ethers, also known as oxymethylene ethers (OMEs), are attractive diesel fuel additives, as their addition is able to strongly reduce the soot formation in compression-ignition (CI) engines. Recently, the concept of e-fuels has been proposed, which aims to produce synthetic, carbon neutral fuels from water and carbon dioxide (CO<sub>2</sub>) by renewable electricity via catalytic conversion. OMEs, which can be synthesized from CO<sub>2</sub>-based methanol, are regarded as one of the most promising classes of e-fuels, and are thus attracting growing interest from both academic research and industry.

In order to investigate and understand the combustion behavior of OMEs in practical devices by means of computational fluid dynamic (CFD) simulations, accurate chemical kinetic mechanisms are a prerequisite. While studies on larger OMEs are scarce in the literature, the combustion kinetics of OME1 has been investigated in terms of experimental investigation, chemical modeling, and theoretical calculation. These studies provide a deep insight into the oxidation chemistry of OME1 and, more importantly, improve our understanding about the common combustion kinetics of the whole class of OMEs. An efficient and effective application of this advanced knowledge can thus strongly simplify and accelerate the mechanism development for larger OMEs.

The primary goal of this study is to develop an accurate chemical mechanism for the auto-ignition of OME2-4 in an efficient way based on the prior knowledge about OME1. The chemical mechanism is developed in two steps. First, an automatic mechanism generation framework based on the concept of reaction classes and rate rules is applied to derive a prior mechanism for OME2-4. Here, all reaction classes relevant in the oxidation of OME1 are taken into account in the generation of reactions for larger OMEs. The rate constants of OME1-specific reactions are taken as rate rules to specify the rate constants of analogous reactions for OME2-4. The application of this automatic process aims to replace the conventional manual derivation of prior mechanisms, which is time-consuming and error-prone. For a good model performance, the mechanism is optimized automatically by calibrating the reaction rate rules and thermochemical properties within their assumed uncertainty limits.

For the validation and optimization of the mechanism, the ignition delay times of OME2-4 are measured in a shock tube (ST) and a rapid compression machine (RCM). All measurements probe a variety of initial conditions and provide an evaluation of the performance of OME2-4 considering homogeneous auto-ignition.

## Experimental investigation

The ignition behaviors of OMEs are studied experimentally at pressures of 10 and 20 bar over the initial temperature range of 559–1137 K for equivalence ratios of 0.5, 1.0, and 2.0. Table 1 summarizes the experiments performed in this study with their respective conditions. The employed shock tube and rapid compression machine have been previously verified and used to determine

the ignition delay times of a number of fuels. Detailed descriptions of these facilities can be found in the literature [1,2].

Fuel	Facility	Condition		
		Pressure [bar]	Temperature [K]	Equivalence ratio [-]
OME2	ST	10	663–1112	1.0
		20	698–1112	0.5, 1.0, 2.0
	RCM	10	559–666	1.0
		20	567–642	1.0
OME3	ST	10	684–1137	1.0, 2.0
		20	703–1066	0.5, 1.0, 2.0
	RCM	10	566–661	1.0
		20	565–681	0.5, 1.0
OME4	ST	10	749–1077	1.0
		20	819–1030	1.0

*Table 1: Experiments for OME2-4.*

### Prior mechanism generation

A prior mechanism is first constructed using an automatic mechanism generator. This automatic framework has been developed in a way to replace the initial step in the conventional mechanism development process, which is the manual derivation of fuel-specific chemistry using prior knowledge of similar molecules and their reaction classes, upon a  $C_0$ – $C_4$  base mechanism. Its major task is to generate the fuel-specific reactions and to specify their rate constants according to the user-defined reaction classes and rate rules, respectively. The application is highly customizable and its modular structure allows for the simple extension and modification of reaction classes within the program.

The generation of reactions within this framework is based on the graph theory [3], which is applied to describe the structures of chemical compounds. A molecular graph represents a Lewis structure, i.e., it describes the atoms in a considered molecule and their connectivity. The graph’s vertices correspond to heavy atoms and two numbers are assigned to each atom group. The first number is a label, which is merely used to name the vertex. The second number is the so-called precedence and represents the information of hydrogen atoms and unpaired electrons of the atom group. Single bonds correspond to the graph’s edges. In contrast, multiple bonds are assigned to vertices instead of edges. These molecule graphs provide on the one hand the necessary information on molecules for model generation. On the other hand, they open the possibility to generate three-dimensional molecule structures for quantum chemistry calculations and to give information for compound identification (e.g. with InChI) as well as for the determination of thermochemical properties.

In the present framework, new reactions are derived according to the reaction classes defined by the user. New species can be constructed and existing species can be modified by deleting or adding vertices, deleting or adding edges, or changing the precedence of a vertex. It should be noted that the purpose of this framework is not the direct generation of a final mechanism. Instead, it only aims to replace the time-consuming and error-prone manual construction of prior mechanisms. The derived prior mechanisms can and should be further improved in terms of reaction pathways, thermochemistry, and reaction rate constants.

In this study, the prior fuel-specific chemistry of OME2-4 is derived by using the framework described above. Recently, Jacob et al. [4] have developed a detailed reaction scheme for OME1, based on the approach of reaction classes. The same reaction classes and rate rules are specified for the mechanism generator. The developed prior mechanism for OME2-4 thus follows the hier-

archical nature of the OME1 mechanism [4]. The extensively validated  $C_0$ – $C_4$  mechanism from Blanquart et al. [5] serves as the base mechanism. A different base mechanism [6] has also been tested but the prediction of ignition delay times is found to be insensitive towards the choice of the base mechanism. The model performance is demonstrated in the following example in terms of the ignition delay times of OME2. Figure 1 shows the comparison of the ignition delay times measured in the ST for OME2 with those computed using the derived prior mechanism. It is found that the mechanism predicts the data with a moderate accuracy.

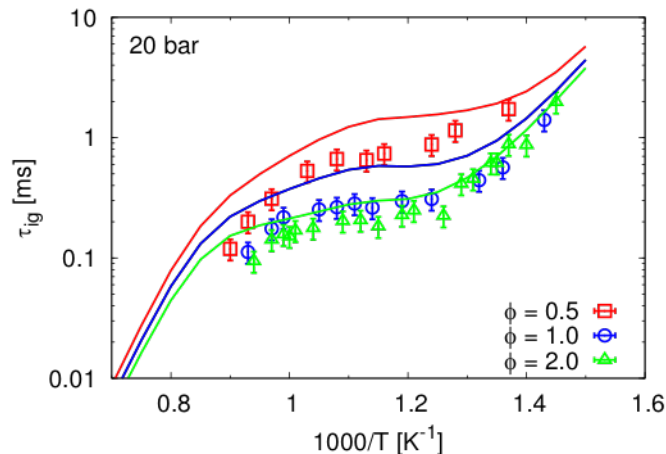


Figure 1: Ignition delay times of OME2 at 20 bar. Symbols denote ST experiments and lines show results calculated using the prior mechanism.

### Mechanism optimization

The automatically generated prior mechanisms need to be improved in terms of reaction pathways, thermochemistry, and reaction rate constants. In the present work, it is assumed that the derived prior mechanism for the auto-ignition of OME2-4 incorporates all necessary reaction paths, as the automatic mechanism generation process considers all relevant reaction classes of OME1. Thus, for a better agreement with the measured data, the rate rules and thermochemical properties are then subjected to an automatic calibration process.

Recently, Cai and Pitsch [7] extended the conventional methods for automatic calibration of chemical kinetic models by performing optimization of reaction rate rules. This methodology enables a chemically consistent optimization and reduces the number of uncertain parameters by categorizing kinetically similar reactions into reaction classes. An additional advantage of this method is that rate rules can be simultaneously optimized for several different fuels and fuel mixtures, as is the present case for the auto-ignition of OME2-4. This method has been recently extended [8] by performing joint calibration of rate rules and thermochemical properties of single species or thermochemical group values, which are used to determine the thermochemical parameters when using the group additivity method. The extended optimization technique is thus applied here to calibrate the reaction rate rules and thermochemical data of the mechanism for OME2-4 within assigned uncertainty limits. For rate rules, an uncertainty factor of four is assumed. The reported ignition delay times are considered as the experimental targets in the optimization process.

Figure 2 shows the numerical ignition delay times obtained using the optimized mechanism in comparison with the measurements. Good agreement is observed between model and experiment. 29 rate rules are selected for calibration due to their notable sensitivities, among which 13 are used for H-abstraction reactions from the fuel. The rate constants [4] of these rate rules were de-

terminated originally based on group additivity rules [9]. A calibration of these rate constants is shown to improve the model performance.

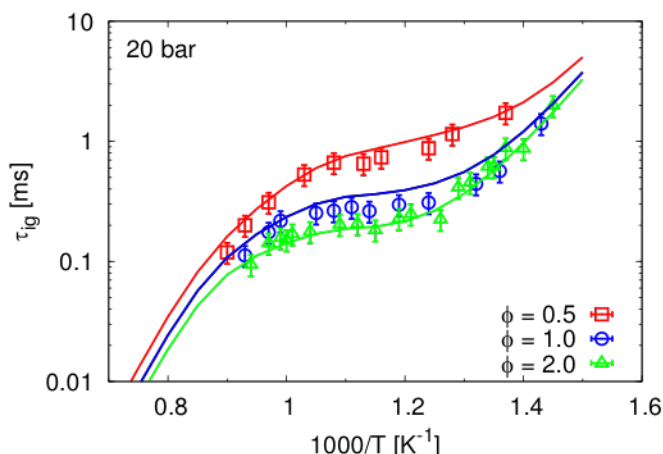


Figure 2: Ignition delay times of OME2 at 20 bar. Symbols denote ST experiments and lines show results calculated using the optimized mechanism.

## Concluding remarks

This study presents a newly developed chemical mechanism for OME2-4. The mechanism is derived first automatically using a reaction class-based mechanism generator. To ensure the chemical validity of the mechanism, all reaction classes found in the oxidation of OME1 are considered in the automatic generation. For good prediction with respect to ignition delay times, the developed mechanism is further optimized automatically in terms of rate rules and thermochemistry. In addition, the ignition delay times of OME2-4 are investigated experimentally in a shock tube and in a rapid compression machine. The measurements cover a wide range of initial conditions and serve as the validation and optimization targets of the mechanism.

Moreover, this study presents a novel model development process, which is composed of automatic mechanism generation and optimization. This process is able to provide very accurate chemical mechanisms. However, it is worthwhile to note that the application of this process is limited and is only valid in the model development for large molecules, for whose short-chain counterparts accurate prior knowledge is available, as is the case for the OMEs presented here.

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## References

- [1] C. Lee et al., *Zeitschrift für Physikalische Chemie* 226 (2012) 1–28.
- [2] K. Zhang et al., *Combustion and Flame* 172 (2016) 116–135.
- [3] A.T. Balaban, *Journal of Chemical Information and Computer Sciences* 25 (1985) 334–343
- [4] S. Jacob et al., *Combustion and Flame*, submitted.
- [5] G. Blanquart et al., *Combustion and Flame* 156 (2009) 588–607.
- [6] Y. Li et al., *Proc. Combust. Inst.* 36 (2017) 403–411
- [7] L. Cai & H. Pitsch, *Combustion and Flame* 161 (2014) 405–415.
- [8] F. vom Lehn et al., in preparation.
- [9] F.H. Vermeire et al. *Combustion and Flame* 190 (2018) 270–283.