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Quantitative measurements of HO₂/H₂O₂ and intermediate species in low and intermediate temperature oxidation of dimethyl ether

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Abstract

As two of the most important species that characterize hydrocarbon low temperature ignition, HO₂ and H₂O₂ formation during dimethyl ether (DME) oxidation was quantified using the same experimental conditions, for the first time, in an atmospheric flow reactor at low and intermediate temperature range. Dual-Modulation Faraday Rotation Spectroscopy (DM-FRS) and Molecular Beam Mass Spectrometry (MBMS) were used to measure HO₂ and H₂O₂ respectively. DME and other important intermediate species such as CH₂O and CO are also measured by MBMS between 400 and 1150 K at different fuel concentrations. Species profiles in the reactor were calculated by using both zero- and two-dimensional computations with different detailed kinetics for cross-validation and comparison with experimental results. The models predict adequately the low and intermediate oxidation temperature windows near 600 and 1000 K, respectively. However, both models over-predicted the DME consumption as well as CO, HO₂ and H₂O₂ formations at the low temperature oxidation window by more than a factor of four. Moreover, although the model predicted reasonably well the formation of CH₂O and CO/CO₂ at the intermediate temperature oxidation window, the concentration of H₂O₂ was also over-predicted, suggesting the large uncertainties existing in the DME low temperature chemistry and in H₂O₂ chemistry at intermediate temperature. Furthermore, to analyze the uncertainty of the low temperature chemistry, a branching ratio of QOOH decomposition to CH₂O was derived using measured DME, CH₂O and CO concentrations. The large difference between the modeled and measured branching ratios of QOOH decomposition suggests an underestimated QOOH decomposition rate to form CH₂O in the current DME models.

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1. Introduction

As the simplest ether exhibiting two-stage autoignition behavior, dimethyl ether (DME) is an excellent target for studying low and intermediate temperature fuel oxidation. Extensive studies of DME ignition delays [1], reactors [2,3], and low- and high-pressure flames have been carried out [4–6]. Several chemical kinetic mechanisms [7–9] have been proposed, however, the models were not able to predict the experimentally measured high-pressure flame speeds [5] and species in low-temperature flow reactors [2,3], in which HO₂ and H₂O₂ related chemistry plays a dominant role. It is well known that HO₂ and H₂O₂ are the two of the most important intermediate species that control the low-temperature and high-pressure autoignition chemistry and the transition to hot ignition for almost all large hydrocarbon fuels [2,5,10], however, they are difficult to quantify in combustion systems. H₂O₂ has been measured indirectly through multi-species laser diagnostics [11] and photofragmentation laser-induced fluorescence [12] in shock tube and engine studies respectively. Only three experiments have been reported where H₂O₂ produced by oxidation of a fuel has been directly quantified using MBMS sampling from a flow reactor [2] or cavity ring-down spectroscopy after sampling from a jet-stirred reactor [13,14]. These measurements were limited to temperatures below 750 K for the MBMS measurements [2] and below 950 K for the cavity ring-down measurements [13,14]. Moreover, the fuel oxidation kinetics at intermediate temperature (~1000 K), where OH production via H₂O₂ (+M) → OH + OH is dominant, were not explored in these studies. Direct quantification of HO₂ has only been reported twice in the literature [15,16]. The first reported HO₂ measurement was performed by the authors using Faraday rotation spectroscopy during the oxidation of DME in a flow reactor [15]. However, the axial temperature uniformity in this experiment was poor and large temperature gradients were present. As such, the results could not be used to validate chemical kinetics. The second reported measurement of HO₂ as a result of the oxidation of *n*-butane was carried out by using the fluorescence assay by gas expansion technique on gas sampled from a jet-stirred reactor [16]. To our knowledge, to date no direct combined HO₂ and H₂O₂ measurements under the same experimental conditions in a flow reactor have been conducted in the literature for combustion kinetic studies.

The goal of the present study is to quantify HO₂/H₂O₂ and other intermediate species of DME oxidation in a flow reactor by using both FRS and MBMS over a broad temperature window (400–1150 K) covering both low-temperature and intermediate-temperature fuel oxidation. The

data will be used to assess the kinetic model by comparing to model predictions. In this paper, HO₂ formation of from oxidation of 0.5% DME in a flow reactor was measured by using FRS. This is followed by H₂O₂, CH₂O, CO and other species measurements using MBMS with a 0.5% DME concentration. The MBMS measurement was also extended to higher fuel concentrations (0.88%) to ensure higher experimental accuracy for MBMS. The experimental results are compared with zero- and two-dimensional simulations with different kinetic models. Finally, a branching ratio analysis of QOOH to CH₂O and CO is conducted and the uncertainty of the kinetic models is assessed.

2. Experimental and diagnostic methods

2.1. Reactor and experimental conditions

The present laminar flow reactor consists of a 355 mm length straight quartz tube with a 17 mm inner diameter (ID), in which the heated reactants are introduced through a 100 mm length and 2 mm ID inlet channel. Volumetric flow rates of argon, helium, oxygen are regulated with mass flow controllers (MKS) while DME is supplied by a pre-calibrated sonic nozzle. To prevent any preliminary reaction before the admission of the reactant into the reactor, oxygen and the 400 K preheated DME/Ar/He mixture are combined just before the inlet channel. To make a significant improvement in the axial temperature uniformity for the flow reactor compared to a 2-stage heating arrangement used in the prior work [15], a 4-stage heating arrangement was employed in this study. In this arrangement, a total of four heaters were independently PID-controlled within ±1 K over the reactor. A schematic of the 4-stage heating configuration, gas mixing, and positions of thermocouples is provided in [Supplemental Material \(Fig. S1\)](#), along with representative temperature distribution profiles ([Fig. S2](#)).

The experimental conditions used in the present study are summarized in [Table 1](#). Conditions (1) and (2) have the same fuel/oxygen concentration ratios for both HO₂ and H₂O₂ measurements. In Condition (3), fuel and oxygen concentration are adjusted to increase H₂O₂ signal for the MBMS measurements.

2.2. Quantitative laser measurement of HO₂

FRS is used in this study for *in situ* quantification of HO₂ using its unique paramagnetic property. In FRS, a linearly polarized laser beam is spatially overlapped with an oscillating magnetic field that is applied to the gas flow at the reactor exit containing HO₂. Through the resonant Faraday Effect, the optical transitions of HO₂ are

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