



Experimental and kinetic modeling study of the shock tube ignition of a large oxygenated fuel: Tri-propylene glycol mono-methyl ether



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ABSTRACT

Tri-propylene glycol monomethyl ether (TPGME) is an important oxygenated fuel additive that can be used to reduce soot in diesel engines. However, a validated chemical kinetic model that incorporates the low- to high-temperature chemistry, needed to simulate ignition in a diesel engine is not available for TPGME. In addition, no fundamental experimental data are available that can be used to validate a TPGME mechanism. In *this study*, a surrogate chemical kinetic model for TPGME that includes low- and high-temperature chemistry has been developed, and shock tube ignition delay time data has been acquired for its validation at 0.25% TPGME for temperatures in the range of 980–1545 K, at pressures of 10 and 20 atm, and at equivalence ratios of $\phi = 0.5, 1.0$ and 2.0. The predictions from the model have been compared to the experimental measurements with good agreement. Under the experimental conditions investigated in the shock tube, TPGME was found to be consumed by molecular elimination reactions and also H-atom abstraction by H atoms and by OH and HO₂ radicals. In performing sensitivity analyses it was found that the ignition of TPGME is most sensitive to reactions involving propene. Considering how the sensitivity analyses change with pressure, the most sensitive reactions involved H atoms at 10 atm and HO₂ radicals at 20 atm. With respect to the effect of equivalence ratio, reactions involving H atoms are relatively more sensitive under fuel-rich conditions while those involving HO₂ radicals are relatively more sensitive under fuel-lean conditions. Further experimental work is needed to enable validation of the model under low-temperature conditions. TPGME was compared to *n*-heptane which has similar ignition properties based on Cetane Number. Predictions showed that TPGME has a higher overall reactivity compared to *n*-heptane. In addition, TPGME is shown to produce significantly less soot precursor species when TPGME predictions are compared to *n*-heptane.

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1. Introduction

Tri-propylene glycol monomethyl ether (TPGME) is an attractive oxygenated additive that is effective in reducing soot emissions in diesel engines [1–3]. Gonzalez et al. [2] found TPGME and dibutylmaleate (DBM) were the most promising oxygenates out of 8 oxygenates tested for addition to a low-sulfur diesel fuel for reduction of particulate emissions. They determined that adding 20% by volume of TPGME to diesel fuel reduced particulate emissions in a diesel engine by 47%. Investigating these two most promising oxygenate additives, Mueller et al. [1] found that TPGME was more effective in reducing soot than DBM for all test

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conditions investigated in an optical diesel engine. They investigated 20% TPGME and 80% 2,2,4,4,6,8,8-heptamethylnonane (a diesel reference fuel) as an oxygenated “diesel” fuel mixture. Kinetic model calculations in their study showed that 30% of the oxygen contained in DBM is unavailable for reducing soot precursors whereas all of the oxygen in TPGME is available. In a constant volume combustion chamber that mimics conditions in a modern diesel engine, Manin et al. [3] found that a 50/50 mixture of TPGME and *n*-hexadecane (a diesel primary reference fuel) gave lower sooting levels than a biodiesel methyl ester surrogate composed of neat methyldecanoate. They attributed this difference in sooting levels to “chemical structural differences on how the oxygen is bonded in the two oxygenated molecules”.

TPGME has a low toxicity and vapor pressure and is currently used practically as an industrial solvent, chemical intermediate, and in inks for ballpoint or felt-tipped pens [4]. Commercially, TPGME is produced only as a mixture of eight isomers, Fig. 1.

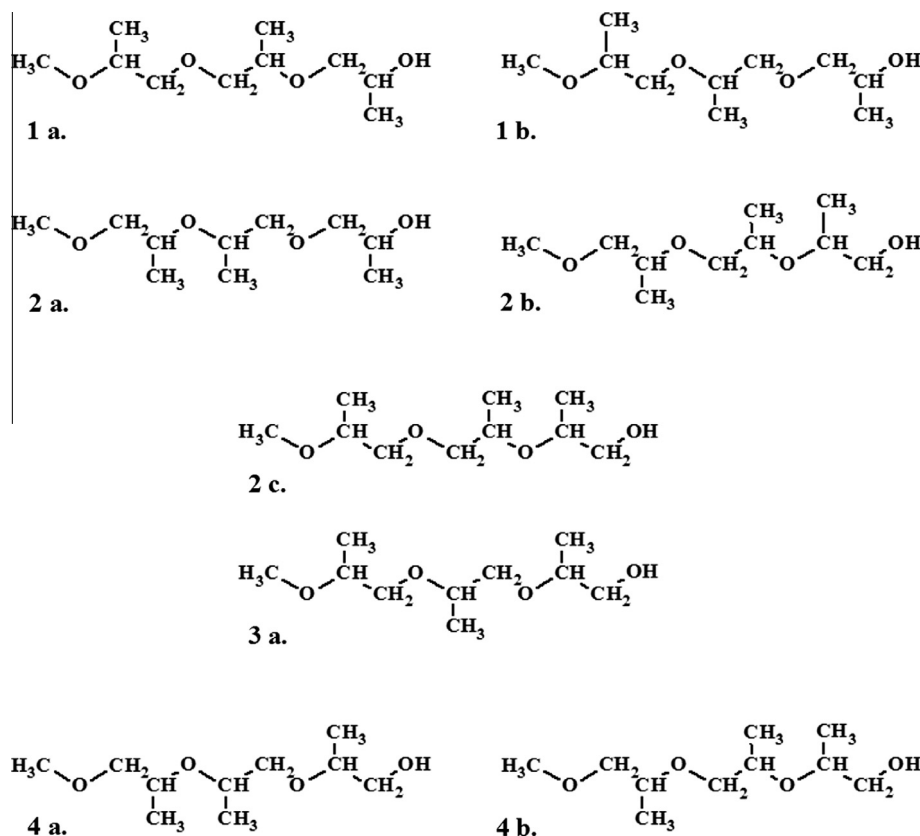


Fig. 1. Structural isomers present in the isomeric mixture studied ranked in 4 groups according to their expected reactivity. (Group 1 has the highest expected reactivity.).

Propylene glycol ethers in general are manufactured in closed reactors using propylene oxide and methanol as precursors. In order to produce high yields of TPGME, high pressure, temperature and molar concentrations of propylene oxide and methanol are required and the eventual isomeric mixture of TPGME is isolated via distillation [4,5]. The isomers of the mixture have similar boiling points (~ 243 °C) and thus it was impractical to separate and quantify them; therefore to simplify modeling of the mixture, one isomer was chosen as a surrogate to represent the eight-isomer mixture. Isomer 3a (Figs. 1 and 2) was chosen as a surrogate for the mixture because its high temperature mechanism has been previously developed and was available [1]. If the isomers are ranked into 4 reactivity groups (Fig. 1), it is expected to be in the third group based on reactivity arguments given in the Reaction Rate Constant Section 3.1.

TPGME has been used in research diesel engines yielding near non-sooting combustion. This effect has motivated an interest in the mechanism of the oxidation of TPGME. A surrogate chemical kinetic mechanism for TPGME will help us understand and optimize its combustion in engines. However, a TPGME mechanism that is valid at high pressures and over the low- to high-temperature range associated with combustion in engines is not available. In order to develop a model, fundamental experi-

mental data is also required in order to provide validation targets which have not previously been available.

From a molecular-structure point of view, TPGME is interesting. It is highly branched with four oxygen atoms distributed throughout the molecule, Fig. 1. It contains both the alcoholic and ether moiety, with secondary C–H bonds adjacent to the alcoholic functional group and primary, secondary and tertiary C–H bonds adjacent to the ether moieties distributed throughout the molecule. Most other oxygenated fuels investigated previously in the literature (methanol [6], *iso*-butanol [7], dimethyl ether [8,9] and methyl *tert*-butyl ether [10] etc.) are much smaller than TPGME in molecular size and are either lightly-branched or straight-chained in their skeletal structure. These characteristics of TPGME represent a challenge for chemical kinetic model development.

A chemical kinetic model for TPGME has been developed previously [1,11] to address its high-temperature chemistry and production of soot precursor species under conditions in diesel engines (high pressures 99 atm and low temperatures 767 K), and this model also took the surrogate approach, by only considering the isomer shown in Fig. 2. Westbrook et al. [11] presented comparisons of a range of oxygenated fuel additives (methanol, ethanol, dimethyl ether, dimethoxy methane, methyl butanoate, TPGME, dimethylcarbonate and DBM) and their effect on the formation of soot precursor species (ethylene, acetylene, propyne, etc.). It was found that the formation of these species was somewhat reliant on the percentage oxygen by weight in the overall fuel mixture (*n*-heptane + oxygenated additive in “air”). Also, it was noted that the even distribution of O-atoms throughout the TPGME molecule meant that its soot reduction capabilities were quite efficient, preventing the C-atoms in the molecule from proceeding to form soot precursor species. Due to a lack of fundamental data, no validation targets were available for this model, and its predictions were purely theoretical. Although this model may have been

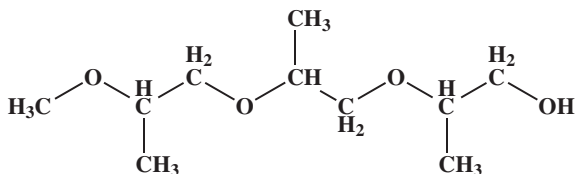


Fig. 2. Isomer 3a chosen to represent TPGME mixture for model development.

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