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Experimental and kinetic modeling study of the low- and intermediate-temperature oxidation of dimethyl ether



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ABSTRACT

Recent experiments on low-temperature oxidation of dimethyl ether (DME) at atmospheric pressure reveal much lower fuel conversion than the predictions of all published models. Consistent with previous measurements, the present work on DME oxidation in a laminar flow reactor between 400 and 1160 K at atmospheric pressure also confirmed this behavior. To reduce the gap between model predictions and experimental results, both regarding key oxygenated species and fuel conversion, an extended and updated kinetic model of DME oxidation was developed from the widely used model of Z. Zhao, M. Chaos, A. Kazakov, F.L. Dryer, Int. J. Chem. Kinet. 40 (2008) 1–18. The development of the model focused on the reaction sequences that affect the low-temperature oxidation reactivity. In particular, the reactivity of DME oxidition in the low-temperature regime and at atmospheric pressure can now be predicted. This is possible upon the inclusion of an additional, chemically-activated pathway of CH₃OCH₂ reaction with O₂, as well as of the new decomposition chemistry of OCH₂OCHO radical, investigated theoretically in this work. The present model was examined against species concentrations in DME oxidation from low to intermediate temperatures and shock tube ignition delay times. It shows satisfactory performance in reproducing the respective literature data.

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1. Introduction

Combustion processes need to become cleaner and more efficient to meet stricter emission regulations and limited fossil fuel resources. An important attempt to address combustion energy challenges is the introduction of alternative fuels, especially bioderived fuels. Generally, typical biofuels may reduce the emissions of polycyclic aromatic hydrocarbons (PAHs) and soot, while the formation of carbonyl compounds such as formaldehyde, acetaldehyde, acetone, and higher aldehydes and ketones often increases [1]. It is warranted to comprehensively study the combustion chemistries and emission properties of potential biofuels before their large-scale use in industry and transportation to examine whether they are environmentally friendly. An attractive renewable fuel is dimethyl ether (DME) which presents low soot and NO_x emissions and a high cetane number. It has thus been proposed as an alternative fuel and as an additive to diesel fuel

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Due to its promising properties and potential as an alternative fuel, DME has been investigated extensively in the past decade including experiments such as pyrolysis [5–11], oxidation [4,5,8,12-24] and flames [25-36], and theoretical calculations [7-9,17-19,37-39], covering a wide range of temperatures and pressures. Based on these experimental and theoretical studies, detailed kinetic models for DME combustion have been developed [5,7,15,25,40]. In previous work, some experiments [13-16,21, 22,24] addressed the low-temperature oxidation of DME. For example, earlier studies at relatively high pressure include experiments in a shock tube [13], jet-stirred reactor (JSR) [14] and flow reactor [15]. These measurements can be reproduced by previously published models [5,7,15,25,40]. However, in recent studies, Guo et al. [21] investigated DME oxidation from 490 to 750 K at atmospheric pressure in a flow reactor, and found that the model developed by Zhao et al. [7], named as "Zhao model" herein, predicted a much higher oxidation reactivity than their measurements. This observation was confirmed by Herrmann et al. [23] in their DME oxidation experiments with different equivalence ratios. More recently, Kurimoto et al. [24] also found discrepancies between



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Table 1

Experimental conditions of the low-temperature oxidation of DME.

Oxidation	$X_{\rm DME}$	X ₀₂	X _{Ar}	P/atm	Total flow rate (SLM) ^a	Residence time (s)
Exp. 1	1.25	3.75	95	1	0.5	b
Exp. 2	1.25	3.75	95	1	0.5	b
Exp. 3	1.25	3.75	95	1	c	1.5

Note: Exp. 1: flow reactor oxidation in Bielefeld; Exp. 2: flow reactor oxidation in Hefei; Exp. 3: JSR oxidation in Hefei.

^a Std. conditions: 273.15 K, 1 atm.

^{b,c} Change with temperature.

the predictions of the Zhao model [7] and their experimental results from a flow reactor. They improved the Zhao model to reproduce the measured fuel conversion by adjusting the branching ratio of the second oxygen addition channel and its competitive channel of the important QOOH intermediate to CH_2O . Moreover, some further advances of chemical kinetics and experimental diagnostics have offered useful insight regarding the key reactions [9,17–19,38,41] that affect the oxidation reactivity of DME in the low-temperature regime.

In this work, DME oxidation in a laminar flow reactor was investigated in the low- and intermediate-temperature regimes from 400 to 1160 K at atmospheric pressure. With a molecular-beam mass spectrometer, mole fraction profiles of reactants, intermediates and major products were measured. The modeling part started with the Zhao model [7] in which some key reactions and their related rate constants were updated with information from the above-mentioned recent experimental and theoretical investigations [9.17–19.38.41]. Furthermore, theoretical calculations were performed to improve this mechanism. In particular, our high-level quantum calculations on the decomposition chemistry of the OCH₂OCHO radical confirms a new formic acid pathway which was not included in previous models [5,7,15,25,40]. The present model shows good agreement with data in this work and further experimental results reported in the literature [13-15,21,22,24]. We believe that these results are helpful for the understanding of the low-temperature oxidation process of DME and may lead to further development of a comprehensive DME low-temperature oxidation mechanism in the future.

2. Experimental method

DME oxidation was investigated in detail using different experimental set-ups. One experiment was performed in a laminar flow reactor coupled to an electron ionization molecular-beam mass spectrometer (EI-MBMS) at Bielefeld University. The other two experiments, a laminar flow reactor [42,43] and a JSR [44], were coupled to photoionization molecular-beam mass spectrometry (PI-MBMS) at the National Synchrotron Radiation Laboratory in Hefei, China. The measurement in Hefei was focused on the investigation of the low-temperature regime oxidation and the identification of the species via photoionization efficiency (PIE) spectra, to support the results of the Bielefeld flow reactor experiment. Thus, only the Bielefeld set-up is described here. Information on the Hefei set-ups can be found in the Supplementary Material. The experimental conditions of the three experiments are shown in Table 1.

As a continuous development of our previous studies [22,23], a new apparatus for the analysis of low-temperature oxidations was designed in the present work. The laminar flow reactor used in this study consisted of a fused silica tube with an inner diameter of 8 mm and a total length of 830 mm. As shown in Fig. 1, the reactor was directly coupled to the time-of-flight mass spectrometer as a molecular beam experiment. The used flange system (Fig. 1, right panel) was important to optimize the position of the quartz nozzle inside the reactor tube. The exhaust gas was pumped via four outlet tubes that are positioned symmetrically enabling undisturbed sampling. The reactor tube can be heated by three independent heating sections. The length of the three heating zones (T1, T2, and T3) is approximately 300, 200, and 200 mm, respectively. Each part was monitored by a Ni-Cr/Ni thermocouple. It should be noticed that the wall reactions in the present quartz flow tube are expected to be negligible due to the small surface area to volume ratio of 5 cm^{-1} , compared with previous studies [5,15,16,21,45,46], and we did not see any indications of surface reactions.

As shown in Fig. 1, the electron–ionization time-of-flight mass spectrometer (Kaesdorf) was directly adapted to the laminar flow reactor. The gas was sampled via a quartz nozzle (\sim 50 µm orifice diameter) and expanded into the 1st pumping stage (Fig. 1, left panel) pumped down to 10^{-4} mbar by a turbo-molecular pump. The formed molecular beam was further sampled by a copper skimmer at the 2nd pumping stage, and then extracted to the



Fig. 1. Schematic diagram of the laminar flow reactor coupled with a molecular-beam mass spectrometer (left panel); flange system connected to the flow reactor and the MBMS system (right panel).

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