A comprehensive kinetic model for Dimethyl ether and Dimethoxymethane oxidation and NOx interaction utilizing experimental laminar flame speed measurements at elevated pressure and temperature

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Supplementary material is available
Abstract

Laminar flame speeds of dimethyl ether and dimethoxymethane at pressures from 1 to 5 bar and initial temperatures from 298 to 373 K were determined experimentally using a constant volume spherical vessel and a heat flux burner setup. This study is the first to report dimethoxymethane laminar flame speeds at a pressure higher than 1 bar. Using these experimental data along with data available in the literature, a new kinetic model for the prediction of the oxidation behavior of dimethyl ether and dimethoxymethane in freely propagating and burner stabilized premixed flames, in shock tubes, rapid compression machines, flow reactors, and a jet-stirred reactor has been developed. The experimental results from the present work and literature are interpreted with the help of the derived kinetic model. This newly developed reaction mechanism considers the redox chemistry of NOx to accommodate the influence of the oxygen level on the onset of fuel conversion and interconversion of NO and NO2. The current model suggests that an increased O2 level promotes the HO2 production, which in turn leads to the formation of OH radicals, which promotes the combustion of the fuel/air mixture under lean conditions. The increase of OH radical concentrations is mainly via the NO/NO2 interconversion reaction channel, NO+HO2=NO2+OH, NO2+H=NO+OH, CH3OCH3+NO2=CH3OCH2+HONO, followed by the thermal decomposition of HONO. This work extends the kinetic database and helps to improve the understanding of dimethyl ether and dimethoxymethane combustion behavior. The kinetic model presented in this work can serve as a base model for hydrocarbons and oxygenated fuels higher than C2.

Keywords: Dimethyl ether, Dimethoxymethane, laminar flame speed, kinetic modeling, NOx
1. Introduction

Compression ignition (CI) engines are still facing the challenge of a trade-off between emission control for oxides of nitrogen (NO\textsubscript{x}) and particulate matter (PM), which are harmful to the environment and human health [1,2]. In addition, transport sectors have significant challenges to mitigate greenhouse gas emissions for transitioning towards low-carbon mobility. To this end, oxygenated alternative fuels can help in reducing carbon footprint by optimizing the engine-fuel system for a sustainable future. Dimethyl ether (DME, CH\textsubscript{3}OCH\textsubscript{3}) is one of the attractive oxygenated alternative fuels, which is non-toxic, and burns cleanly. In addition, its high cetane value (e.g., 55-60) and quiet combustion [3], as well as its inexpensive fueling system, make it a promising diesel alternative fuel that could meet increasingly stringent environmental regulations. Because it lacks carbon-to-carbon bonds, the use of DME as an alternative to diesel can eliminate particulate matter emissions, and thus its use as a transportation fuel may negate the need for costly diesel particulate filters. Experimental studies show that diesel engines fueled with DME can achieve high thermal efficiency and ultra-low emissions [3,4]. As a blend, the influence of DME-Diesel blends on the emission characteristics of a naturally aspirated Diesel engine has been investigated by several researchers before [5–7]. It has been observed that DME-Diesel blends produce less soot compared to neat Diesel fuel, which can be attributed to the higher oxygen content of DME. NO\textsubscript{x} emissions were observed to be lower by adding DME in Diesel, while HC and CO emissions exhibited an increasing trend [5]. However, there are some disadvantages of using DME. Using DME as a blend to Diesel fuel increases the vapor pressure, lowers the fuel viscosity [5] and may result in reduced solubility at lower temperatures [5,8]. To counteract a possible vapor lock due to the higher vapor pressure, the engine’s fuel supply system has to be modified. The lower viscosity leads to a change in injection
spray behavior, which results in a further modification in the injection system [9,10]. Therefore, other oxygenates with lower vapor pressure and higher viscosity are more attractive as diesel fuel additives.

Poly(oxyethylene) dimethyl ethers (POMDMEs) with the general empirical formula CH$_3$–O–(CH$_2$–O)$_n$–CH$_3$ are also attractive as alternative fuels as their larger molecular structure results into low vapor pressures and high viscosity as compared to DME [11]. They also have the potential to reduce soot formation. POMDMEs are non-toxic offering the properties to be a good candidate as a co-fuel in Diesel fuel. Such blends have shown a significant reduction of soot emissions [12–14]. The presence of activated methylene groups bound to oxygen atoms (–O–CH$_2$–) in the chemical structure of the POMDMEs leads to the formation of hydroperoxides in an early stage of the combustion. These hydroperoxides decompose into OH-radicals which subsequently degrade soot precursors by oxidative processes [15,16]. The study form [13,17] also found that the reduction of particulate matter correlates with the oxygen content and not with the chemical nature of the oxygen-containing species. The number of oxymethylene groups ($n$) influences the properties of the fuel. As $n$ is increased, the cetane number rises, and diesel-like boiling point temperatures can be reached [11,18]. The above discussion leads to the conclusion that POMDMEs are more suitable candidates compared to DME. The POMDME with $n = 1$ is dimethoxymethane, CH$_3$–O–CH$_2$–O–CH$_3$, (DMM), also called methylal, which is also discussed as Diesel fuel additive [8,19]. Experiments have shown that using blends of DMM and diesel fuel still requires engine modifications [19]. However, POMDME with $n = 2$–5 blended with diesel fuel can be used without requiring to modify the engine’s infrastructure [20]. Due to their physical properties, POMDMEs ($n > 1$) can overcome the disadvantages of DME or DMM related to blending fuels [11]. DMM is
the smallest member of the POMDMEs family, and understanding its chemistry forms the base to characterize the combustion kinetics of higher POMDME \(n > 1\).

The oxidation chemistry of DME has been extensively studied (see Rodriguez et al. [21]). In CI engines exhaust products are often recirculated to the combustion chamber. The use of oxygenated fuels in the CI engine in neat or as additive requires the study on fuels and NO\(_x\) interaction. In our previous work [22] we studied the methanol/ethanol/NO\(_x\) interaction. In this study, we investigate the DME/NO\(_x\) system taking into account the available experimental data from the literature. Unlike DME, the combustion behavior of DMM has yet to be rigorously explored experimentally and theoretically. There are only a few studies reported in the literature which mainly focused on a single reactor at particular conditions [23]. Here, we briefly review some of the earlier and more recent works on DMM which are summarized in Table 1: Daly et al. [24] performed experiments in a jet-stirred reactor to study the oxidation of DMM. The kinetic model developed in their work mainly relied on the estimated rate parameters obtained from the analog to similar reactions of hydrocarbons, dimethyl ether, and diethyl ether. Dias et al. [25] studied fuel-lean and fuel-rich burner stabilized premixed DMM/oxygen/argon flames and used these data to develop and validate their model. Sun et al. [26] studied the influence of DMM and dimethyl carbonate (DMC) blending on species formation in an ethane premixed flame in addition to the neat DMM premixed flame study. They also constructed a kinetic model based on the earlier published literature targeting modeling of the flames data only.

Zhang et al. [27] reported ignition delay times (IDTs) of DMM/O\(_2\)/Ar obtained in a shock tube (ST). They used two DMM mechanisms [25,28] from literature to model their experimental data but neither of the mechanism could satisfactorily predict the IDTs. Oxidation of DMM in a plug flow reactor at atmospheric and high pressures was studied by Marrodán et al. [29,30]. They
constructed the kinetic model for DMM oxidation based on their previous study and published literature [25]. Their study further suggests that DMM chemistry is not yet fully understood.

Recently, Vermeire et al. [23] studied the pyrolysis and oxidation of DMM experimental in a jet-stirred reactor. They performed a theoretical study for relevant peroxy species related to dimethoxymethane. Further, they calculated the thermodynamic properties of those peroxy species as well as rate parameters for important reactions and developed a kinetic model. Similarly, Sun et al. [31] performed an experimental and modeling study of DMM oxidation in a jet-stirred reactor. They validated their model against their experimental data but did not validate against the other experimental data available from the literature. In 2019, Jacobs et al. [32] performed an experimental and modeling study of DMM auto-ignition timing in a shock tube and rapid compression machine (RCM). The developed model was validated against a wide range of experimental data including their work and other published experiments. In general, their work showed a good agreement against measurements. However, the model from their study was not validated against the speciation in flames.

To our knowledge, the only reported DMM laminar flame speed measurements to date are from the work of Gillespie [33]. Laminar flame speed experimental data for DME at higher pressure (engine relevant condition) are scare. In general, the experimental database for DMM is not yet broad enough. Recently, there have been various experimental studies on DMM which can be used to improve the development and validation of DMM models. Uncertainties are found in the rate kinetic data as well as in the thermochemistry. Further experimental data are needed to allow further improvements of the kinetic models and enhance the understanding of DMM kinetics. Recent experimental studies, including our present work, which can be used for model development and validation of DME and DMM reaction kinetics, are summarized in Table 1.
There is no generally applicable kinetic model for DME and DMM combustion also covering NO\textsubscript{x} chemistry over a wide range of experimental conditions. This clearly identifies the need for an in-depth analysis of DME/DMM – NO\textsubscript{x} chemistry interactions.

The aim of the present work is thus twofold:

1) To conduct laminar flame speed measurements of DME and DMM at elevated pressures and temperatures, which will extend the existing database, thus allowing model improvement and development reliably. Moreover, for the first time, DMM laminar flame speeds at higher pressure are provided.

2) To extend our recently published mechanism [34] for predicting the combustion behavior of DME and DMM and the NO\textsubscript{x} effects on the overall oxidation kinetics.

This work is an ongoing effort to develop a reliable and comprehensive mechanism for fuel/NO\textsubscript{x} interaction. In addition, the model derived in this work is thoroughly tested against a large data pool comprising of laminar flame speeds (LFS), ignition delay times (IDT), speciation in jet-stirred reactors (JSR), plug flow reactors (PFR), and burner stabilized flames (BSF). The development and compilation strategy for our baseline mechanism is described in our previous work [35]. The present study is conducted in a similar manner aiming to construct a robust and reliable kinetic model for combustion modeling application.
Table 1: Summary of the experimental studies pertinent to DME and DMM. Only the DME data obtained during this work are listed below (see Rodriguez et al. [24] for a comprehensive summary of DME literature data).

<table>
<thead>
<tr>
<th>Experimental devices</th>
<th>Measured properties</th>
<th>Experimental conditions</th>
<th>Model</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat flux burner and Constant volume vessel</td>
<td>Laminar flame speed</td>
<td>1.5 bar, 298 - 373 K, $\phi = 0.6 - 1.9$ for DME/air</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Heat flux burner</td>
<td>Laminar flame speed</td>
<td>1 bar, 373 K, $\phi = 0.8 - 1.2$ for DME/CH$_4$/air</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Heat flux burner</td>
<td>Laminar flame speed</td>
<td>1 atm, 298 - 358 K, $\phi = 0.6 - 1.85$ for DMM/air</td>
<td>No</td>
<td>Gillespie [33]</td>
</tr>
<tr>
<td>Heat flux burner and Constant volume vessel</td>
<td>Laminar flame speed</td>
<td>1.5 bar, 298 - 373 K, $\phi = 0.6 - 1.85$ for DMM/air</td>
<td>Yes</td>
<td>This work</td>
</tr>
<tr>
<td>Flow reactor</td>
<td>Speciation</td>
<td>20-60 bar, 373 - 1073 K, $\phi = 0.05 - 1.428$ for DMM/O$_2$/N$_2$</td>
<td>Yes</td>
<td>Marrodán et al. [29]</td>
</tr>
<tr>
<td>Flow reactor</td>
<td>Speciation</td>
<td>1 atm, 573 - 1373 K, $\phi = 0.028 - 2.5$ for DMM/O$_2$/N$_2$</td>
<td>Yes</td>
<td>Marrodán et al. [30]</td>
</tr>
<tr>
<td>Jet stirred reactor</td>
<td>Speciation</td>
<td>5.07 bar, 800 - 1200 K, $\phi = 0.444 - 1.778$ for DMM(0.15% mol)/O$_2$/N$_2$, $\tau = 2.83$ s</td>
<td>Yes</td>
<td>Daly et al. [24]</td>
</tr>
<tr>
<td>Jet stirred reactor</td>
<td>Speciation</td>
<td>1.07 bar, 500 - 1100 K, for DMM (1% mol)/O$_2$/He, $\tau = 2.83$ s</td>
<td>Yes</td>
<td>Vermeire et al. [23]</td>
</tr>
<tr>
<td>Jet stirred reactor</td>
<td>Speciation</td>
<td>0.986 and 10 atm, 460 - 1200 K, $\phi = 0.2 - 1.5$ for DMM (2% mol)/O$_2$/Ar and DMM (1% mol)/O$_2$/N$_2$, $\tau = 3$ and 0.7 s</td>
<td>Yes</td>
<td>Sun et al. [31]</td>
</tr>
<tr>
<td>Jet stirred reactor</td>
<td>Speciation</td>
<td>1.0 atm, 500 - 1100 K, for DMM (0.5% mol)/O$_2$/Ar, $\tau = 2.0$ s</td>
<td>Yes</td>
<td>Gao et al. [36]</td>
</tr>
<tr>
<td>Shock tube</td>
<td>Ignition delay time</td>
<td>2 - 10 atm, 1103 - 1454 K, $\phi = 0.5 - 2.0$, for DMM/O$_2$/Ar</td>
<td>No</td>
<td>Zhang et al. [37]</td>
</tr>
<tr>
<td>Shock tube</td>
<td>Ignition delay time</td>
<td>2 - 10 atm, 1100-1600 K, $\phi = 1.0$, for DMM/O$_2$/Ar</td>
<td>Yes</td>
<td>Hu et al. [38]</td>
</tr>
<tr>
<td>Shock tube and Rapid compression machine McKenna Burner</td>
<td>Ignition delay time</td>
<td>1-40 bar, 590-1215 K, $\phi = 1.0$, for DMM/air</td>
<td>Yes</td>
<td>Jacobs et al. [32]</td>
</tr>
<tr>
<td>McKenna Burner</td>
<td>Speciation</td>
<td>5 kPa, 298 K, $\phi = 0.24$ and 1.72 for DMM/O$_2$/Ar</td>
<td>Yes</td>
<td>Dias et al. [25]</td>
</tr>
<tr>
<td>McKenna Burner</td>
<td>Speciation</td>
<td>4 kPa, 298 K, $\phi = 2.0$ for DMM (25% mol)/O$_2$/Ar</td>
<td>Yes</td>
<td>Sun et al. [26]</td>
</tr>
</tbody>
</table>
2. Experimental Investigations

Laminar flame speeds of DME/air and DMM/air were experimentally investigated at two different facilities: Technische Universität Bergakademie Freiberg (TU-Freiberg) and King Abdullah University of Science and Technology (KAUST). At TU-Freiberg a Heat Flux burner (HFB) was utilized while in KAUST a constant volume spherical vessel (CVSV) setup was used. Details of the experiments are described below.

**HFB at TU-Freiberg**: The adiabatic laminar flame speed was investigated by a Heat Flux burner, which was initially proposed by de Goey et al. [39]. This method is based on the compensation of heat loss for flame stabilization by a heat influx to the inflowing fuel-air mixture while passing the heated burner plate (perforated with a porosity of 0.46). Thus, as the main advantage, a stabilized flat flame is generated at which the laminar flame speed, LFS, is measured under quasi adiabatic conditions [40]. A detailed description of the Heat Flux test rig, including the evaluation of uncertainties and the process of data analysis, can be found elsewhere [41–43]. The experimental methodology of the present work is outlined in the following. A piston accumulator was used as a tank to investigate the LFS of the liquid fuel DMM. Furthermore, the fuel was accurately dosed with high precision by employing a mini core-Flow type (Bronkhorst M12V14I model) mass flow controller. The liquid fuel was then converted into the gas phase in the direct evaporator (aSTEAM DV-4 from aDROP). To avoid condensation, all the lines downstream of the evaporator were equipped with heating tape. A thermal Mass Flow Controller (MFC, type EL-FLOW) from Bronkhorst was used to introduce air. The fuel-air mixture was conditioned in a heating bath to the desired preheating temperature of the unburned gas mixture and was fed into the tempered premixing chamber of the burner.
A second heating bath was used to preheat the burner plate to a temperature $\Delta T = 70$ K above the unburned gas mixture temperature. The burner plate was isolated from the downstream part of the burner by a ceramic seal. This temperature gradient compensates the heat losses of the flame and therefore creates a quasi-adiabatic flame.

In addition, two mass flow controllers were used for dosing the gaseous DME and methane that were also investigated in this study. The initial gas temperatures varied between 300 K and 373 K. DME and DMM were provided by ASG Analytik and had purities of >99.8 %. The Heat Flux method aims to stabilize an adiabatic flame above the burner plate, which is characterized by a constant radial temperature profile. Thus, the parabolic coefficient, $C$ equals zero. In this state, the unburned gas velocity and LFS are identical. A detailed description of the procedure and all correlations between the parameters are given by Bosschaart and de Goey [44]. To determine the temperature profile of the burner plate, eight type T thermocouples (class 1) were used. About 350 single measurements in the near adiabatic region were taken into account to calculate five C-Values with their corresponding inlet velocities. Linear interpolation was used to determine the unburned gas velocity at which the C value equals zero.

**CVSV at KAUST:** The CVSV has an inner diameter of 330 mm and is equipped with two orthogonal pairs of quartz windows of 120 mm diameter. The initial temperature of the mixture was recorded at two different locations inside the vessel to assure the thermal homogeneity of the mixture. The DMM or DME and dry air mixture were prepared in the vessel according to the required partial pressures of the gaseous components. The required amount of liquid DMM was injected inside the vessel using a gas-tight micro-syringe under vacuum, while the gaseous DME was injected directly inside the chamber through the inlet valve. Mixtures were ignited by using two spark electrodes (1.2 mm diameter), forming a V-shape configuration at the center of the
vessel with a 1 mm gap. The average spark ignition energy was set to 24 mJ. Flame propagation was recorded by schlieren photography with a high-speed camera (Photron; FastCam Ultima APX 120K) at 4000 fps and 512×512 pixels. For the spherically propagating laminar flames, the propagating flame speed, $S_n$, is evaluated as $S_n = \frac{dR_f}{dt}$, where $R_f$ is the schlieren flame radius, and $t$ is time. The spherical propagating flame is subjected to flame stretch, and thus $S_n$ represents the stretched laminar flame speed. The stretch rate in spherical flame, $\kappa$, is defined as: $(1/A) \frac{dA}{dt} = \frac{2}{R_f} S_n$, where $A$ is the flame surface area. Various correlations between $S_n$ and $\kappa$ have been proposed to estimate the unstretched flame speed, $S_s$. A non-linear relationship \cite{45} was found to be most appropriate for extracting $S_s$ from the measured data using the following correlation: 

\[(S_u/S_s)^2 \ln(S_u/S_s)^2 = -2L_b \kappa/S_s,\]  

where $L_b$ is the burned gas Markstein length. In this correlation, $S_s$ and $L_b$ can be deduced from the linear extrapolation in a plot of $\ln(S_u)$ versus $\kappa/S_n^2$. After extracting $S_s$, the un-stretched laminar flame speed, $S_L$, is obtained by the mass balance over $S_s$ as $S_L = S_s/\sigma$, where $\sigma$ is the expansion coefficient, i.e., the ratio of the unburnt mixture density, $\rho_u$, to the burnt gas density, $\rho_b$.

3. Kinetic modeling

The mechanism proposed here extends our recent work \cite{34}, which was developed to predict nitromethane (CH$_3$NO$_2$) pyrolysis, oxidation, and NO$_x$ chemistry interaction. Our mechanism \cite{34} was validated for C$_1$-C$_2$ fuels e.g., methane (CH$_4$), acetylene (C$_2$H$_2$), ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$), methanol (CH$_3$OH), acetaldehyde (CH$_3$CHO) and ethanol (C$_2$H$_5$OH) and also for ammonia (NH$_3$) over a wide range of experimental conditions. We demonstrated that the kinetic model satisfactorily captured the oxidation kinetics of C$_1$ - C$_2$ hydrocarbon/oxygenated - NO$_x$ chemistry interaction as well as NO formation in C$_1$ - C$_2$ premixed flames. The currently developed mechanism is based on the earlier published literature (modeling, experimental and theoretical).
along with the NO$_x$ sub-mechanism to include cross-reactions between nitrogen and carbon species. The detailed mechanism describing the oxidation of DME was included in our recent work [34]; however, validation against experimental data was not presented. Therefore, this study aims to validate the DME chemistry provided in the literature. The elementary reactions in the DME sub-mechanism are compiled from several contributions [46–61]. Additional cross-reactions between carbon and nitrogen chemistry, which are essential for DME/NO$_x$ interaction, are also included (see the list in Table 2).

Table 2: List of crucial cross-reactions between carbon and nitrogen family to accommodate DME/NO$_x$ interaction.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OCH$_3$-DME+NO=CH$_3$OCH$_2$+HNO</td>
<td>[62]</td>
</tr>
<tr>
<td>CH$_3$OCH$_3$-DME+NO$_2$=CH$_3$OCH$_2$+HONO</td>
<td>[62]</td>
</tr>
<tr>
<td>CH$_3$OCH$_2$+NO$_2$=CH$_3$OCH$_2$O+NO</td>
<td>[62]</td>
</tr>
<tr>
<td>CH$_3$OCH$_2$O+NO$_2$=CH$_3$OCHO+HONO</td>
<td>[62]</td>
</tr>
<tr>
<td>CH$_3$OCH$_2$O+NO=CH$_3$OCO+HNO</td>
<td>[62]</td>
</tr>
<tr>
<td>CH$_3$OCH$_2$O$_2$+NO=CH$_3$OCH$_2$O+NO$_2$</td>
<td>[63]</td>
</tr>
<tr>
<td>CH$_3$OCH$_2$O$_2$+HONO=CH$_3$OCH$_2$O$_2$H+NO$_2$</td>
<td>[62]</td>
</tr>
<tr>
<td>CH$_3$CO$_3$+NO=CH$_3$CO$_2$+NO$_2$</td>
<td>[64]</td>
</tr>
</tbody>
</table>

The main aim of this work is to include DMM (CH$_3$OCH$_2$OCH$_3$) species as a fuel and to extend the validation range of our nitrogen chemistry. The inclusion of this species and their reactions have required updates to the previous model. The complete reaction mechanism is provided in the supplementary material (SM).
A detailed description of the DMM sub-mechanism, which is included in the present work (pw), and the adaptation of the rate parameters are briefly explained below, highlighting the important reactions and their kinetics.

3.1 DMM sub-mechanism:

Unlike DME kinetics, the rate constants of the elementary reactions involved in DMM chemistry have not been studied extensively experimentally and/or theoretically. Most of the reaction rate parameters used in DMM sub-mechanism stem from the recent modeling studies [23,31,32,65] which were estimated using the analogy with DME or diethyl ether (DEE). In this work, the DMM sub-mechanism is built by utilizing the published models.

During the initial stage of pyrolysis, DMM can undergo dissociation or decomposition thermally via six possible channels, which are listed below:

\[
\begin{align*}
\text{CH}_3\text{OCH}_2\text{OCH}_3(+\text{M}) &= \text{CH}_3\text{OCH}_2\text{O}+\text{CH}_3(+\text{M}) \quad \text{(r1)} \\
\text{CH}_3\text{OCH}_2\text{OCH}_3(+\text{M}) &= \text{CH}_3\text{OCH}_2+\text{CH}_3\text{O}(+\text{M}) \quad \text{(r2)} \\
\text{CH}_3\text{OCH}_2\text{OCH}_3(+\text{M}) &= \text{CH}_3\text{OH}+\text{CH}_3+\text{HCO}(+\text{M}) \quad \text{(r3)} \\
\text{CH}_3\text{OCH}_2\text{OCH}_3(+\text{M}) &= \text{CH}_3\text{OCH}_3\text{-DME}+\text{CH}_2\text{O}(+\text{M}) \quad \text{(r4)} \\
\text{CH}_3\text{OCH}_2\text{OCH}_3 &= \text{CH}_3\text{OCH}_2\text{OCH}_2+\text{H} \quad \text{(r5)} \\
\text{CH}_3\text{OCH}_2\text{OCH}_3 &= \text{CH}_3\text{OCHOCH}_3+\text{H} \quad \text{(r6)} \\
\end{align*}
\]

The reaction rate parameter of r1 is taken analogous to \(\text{CH}_3\text{OCH}_3(+\text{M})=\text{CH}_3\text{O}+\text{CH}_3(\text{M})\) [46]. Rate parameters of the reaction r2, producing methoxymethyl (\(\text{CH}_3\text{OCH}_2\)) and methoxy (\(\text{CH}_3\text{O}\)) radical, is are assumed to be similar to \(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3=\text{CH}_3\text{CH}_2\text{O}+\text{CH}_3\text{CH}_2\) [66]. Further, the reaction rate parameters of the reaction r3 were adopted from the work of [32] which was obtained by analogy with DEE thermal dissociation channel producing ethane and ethanol. In the experimental and modeling study of Hu et al. [38], this reaction (r3) was found to be the most important
promoting oxidation kinetics of DMM. This reaction was also identified to be among the important reactions in the work of Jacobs et al. [32] at higher temperatures. In recently published models, this reaction was not taken into account [23,65]. The reaction rate of r4 is adopted from the work Sun et al. [65] who obtained this rate parameter via analogy from the DEE model of [66].

Furthermore, the other possible channels are the H-loss from primary and secondary carbon sites of DMM (reaction r5 and r6), the rate parameters of which are adopted from the modeling work of [32].

DMM can also undergo H-atom abstraction by radicals H, OH, O, CH₃, CH₃O, CH₃O₂, CH₂OH, OCHO, CH₂OCHO, CH₃OCO, CH₃OCH₂, and O₂. The abstraction of an H-atom can occur either at the terminal methyl group, leading to the formation of radical CH₃OCH₂OCH₂ (R1) or at the central methylene group leading to the formation of radical CH₃OCHOCH₃O (R2).

The rate constants for the H abstraction from DMM by H-atom

$$\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{H} = \text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{H}_2 \quad (r7)$$

$$\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{H} = \text{CH}_3\text{OCHOCH}_3 + \text{H}_2 \quad (r8)$$

was computed by Kopp et al. [67] using a high-level ab-initio/statistical rate theory calculations over a temperature range of 500 - 2000 K showing a branching ratio of 0.372 for $k_{r7}/k_{r8}$. This reaction was also experimentally studied by Golka et al. [68] in a shock tube and proposed a rate constant at a temperature range of 850 – 1100 K. The reported total rate constant was factor 5 higher than that of Kopp et al. [67] theoretical predictions. For this work, we adopted the rate parameters from Kopp et al. [67] that are valid for a wider temperature range. However, we note here that the discrepancy between the results of two recent studies warrants more future experimental investigation. The rate constant of H-atom abstraction by OH radical

$$\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{OH} = \text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{H}_2\text{O} \quad (r9)$$
\[ \text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{OH} = \text{CH}_3\text{OCHOCH}_3 + \text{H}_2\text{O} \quad (\text{r10}) \]

is adopted from the theoretical work (temperature range 200 - 3000 K) of He et al. [69]. The rate constant of this reaction was recently studied experimentally by Bänsch and Olzmann [70] in a flow reactor over 297-570 K who reported deviations above 400 K (lower rate constant) in comparison with other published values. The reaction of DMM with OH is one of the essential reactions in predicting accurately the ignition delay time as well as speciation in jet-stirred and flow reactors. DMM does not exhibit such a pronounced negative temperature coefficient (NTC) region as shown by DME (see section 5). However, the branching ratio of this reaction was found to have a pronounced effect in the NTC region during DMM oxidation. The rate constant of H-atom abstraction by CH₃ radical is adopted from Kopp et al. [67]. Similarly, rate parameters of H-atom abstraction reactions by O₂, O, HCO, CH₂O, CH₂OH, CH₃OCO, CH₂OCHO, and CH₃OCH₂ is adopted from the modeling work of Vermeire et al. [23]. The reaction of DMM with HO₂

\[ \text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{HO}_2 = \text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{H}_2\text{O}_2 \quad (\text{r11}) \]

\[ \text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{HO}_2 = \text{CH}_3\text{OCHOCH}_3 + \text{H}_2\text{O}_2 \quad (\text{r12}) \]

were found to be the most sensitive reaction in predicting the speciation history of DMM oxidation in jet-stirred and flow reactors. In this study, we adopted the rate parameter of this reaction from the modeling work of He et al. [69] which provided better results for a wide range of experimental conditions investigated. In addition, reactions

\[ \text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{CH}_3\text{O} = \text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{CH}_3\text{O}_2\text{H} \quad (\text{r13}) \]

\[ \text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{CH}_3\text{O} = \text{CH}_3\text{OCHOCH}_3 + \text{CH}_3\text{O}_2\text{H} \quad (\text{r14}) \]

were also very sensitive in predicting the ignition delay times, particularly during transitioning from low to intermediate temperature region. The rate parameter of this reaction is adopted from
the modeling work of Sun et al. [31] and is increased by factor 2 for better agreement with the experimental ignition delay times.

The formed radicals R1 and R2 from the above process can also undergo thermal dissociation *via* the following reactions

\[
\text{CH}_3\text{OCH}_2\text{OCH}_2/\text{CH}_3\text{OCHOCH}_3 = \text{CH}_3\text{OCH}_2 + \text{CH}_2\text{O}
\]

\[
\text{CH}_3\text{OCH}_2\text{OCH}_2/\text{CH}_3\text{OCHOCH}_3 = \text{CH}_3\text{OCHO} + \text{CH}_3.
\]

Radical R1 and R2 can also isomerize \(\text{CH}_3\text{OCH}_2\text{OCH}_2 = \text{CH}_3\text{OCHOCH}_3\). The rate parameters of these reactions are adopted from the theoretical and modeling work [32].

For the low-temperature chemistry of DMM, we followed the reaction classes suggested by Jacobs *et al.* [32] which are mainly based on literature. The complete low-temperature chemistry (reaction classes from 7 to 21) and their reaction rate parameters for DMM are also adopted from the modeling work of [32].

The complete mechanism is composed of 173 species and 1381 reversible reactions.

4. **Thermochemistry and transport properties**

The thermochemistry and transport properties of the species in the mechanism remains the same as in our previous study [34]. The thermochemistry and transport properties of the additional species in the DMM sub-mechanism are adopted from [32].

5. **Results and Discussion**

The DME/DMM/NO\(_x\) kinetic model compiled in this study has been validated against a large set of experimental data that includes the newly measured data in the present work and literature data. The validation targets include: laminar flame speeds, ignition delay times, speciation in jet-stirred and flow reactors, as well as premixed burner stabilized flames. To our knowledge, this is the first study that investigates the complete oxidation kinetics of DME, DMM and NO\(_x\) interaction in a
multi set-up approach. In the sections below, the lines in each figure represent the simulation results of the present kinetic model; whereas the symbols represent experimental data unless stated differently. All simulations were performed using the LOGEresearch v1.10.0 [71] software package.

5.1 Laminar flame speed

5.1.1 DME and DME/CH\textsubscript{4} laminar flame speed

Figure 1 displays the laminar flame speed data of DME/air for varying equivalence ratio (\(\phi\)). Figure 1a shows the laminar flame speed at 1 atm and 298 K. As can be seen, our kinetic model excellently predicts our experimental data including the literature data for fuel-lean and stoichiometric conditions while slightly overpredicting for fuel-rich conditions. However, the modeling results agree well with the measurements from Qin 2005 [72] and Song 2013 [73] towards fuel-rich conditions. Experiments show the maximum flame speed at \(\phi = 1.1\) and the model predicts the same. The flame speeds obtained in this work show excellent agreement with literature data.

Similarly, Figure 1b shows the laminar flame speed at 3 bar, 5 bar, 5 atm, and 10 atm respectively. The model (from this work) captures the experimental trends from lean to stoichiometric conditions very well. At 3 and 5 bar the model slightly underpredicts the laminar flame speed at \(\phi = 0.8-1.2\) but shows much better agreement at the rich side for 5 bar. Comparing Figure 1a and Figure 1b at \(\phi = 1.0\) it is found that laminar flame speed of DME/air is decreased by 35.5\% at 5 bar compared to the data at 1 bar. Experimental data at 10 atm from de Vries et al. 2011 [74] and Qin et al. 2005 [72] contradict each other, while our model closely agrees with the measurements from Qin et al. 2005 [72].
Figure 1: Laminar flame speed of DME/air at 298 K and 1 atm (a), at 5 and 10 atm (b). Symbols: present work (pw) and from published literature [72–81]. Lines: this work. In Fig. (a) present work is conducted at 1 bar while literature reported data are either taken and 1 bar or 1 atm.

Figure 2 illustrates the laminar flame speed of DME/air at 1 bar and 373 K from present work together with the model prediction. It can be observed in Figure 2 that model predictions are in excellent agreement with the measurement from fuel-lean to stoichiometric conditions, but slightly over-predicts at the fuel-rich side. However, the model follows the experimental trend very well for all $\phi$. Furthermore, comparing Figure 1a and Figure 2 at $\phi = 1.0$ it is found that an increase in temperature of 75 K increases the laminar flame speed by factor 1.42. The results of additional model validation for DME/air for different pressures and temperatures are further illustrated in SM (Figs. S1 and S2)
Figure 2: Laminar flame speed of DME/air at 1 bar and 373 K. Symbols: present work. Line: this work.

To outline important reactions for DME/air laminar flame speeds, a reaction sensitivity analysis is conducted which is presented in Figure 3 for $\phi = 1.1$ at 298 K and different pressure (1, 3 and 5 bar respectively). The 15 most sensitive reactions are shown; positive sensitivity means reaction promotes the reactivity (enhances the flame speed) and negative sensitivity means the reaction retards the reactivity (decreases flame speed).

Interestingly it can be observed in Figure 3 that most of the sensitive reactions appear from the core H$_2$/CO mechanism. The chain branching reaction from the hydrogen chemistry ($O_2$+H=OH+O) is the most sensitive reaction for all three pressure. Furthermore, the majority of reactions show a decreasing sensitivity trend with an increase in pressure. While reactions: H+OH+M=H$_2$O+M, CH$_3$+H(+M)=CH$_4$(+M) and H+O$_2$(+M)=HO$_2$(+M) which are chain-terminating show an increasing sensitivity trend.
Figure 3: Normalized reaction sensitivity analysis for DME/air laminar flame speed at $\phi = 1.1$, pressure of 1, 3 and 5 bar, and 298 K.

Moreover, in this study, we also present laminar flame speed measurements of DME/CH$_4$/air blends at three different equivalence ratios ($\phi = 0.8, 1.0$ and 1.2) at 1 bar and 373 K. Figure 4 shows the laminar flame speed of DME/CH$_4$/air blend as a function of DME concentration in the fuel stream. It can be observed that for $\phi = 0.8$ and 1.0 the model is in close agreement with the measurements as the DME concentration in the fuel stream is increased. The model over predicts the flame speed by $\sim 6\%$ for $\phi = 1.2$. We note that in this work, no attempt is made to optimize the model targeting DME/CH$_4$ blend.
Figure 4: Laminar flame speed of DME/CH₄/air at 1 bar and 373 K and various DME concentration (by vol%) in DME/CH₄ blend. Symbols: present work. Line: this work.

5.1.2 DMM laminar flame speed

Figure 5 shows the laminar flame speed measurements for DMM/air at 1 bar and 373 K (a) and 298 K at three different pressure (1, 3 and 5 bar) (b) obtained in this work along with the model predictions.

In Figure 5a, it can be observed that the model predictions are in excellent agreement with measurements for all equivalence ratios investigated. The experiments show peak flame speeds at $\phi = 1.2$ for both temperatures. For DME/ air the peak flame speed position was measured at $\phi = 1.1$ (Figure 1a and Figure 2). However, for DMM/air, the model suggests the peak flame speed at $\phi = 1.15$. It should be noted that laminar flame speed at $\phi = 1.15$ was not measured in the present work. Comparing laminar flame speed (experimental data from present work) of DME/air and DMM/air at $\phi = 1.0$ for 298 and 373 K (Figure 1a, 2 and 5a), we do not find any difference in the flame speed of these two fuels (for DME/air it is $43.16\pm0.96$ and $61.38\pm1.31$ cm/s, and for DMM/air it is $42.98\pm0.05$ and $59.79\pm1.54$ cm/s respectively) which are within the experimental uncertainty.

Figure 5b displays the laminar flame speed of DMM/air at 298 K and 1, 3 and 5 bar respectively. It can be observed that at 3 and 5 bar and $\phi = 1.2$ the model underpredicts the laminar flame speed.
by 8.6% and 11.1% respectively. Furthermore, laminar flame speed of DMM/air decreases as pressure increases with a similar trend as observed for DME/air in Figure 1b. Laminar flame speed of DMM/air decreases by 21.5% and 32% at 3 and 5 bar respectively compared to 1 bar. The influence of pressure on decreasing the laminar flame speed is reduced as the pressure increases (see Figure 5b). We note that this study is the first to report the laminar flame speed of DMM/air above 1 bar.

Figure 6 compares the model prediction against the experimental data from the present work and literature. Figure 6a shows the laminar flame speed of DMM/air at $\phi = 1.2$ and 1 bar as a function of temperature. It can be observed that the model slightly overpredicts the flame speed but is within the error margins of the experiment. Similarly, Figure 6b shows the laminar flame speed of DMM/air as a function of equivalence ratio at different temperatures. It can be observed in this figure that measurements from this work (at 298 K) are in excellent agreement with the measurements from Gillespie et al. [33] showing the reliability of the present measurements. Furthermore, the model predictions agree with the measurements for the whole range of equivalence ratio and temperatures investigated. It can also be observed in Figure 6 that with an increase in the initial temperature the laminar flame speed also increases.

Furthermore, to explore the important reactions for predicting the laminar flame speeds of DMM/air, a sensitivity analysis was performed at varying pressures. Figure 7 displays the normalized reaction sensitivity for the top 15 reactions at $\phi = 1.1$, 298 K and 1, 3 and 5, respectively. It can be observed that the highest sensitivity is shown by the reaction $\text{O}_2+\text{H}=\text{OH}+\text{O}$ for all the conditions. Most of the sensitive reactions and the sensitivity direction of reactions are similar to the DME/air case (in Figure 3). However, $\text{H}+\text{HO}_2=\text{H}_2+\text{O}_2$ (chain-terminating) and $\text{H}+\text{HO}_2=\text{OH}+\text{OH}$ (chain branching) reactions show increased sensitivity with increasing pressure.
(Figure 7) contrary to DME/air (Figure 3). This observation leads to the conclusion that DMM fueled flames may have more complex radical pools compared to DME. As pointed out by [15,16] that the presence of activated methylene groups bound next to oxygen atoms (–O–CH₂–) in the chemical structure of the POMDMEs leads to the formation of hydroperoxides in an early stage of the combustion. This could explain the above reactions (H+HO₂=H₂+O₂ and H+HO₂=OH+OH) showing different sensitivity compared to DME.

Figure 5: Laminar flame speed of DMM/air at 1 bar, 298 K and 373 K (a); at 1, 3 and 5 bar and 298 K (b). Symbols: present work. Lines: this work.
Figure 6: Laminar flame speed of DMM/air at 1 bar, $\phi = 1.2$, and 323 - 373 K (a); 1 bar and 298 – 373 K (b). Symbols: present work (pw) and from published literature [33]. Lines: this work.

Figure 7: Normalized reaction sensitivity analysis for DMM/air laminar flame speed at $\phi = 1.1$, 298 K and three different pressure (1, 3 and 5 bar).
5.2 Speciation in a jet-stirred reactor

5.2.1 DME oxidation in a jet-stirred reactor

Figure 8 shows the evolution of species mole fractions with temperature during the oxidation of DME under the varying JSR experimental conditions of Dagaut et al. [59]. As seen, in Figure 8a, the onset temperature of DME and O$_2$ consumption is well captured by the model. An NTC region around 600 K is observed which is more visible in the O$_2$ profile compared to DME. Also, Figure 8a-d illustrate that the current model predicts other major species (H$_2$, CO, and CO$_2$) and intermediate species (CH$_4$, C$_2$H$_4$, and C$_2$H$_6$) within the experimental uncertainty (25%) satisfactorily.

We now briefly discuss the reaction paths and the important reactions during DME oxidations under the conditions of Figure 8 at 900 K (where 60% of DME is consumed) with the help of the mass flux analysis shown in Figure 9 and the sensitivity analysis (towards DME) shown in Figure 10. In Figure 9, integrated mass flux based on C-atoms is shown (only major paths are shown). Based on the carbon atom mass flux, DME mainly undergoes H-atom abstraction (97%) reacting with OH, H and HO$_2$ radicals to CH$_3$OCH$_2$ radical. Among these, H-atom abstraction by OH radical contributes the most and the least is contributed by the HO$_2$ radicals. In line with the sensitivity analysis, these three reactions appear among the most sensitive reaction (see Figure 10). The CH$_3$OCH$_2$ radical mainly undergoes thermal unimolecular dissociation (96%) to form CH$_3$ and CH$_2$O (CH$_3$OCH$_2$=CH$_3$+CH$_2$O). The CH$_3$ radical formed can either undergo self-recombination to form C$_2$H$_6$ (34%) or react with CH$_2$O, HO$_2$, and DME to form CH$_4$ (27%, path now shown here). Interestingly the reaction CH$_4$+O$_2$=CH$_3$+HO$_2$ exhibits the highest sensitivity. The formed C$_2$H$_6$ (96%) mainly undergoes H-atom abstraction by OH to form C$_2$H$_5$. Most of the C$_2$H$_5$ (65%) formed reacts with O$_2$ to form C$_2$H$_5$O$_2$ and 22% also reacts with HO$_2$ radicals to form
C₂H₅O. Overall, the degradation of DME based on carbon atom mass flux analysis in Figure 9 leads to CH₂O as the main intermediate product. In line with the sensitivity analysis (Figure 10), the reactions involving CH₂O are also among the most sensitive reactions. Reaction flow and sensitivity analysis at 600 K (in NTC region) is also performed, the results of which are shown in Fig. S3 and Fig. S4 in SM. Unlike in the case at 900 K (Figure 9), flow analysis reveals that all of the DME (at 600 K) undergoes H-atom abstraction via OH radical to from CH₃OCH₂+H₂O and almost all of the formed CH₃OCH₂ radical (94%) undergoes O₂ addition channel. The reaction flow analysis (based on C-atom) at this temperature (600 K) can be summarized as DME →

\[ \text{CH}_3\text{OCH}_2 \xrightarrow{+\text{O}_2} \text{CH}_3\text{OCH}_2\text{O}_2 \xrightarrow{\text{isomerization}} \text{CH}_2\text{OCH}_2\text{O}_2\text{H} \xrightarrow{+\text{O}_2} \text{O}_2\text{CH}_2\text{OCH}_2\text{O}_2\text{H} \]

\[ \xrightarrow{-\text{OH}} \text{HO}_2\text{CH}_2\text{OCHO} \xrightarrow{-\text{OH}} \text{OCH}_2\text{OCHO} \rightarrow \text{HCO} (+\text{CH}_2\text{O}, +\text{HOCHO}). \]

Additional model validation of DME in a JSR is provided in SM (Fig. S7 – Fig. S10).

Figure 8: Oxidation of DME(CH₃OCH₃)/O₂/N₂ at φ = 1.0, 10 atm, and τ = 1.0 s in a jet-stirred reactor. Symbols: experimental data from [59], Lines: this model.
Figure 9: Reaction flow analysis based on C-atom during oxidation of DME/O$_2$/N$_2$ in a jet-stirred reactor for the condition shown in Figure 8 at 900 K. “therm-“ and “iso-“ means thermal dissociation and isomerization respectively.

Figure 10: Normalized reaction sensitivity at 900 K during DME/O$_2$/N$_2$ oxidation at 10 atm for the condition shown in Figure 8 towards DME.

5.2.2 DMM oxidation in a jet-stirred reactor

Figure 11 illustrates the species mole fractions (symbols) as a function of temperature measured by Sun et al. [31] during the oxidation of DMM/O$_2$/N$_2$ in a JSR at $\phi = 0.5$ and 10 atm. As we can
see in Figure 11 (b and d) CH$_2$O and CH$_3$OH are detected in an experiment before the fuel starts decomposing which is unlikely. The authors [31] did not provide any explanation regarding the early appearance of these species. To model the experiment, we added CH$_2$O and CH$_3$OH (5x10$^{-5}$ mole fraction) in the inlet mixture. The simulation without CH$_2$O and CH$_3$OH in the inlet mixture was also performed (see Fig. S11 in SM) and the model predictions are similar. As can be seen in Figure 11a, the model predicts the onset temperature of DMM consumption well. However, for temperature range from 840 to 1040 K, the model slightly overpredicts the DMM concentrations. Unlike in the case of DME oxidation (Figure 8), we do not observe the marked NTC region (see also section 5.5) for DMM. For major species, H$_2$O, H$_2$, CO, and CO$_2$ modeling results follow the experimental trend very well and are in close agreement with the measurements. It is seen in Figure 11b that the model underpredicts the peak of CH$_2$O mole fraction by ~20% but follows the experimental trend very well over the temperature range investigated. Similarly, another crucial intermediate product during DMM oxidation is methyl format (CH$_3$OCHO) and model prediction is in good agreement with the measurements. For other species in Figure 11d, it can be observed that the model accurately predicts the C$_2$H$_4$ concentration profile while overpredicts the peak CH$_4$ concentration by factor 1.8. A small peak around 870 K is observed for CH$_3$OH in the experiment while the model does not exhibit such peak and underpredicts by factor 2 at this temperature.

To explore the important reactions for DMM degradation we now briefly discuss the reaction paths for the condition shown in Figure 11 with the help of mass flux analysis (Figure 12) and reaction sensitivity analysis (Figure 13) at 900 K. In Figure 12, integrated mass flux based on C-atoms is shown (only major paths are shown). Reaction path analysis reveals DMM is exclusively consumed via H-atom abstraction (from the terminal and central carbon atom) by OH (reaction r9 and r10) and HO$_2$ (reaction r11 and r12) radical forming CH$_3$OCH$_2$OCH$_2$ (R1, 51%) and
CH₃OCHOCH₃ (R2, 48%). The former radical has the highest contribution in consuming DMM while the least is contributed by later. In line with the sensitivity analysis in Figure 13, these reactions (r₉, r₁₀, r₁₁ and r₁₁₂) are among the most sensitive reactions. Most of the R1 radical (96%) undergoes thermal dissociation to form CH₃OH₂ and CH₂O (R1 = CH₃OCH₂+CH₂O). The entire formed CH₃OCH₂ radical undergoes thermal dissociation to give CH₃+CH₂O. The minor path (4%) that consumes R1 radical is via the O₂ addition to give R1O₂ and most of the formed R1O₂ mainly isomerizes to give Q1OOH (CH₃OCHOCH₂O₂H) by H-atom transfer from the central carbon atom. Further, most of the formed Q1OOH radical (71%) undergo isomerization to form 1,3,5-trioxane (C₃H₆cy13). The formed C₃H₆cy13 reacts with OH and HO₂ radical to give methyl formate (CH₃OCHO) and methoxycarbonyl (CH₂OCO) via reactions C₃H₆cy13+OH/HO₂ = CH₃OCHO/CH₂OCO + HCO/CH₂O + H₂O/H₂O₂. The formed CH₃OCHO undergoes H-atom abstraction reacting with OH and H-atom to form CH₂OCHO and CH₂OCHO (not shown here).

During the DMM decomposition, CH₃OCHO is one of the main intermediate product. However, for both the fuels (DME and DMM) at 900 K, the highest sensitivity is exhibited by the same reaction CH₄+O₂=CH₃+HO₂ (Figure 10 and Figure 13). It can also be observed that the majority of the reactions in the sensitivity analysis (Figure 10 and Figure 13) involve OH and HO₂ radical indicating the increased importance of these radicals in the radical pool and reactions related to them.

To investigate the reaction paths and important reactions at low temperature during DMM oxidation, reaction flow and sensitivity analysis at 600 K is also performed (for the condition of Figure 11) which are shown in Figs. S5 and S6 in SM and discussed there. Additional illustrations for the model validation of DMM in a JSR are provided in the SM (Fig. S12 – Fig. S14).
Figure 11: Oxidation of DMM(CH$_3$OCH$_2$OCH$_3$)/O$_2$/N$_2$ at $\phi = 0.5$, 10 atm, and $\tau = 0.7$ s in a jet-stirred reactor. Symbols: experimental data from [31], Lines: this model. CH$_3$OH and CH$_2$O (5x10$^{-5}$ mole fraction) added in the initial mixture for simulation.
Figure 12: Reaction flow analysis based on C-atom during oxidation of DMM/O₂/N₂ in a jet-stirred reactor for the condition shown in Figure 11 at 900 K. “therm-“ and “iso-“ means thermal dissociation and isomerization respectively.

Figure 13: Normalized reaction sensitivity at 900 K during DMM/O₂/N₂ oxidation at 10 atm for the condition shown in Figure 11 towards DMM.
5.3 Oxidation of DME in presence of NO

Unlike hydrocarbon-fuel/NO\textsubscript{x} system, studies related to the oxygenated-fuel/NO\textsubscript{x} system are scarce. To our knowledge, only a few studies have systematically investigated the DME/NO\textsubscript{x} system to date [62,82–84]. As discussed earlier, the use of oxygenated fuels produces less NO\textsubscript{x}, which can possibly be, attributed to less favorable conditions for thermal NO formation. This issue did not catch much attention for a detailed study (oxygenated fuel-NO\textsubscript{x} interaction).

Nitrogen oxides may interact with DME in different ways, depending on the reaction conditions. Under reducing (oxygen-deficient) conditions, NO may be reduced by reaction with hydrocarbon radicals produced during the oxidation of DME in reburn-type reactions [85]. In oxidizing (oxygen-enrich) conditions, the presence of NO\textsubscript{x} may promote the DME conversion through a mutually sensitized oxidation process, similar to that observed for methanol and ethanol [22,86] oxidation.

Figure 14 shows the results for the oxidation of DME in the presence of NO in a flow reactor studied by Alzueta et al. [82] for three different equivalence ratios at atmospheric pressure. Figure 14a shows the conversion of DME which mainly reacts with the radical pool (OH/HO\textsubscript{2}/CH\textsubscript{3}) producing CH\textsubscript{3}OCH\textsubscript{2} radical. In particular, the results obtained under very lean conditions show a shift to lower temperatures (see Figure 14). However, under rich and stoichiometric conditions, no appreciable effect of the NO concentration on DME conversion is seen up to a temperature of about 1100 K. As seen in Figure 14, there is a significant influence of the oxygen concentration on the presence of nitric oxide. For $T = 780$-$980$ K, a significant influence of the O\textsubscript{2} concentration on NO oxidation was observed (see Figure 14c).
At 890 K, the model suggests that once the CH$_3$OCH$_2$ radical is formed, this radical mainly dissociates thermally to yield CH$_3$ and CH$_2$O under very lean conditions. However, reaction with O$_2$ also becomes important: CH$_3$OCH$_2$ also reacts with O$_2$ to mainly form CH$_3$OCH$_2$O$_2$. The less reactive hydroperoxyl (HO$_2$) radicals (HO$_2$ production and consumption will be discussed below) reacts with NO forming the more reactive OH radicals via the reaction NO+HO$_2$=NO$_2$+OH expediting the fuel reactivity. Thus, formed NO$_2$ may react with H-atoms to produce NO+OH resulting in a net increase of OH radicals, which further promotes DME oxidation under low-temperature conditions. This reaction (NO$_2$+H=NO+OH) is also the primary route for H-atom consumption. However, NO$_2$ can also react with DME and CH$_3$ via the following reactions:

$$\text{DME} + \text{NO}_2 = \text{CH}_3\text{OCH}_2 + \text{HONO}$$ and $$\text{CH}_3\text{NO}_2(\text{+M}) = \text{CH}_3 + \text{NO}_2(\text{+M}).$$

The formed HONO will thermally dissociate to yield NO and OH recycling back NO and producing reactive OH radicals in the process. Further, nitromethane (CH$_3$NO$_2$) reacts with OH to form CH$_2$NO$_2$ (CH$_3$NO$_2$+OH=CH$_2$NO$_2$+H$_2$O), and CH$_2$NO$_2$ can undergo thermal dissociation to produce CH$_2$O and NO which further adds to the recycling of NO. The reactions of NO+HO$_2$=NO$_2$+OH and NO$_2$+H=NO+OH are also responsible for the NO/NO$_2$ interconversion process. The sensitization effects of NO under very lean condition can be attributed to the formation and consumption of HO$_2$ radicals. In lean conditions, CH$_3$ radicals react with NO$_2$ to form CH$_3$O and NO (CH$_3$+NO$_2$=CH$_3$O+NO), the CH$_3$O radicals thermally dissociate to give CH$_2$O and H-atom. CH$_2$O further reacts with OH radical producing HCO via CH$_2$O+OH=HCO+H$_2$O reaction. HCO may dissociate into H and CO or may react with O$_2$ to form HO$_2$ via HCO+O$_2$=CO+HO$_2$ reaction. Also, H + O$_2$ reactions can be another route of HO$_2$ formation. HO$_2$ eventually oxidizes NO to produce NO$_2$ and OH (NO+HO$_2$=NO$_2$+OH) resulting in the overall enhancement of the oxidation behaviour of the fuel under investigation. As the O$_2$
concentration in the system is increased, HO₂ production via the reaction HCO+O₂=CO+HO₂ and H+O₂(+M)=HO₂(+M) get promoted which eventually increase OH radical pool which is the most important radical responsible for DME decomposition. At very lean conditions, mutually sensitized oxidation kinetics of DME and NO was observed; however, for stoichiometric and fuel-rich conditions, such sensitization effects were not found.

Furthermore, it can be observed in Figure 14a that the onset of DME oxidation is shifted towards higher temperatures for near stoichiometric and rich conditions. This is due to the inhibiting effect of NO under oxygen-deficient environments. Thus, one can conclude that depending upon the equivalence ratio, NO either promote or inhibit the oxidation process. In stoichiometric and fuel-rich conditions, the experiment shows the onset of NO consumption occurring at ~1100 K, which is well predicted by the model. The model suggests that NO is mainly consumed by the reactions with CH₃, C₂H₃, and HCCO radicals to form HCN, H₂CN, and HCNO via the following reactions:

\[
\begin{align*}
\text{CH}_3 + \text{NO} & \rightarrow \text{HCN} + \text{H}_2\text{O} \\
\text{CH}_3 + \text{NO} & \rightarrow \text{H}_2\text{CN} + \text{OH} \\
\text{C}_2\text{H}_3 + \text{NO} & \rightarrow \text{HCN} + \text{CH}_2\text{O} \\
\text{HCCO} + \text{NO} & \rightarrow \text{HCN} + \text{CO}_2 \\
\text{HCCO} + \text{NO} & \rightarrow \text{HCNO} + \text{CO}.
\end{align*}
\]

The consecutive reactions of H₂CN and HCNO will eventually produce HCN. NO+HO₂=NO₂+OH reaction constitutes a minor pathway which is, in fact, the highest contributing channel for NO consumption under fuel-lean condition. This also explains our inability to observe NO₂ formation under stoichiometric and fuel-rich conditions (Figure 14d).
The model follows the experimental trend very well for all the equivalence ratios over the whole temperature range investigated and accurately predicts the sensitization effects of the DME/NO\textsubscript{x} system. Both CO/CO\textsubscript{2} and NO/NO\textsubscript{2} conversion are predicted very well over the range of investigated conditions.

To our knowledge, there has not been any experimental and theoretical study on the NO\textsubscript{x} effect in DMM/NO\textsubscript{x} system. However, our proposed model will be useful for predicting such NO\textsubscript{x} sensitization effects in the oxidation kinetics of DMM. Further illustrations of model validation for the DME/NO\textsubscript{x} system are provided in the SM (Fig. S25 – Fig. 28).
Figure 14: Oxidation of DME/O$_2$/H$_2$O/NO/N$_2$ in a flow reactor at 1 atm and different $\phi$. DME/O$_2$/H$_2$O/NO = 0.0245 / 3.94 / 3.8 / 0.0508 ($\phi = 0.018$); 0.0497 / 0.147 / 10.5 / 0.0502 ($\phi = 1.0$); 0.05 / 0.073 / 4.78 / 0.0493 ($\phi = 2.0$) balance N$_2$. Symbols: experimental data from [82], lines: this work.

5.4 Speciation in a burner stabilized flame

For burner stabilized flame modeling, a mixture-average transport model, thermal diffusion and radiative heat transfer were considered. The temperature profile is calculated by solving the energy conservation equation, which considers the heat flux to the burner. We calculate the concentrations of all stable species on the burner surface from the gas composition in the feed, and the species
diffusion close to the boundary. For all major radicals, we consider recombination at the burner surface. The undisturbed flame stabilizes above the burner through heat loss, which is calculated from the temperature gradient at the burner surface. The heat loss determines the maximum flame temperature, which is captured well.

5.4.1 DME burner stabilized flame

Figure 15 illustrates the evolution of species profile (mole fraction) with height above burner (HAB) experimentally studied by Liu et al. [87] for DME/O2/Ar premixed burner stabilized flame at φ =1.63 and 5 kPa. Calculations were performed imposing the experimental temperature profile (dashed lines), and by solving the energy conservation equation (solid lines). A comparison between the measured and calculated temperature profiles is shown in the supplementary material of this work (Fig. S29). It can be observed in Figure 15 that the model prediction follows the experimental trend. However, the prediction solving the energy conservation equations shifts the species profile towards the burner surface by 1-1.5 mm. This shift is due to the influence of the probe which causes disturbance of the flame [88]. In Figure 15a, imposing the experimental temperature profile, experimental and modeling results for major species are in good agreement. However, at HAB = 4.5 mm, the model underpredicts the H2O mole fraction profile by 8% and discrepancies between model and measurements are reduced at HAB > 4.5 mm. The predicted H2O mole fraction is within the experimental uncertainty of 15%. Furthermore, for intermediate species, it can be observed in Figure 15b and Figure 15c, imposing the experimental temperature profile, the model accurately predicts the peak positions. Further, for species C2H2 and C2H4 (Figure 15b) the model under predicts the peak concentration by 28% and 30% respectively and for C2H6 it over predicts by 26%. Similarly, for CH4 the model underpredicts by factor 2 and over predicts CH2O by factor 1.8 but follows the experimental trend very well. In Figure 15d, it can be
observed that the model underpredicts peak CH$_3$CHO by factor 2. It should be noted that authors in their work mentioned that for intermediate stable species factor 2 uncertainty in measurements and radical species, uncertainty could be as high as factor 4. However, the present model largely overpredicts CH$_3$OH (by factor 6.5) peak concentration which is outside of the experimental uncertainty range. In present work, no attempt is made to optimize model targeting on CH$_3$OH.

In following the main degradation pathways of DME (Figure 15) are discussed based on C-atom mass flux analysis. Figure 16 shows the integrated mass flux imposing the experimental temperature profile (only major paths are shown). The mass flow analysis in Figure 16 indicates that DME (97%) decomposition happens exclusively via H abstraction by H-atom and OH radical to form CH$_3$OCH$_2$ radical via reactions DME+H/OH=CH$_3$OCH$_2$H$_2$/H$_2$O. CH$_3$OCH$_2$ (97%) dissociates thermally to produce CH$_3$ and CH$_2$O (CH$_3$OCH$_2$=CH$_3$+CH$_2$O). The remaining CH$_3$OCH$_2$ (not shown here) goes to CH$_3$OCH$_2$O$_2$ (1%, CH$_3$OCH$_2$O$_2$=CH$_3$OCH$_2$H$_2$O), CH$_3$OCH$_2$OCH$_3$ (1%, CH$_3$OCH$_2$OCH$_3$+M=CH$_3$OCH$_2$CH$_3$+H) and CH$_3$OCH$_2$O (1%, CH$_3$OCH$_2$+HO$_2$=CH$_3$OCH$_2$O+OH). Further, 25% of formed CH$_3$ undergoes self-recombination to form C$_2$H$_6$ (CH$_3$+CH$_3$+M=C$_2$H$_6$+M), 20% of CH$_3$ react with O-atom to form CH$_2$O (CH$_3$+O=CH$_2$O+H), and 19% of CH$_3$ reacts with an H-atom and OH radical to form CH$_2$-3 (triplet methylene radical) via reactions CH$_2$-3+H$_2$=CH$_3$+H and CH$_3$+OH=CH$_2$-3+H$_2$O. The remaining CH$_3$ goes to CH$_2$-1 (singlet methylene radical) and CH$_2$OH (not shown here) reacting with H-atom and OH radical via reactions CH$_2$-1+H$_2$=CH$_3$+H, CH$_3$+OH=CH$_2$-1+H$_2$O and CH$_3$+OH=CH$_2$OH+H.

Furthermore, C$_2$H$_6$ (97%) formed in the above process goes to C$_2$H$_5$ via H-atom abstraction channel reacting with H, OH and O, in which H-atom has the highest contribution and O-atom contributes the least. Further, most of the C$_2$H$_5$ (71%) formed undergo thermal dissociation
(C_2H_4+H(+M)=C_2H_5(+M)) and H-atom abstraction by H (C_2H_5+H=C_2H_4+H_2) to form C_2H_4 while the later one has the least contribution. C_2H_5 (21%) also reacts with H-atom to form CH_3 radicals \textit{via} reaction CH_3+CH_3=C_2H_5+H. The formed C_2H_4 in the above process reacts with H-atom and OH radicals to form C_2H_3 (C_2H_4+H/OH=C_2H_3+H_2/H_2O). The formed C_2H_3 undergoes thermal dissociation to produce C_2H_2+H; the formed C_2H_2 undergoes H-atom abstraction to give HCCO reacting with O-atom (C_2H_2+O=HCCO+H), and the formed HCCO reacts with H-atom forming CH_2-1 (HCCO+H=CH_2-1+CO). The formed CH_2-1 completely isomerizes to CH_2-3. The CH_2-3 formed from the above process reacts with an H-atom to give CH+H_2. Further, the formed CH undergoes H-atom abstraction reacting with H to form a C-atom (CH+H=C+H_2). Eventually, the formed C-atom reacts with O_2 and a H-atom to produce CO. It can be concluded from the above analysis that in flames fueled by DME, CH_3 is the vital intermediate species. Additional model validation for speciation in DME flames is shown in SM (Fig. S30 – Fig. S33).

Figure 15: Speciation in a DME/O_2/Ar (0.17582/0.32418/0.5, mole fraction) burner stabilized premixed flame at 5 kPa and $\phi = 1.63$. Symbols: experimental data from [87], lines: this work;
dashed lines (imposing experimental temperature profile), solid lines (solving energy conservation equation).

Figure 16: Reaction flow analysis based on C-atom (integrated) for the DME/O₂/Ar flame shown in Figure 15 imposing experimental temperature profile. Only major paths are shown. “therm-“ means thermal dissociation.

5.4.2 DMM burner stabilized flame

The developed mechanism is supposed to provide insights into the DMM degradation pathways; therefore, it is necessary to test and ensure the predictive capability of the model at different experimental setup. Figure 17 displays the speciation in burner stabilized DMM/O₂/Ar premixed flame as a function of HAB experimentally studied by Sun et al. [26] at low pressure (4 kPa) and φ = 2.0. In Figure 17 dashed lines are simulation results imposing the experimental temperature profile and solid lines solving the energy conservation equation. Experimental and simulated mole fraction profiles for the major species (DMM, O₂, Ar, H₂, H₂O, CO, CO₂) are shown in Figure 17a.
Reasonable agreement between experimental and modeling results is observed, providing confidence that the model can capture the global combustion chemistry of DMM. A shift of about 1-1.5 mm between experimental and modeling results is noted, which appears for major species (fuel and oxygen) as well as for all intermediate species. This shift is probably a consequence of larger uncertainties of the flame temperature due to steeper gradients and might also be related to probing perturbations [89]. The authors mentioned in their study [26] that when performing model simulations, they shifted the measured temperature profiles by 1 mm downstream to compensate for the probe effect. Please note that neither the position of the mole fraction profiles nor the temperature profiles were shifted in this study.

Beyond the major species, it is important to discuss the predictive capabilities of the model with respect to small intermediate species. For the majority of intermediate species, the model predicts the maximum mole fraction as well as profile shape satisfactorily. For important C₂ species (C₂H₂, C₂H₄, and C₂H₆) shown in Figure 17b, the model predictions are in good agreement with the measurements. In Figure 17c, peak mole fraction predicted by the model for CH₃CHO is in excellent agreement with the measured peak mole fraction. However, for CH₂CO the prediction is factor 3 higher compared to the measurements. For important C₁ species (CH₃ and CH₄) in Figure 17d, the maximum mole fraction for CH₄ is well predicted by the model. The experiment shows a higher concentration of CH₄ near the burner surface. Furthermore, it can be observed in Figure 17e and Figure 17f, model overpredicts maximum mole fraction of CH₂O by factor 1.65, similarly factor 2.85 higher for CH₃OH, factor 4 higher for DME and factor 2 higher for CH₃O.

The experimental uncertainties were reported as follows: in initial pressure ±1%, in mixture flow rate ±2%, in measured temperature ±100 K. Furthermore, uncertainty for measured major species is factor 1.2 – 1.3, uncertainty for measured intermediate species is reported to be as large as factor...
3-4. The authors also mentioned that the temperature at the burner surface (HAB = 0 mm) could not be experimentally determined and were estimated to be 500 K. Taking into account all these experimental uncertainties, we can conclude that predicted species mole fractions are good and within the experimental uncertainty. Indeed, to study the influence of various uncertainties on the model prediction will be useful and interesting, but beyond the scope of the present study.

To explore important reactions during the DMM oxidation in the flame (Figure 17), a mass flux analysis is performed. Figure 18 shows the integrated mass flux analysis based on C-atoms for the flame shown in Figure 17 (only major paths are shown). The model suggests that most of the DMM goes to CH$_3$OCH$_2$OCH$_2$ (R1) and CH$_3$OCHOCH$_3$ (R2) via H-atom abstraction channel reacting with H-atom (reaction r7 and r8) and OH radicals (r9 and r10), while former has the highest contribution and least is contributed by later. It can also be observed that path forming R1 is favored more (by factor 1.8) compared to R2. Most of the formed R1 radical (99%) undergoes thermal dissociation to produce CH$_3$OCH$_2$ in the process also forming CH$_2$O via the reaction CH$_3$OCH$_2$OCH$_2$=CH$_3$OCH$_2$+CH$_2$O. The formed CH$_3$OCH$_2$ radical (99%, a primary fuel radical of DME) thermally dissociates to give CH$_3$ and CH$_2$O (CH$_3$OCH$_2$=CH$_3$+CH$_2$O). Similarly, the entire R2 radical (100%) is also thermally dissociated to CH$_3$OCHO and CH$_3$ (CH$_3$OCHOCH$_3$=CH$_3$OCHO+CH$_3$). The formed CH$_3$OCHO (87%) reacts with H-atom to CH$_3$OCO and 9% of CH$_3$OCHO goes to CH$_2$OCHO (not shown here). Finally, all of the formed CH$_3$OCO thermally dissociates to give CH$_3$ and CO$_2$ (CH$_3$OCO=CH$_3$+CO$_2$).

Overall, the carbon atom mass flux analysis in Figure 18 can be seen as a two-step process:

- In the first step, almost all of the primary products lead to CH$_3$ radicals.
- The second step is directed to the decomposition of CH$_3$ radicals.
In this flame as well, the CH$_3$ radical is a key intermediate species. The CH$_3$ radical formed in the above process (Figure 18) decomposes through the same reaction channels as described for the DME flame (Figure 16). It is also interesting to observe in Figure 18 that most of the reactions taking part during DMM degradation are H-atom abstractions by H and OH as well as thermal dissociation.

To our knowledge, there has not been any experimental study to date, which reported NO$_x$ measurements in flames fueled by DME and DMM. As already mentioned, the here proposed model is an extension of our previous work [22,34] which was also validated for NO$_x$ formation in C$_1$-C$_2$ hydrocarbon as well as oxygenated premixed flames. Based on our previous work, we believe the proposed model can be used to model NO$_x$ in DME and DMM fueled flames.
Figure 17: Speciation in a DMM/O\textsubscript{2}/Ar (0.25/0.5/0.25, mole fraction) burner stabilized premixed flame at 4 kPa and \( \phi = 2.0 \). Symbols: experimental data from [26], lines: this work; dashed lines (imposing experimental temperature profile), solid lines (solving energy conservation equation).
Figure 18: Reaction flow analysis based on C-atom (integrated) for the DMM/O₂/Ar flame shown in Figure 17 imposing experimental temperature profile. Only major paths are shown. "therm-" means thermal dissociation

5.5 Ignition delay time

Finally, we demonstrate the capability of our model to predict one of the essential features of DME and DMM combustion over a wide range of conditions, the ignition timing.

5.5.1 DME ignition delay time

Figure 19 compares the predicted ignition delay times against shock tube (ST) experimental data from the literature for DME/air blends. The shock tube experimental data are from Li et al. [90] at a pressure of 23 bar and three different equivalence ratios (ϕ = 0.5, 1.0 and 1.5). It can be observed in Figure 19 that the model captures the equivalence ratio dependency of ignition delay times very well and agrees with the measurements for the temperature range investigated.
To explore important reactions for DME/air ignition timing, reaction sensitivity analysis is performed which is shown in Fig. S34 and S35 in SM and discussed there. Further model validation for DME ignition delay times using other published experiments is provided in the SM (Fig. S38).

![Figure 19: Ignition delay time of DME/air at 23 bar and different equivalence ratios (0.5, 1.0, and 1.5). Symbols: experimental data from [90], lines: this work.](image)

**5.5.2 DMM ignition delay time**

Figure 20 compares the predicted ignition delay times against shock tube and rapid compression machine (RCM) experimental data for DMM/air blend at $\phi = 1.0$ at three different pressure (10, 20 and 40 bar). The measurements (symbols) are from [32,33]. We can observe (in Figure 20) that the model captures the pressure dependency of ignition delay times very well for the whole temperature range investigated. The predicted ignition delay times are in excellent agreement with the measurements showing the model capability to perform for the wide range of conditions. Unlike the case of DME (Figure 19), where we can observe the discernible NTC region ($\sim$750-950 K), we do not observe a noticeable NTC region for the DMM despite both fuels have some similarities in terms of chemical structure and bonding.

To outline important reactions of DMM ignition delay time a reaction sensitivity analysis is performed which is shown in Figs. S37 and S38 in SM and discussed there. Additional model
validation for DMM ignition delay times using other published experiments can be found in the supplementary material (Fig. S39).

![Image](image.png)

Figure 20: Ignition delay time of DMM/air at \( \phi = 1.0 \) and various pressure. Symbols: experimental data from [32,33], filled symbols: shock tube measurements, half-filled symbols: RCM measurements. Lines: this work.

6. Conclusion

The laminar flame speed of DME and DMM have been studied experimentally at 1-5 bar, 298-373 K using a constant volume spherical vessel and a heat flux burner. To provide quantitative chemical insights into the kinetics of DME and DMM, a reaction mechanism for the oxidation of DME and DMM including nitrogen chemistry was developed based on the present measurements and published experimental data. Several published experiments have been selected to demonstrate that important features of the DME and DMM chemistry are well captured by the model. Overall, there is a good agreement between model predictions and experimental measurements for a wide range of experimental conditions investigated. It is found that laminar flame speed of DME and DMM increases with increasing initial mixture temperature and decreases as the pressure is increased. It is also found that for stoichiometric conditions the laminar flame speed of DME and
DMM is the same (within the present experimental uncertainty). The peak flame velocity of DME at 1 bar and 298 K is found to be at equivalence ratio 1.1 while for DMM it is at 1.2. DME shows a marked NTC region while DMM does not show the obvious NTC behavior. The kinetic analysis suggests that during DMM oxidation, H-atom abstraction from terminal carbon is favored compared to H-atom abstraction from the central carbon atom. Furthermore, the model reveals that at low-temperature reactions involving OH and HO2 are essential while at high-temperature thermal dissociation reactions and reactions involving H-atom gain importance. The available experimental data from literature has been selected to demonstrate that essential features of the DME/NOx interaction chemistry are well captured by the model.

The oxygen level in the gas mixture significantly influences the onset of DME conversion and NO reduction, which moves towards lower temperature as the mixture gets leaner. The presence of NO is responsible for promoting the reactivity of the system and for sensitized oxidation of DME at lean conditions. Published rate parameters of reactions related to DMM chemistry (experimentally and theoretically) are scare and the ones available in the literature are mainly derived via analogy. Further work is required in this area to enhance the model development and improve the understanding of DMM combustion. The here derived model is capable of serving as the base mechanism for hydrocarbon fuels and oxygenated fuels higher than C2.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: