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An analytical approximation for low- and high-temperature autoignition for dimethyl ether–air mixtures

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Abstract

Dimethyl ether has proven to be one of the most attractive alternatives to traditional fossil oil derived fuels for compression ignition engines. In this study, a skeletal mechanism consisting of 32 species and 49 elementary reactions, based on the detailed mechanism proposed by Fischer et al. [Int. J. Chem. Kinet. 32 (12) (2000) 713–740], is further reduced to a short 36-step mechanism describing first and second stage ignition as well as the rapid transition to final products. A global 4-step mechanism is derived by introducing steady state assumptions of intermediate species. An analytical solution for the ignition delay times of the first stage of ignition in the low temperature regime and the beginning of its transition to the intermediate temperature regime is presented. The important competition of the β-scission and the reaction with molecular oxygen of the hydroperoxy-methoxymethyl radical ($C_2OCH_2O_2H$) is quantified by the introduction of a parameter β, related to the competition of chain-branching and chain-propagation. The calculated values agree very well with those of the 36-step mechanism. Also for the high temperature regime, an analytical solution is presented, which agrees well with the experiments and the values calculated with the 36-step mechanism.

Keywords: Dimethyl ether; Ignition delay time; Reduced chemistry; Analytical solution

1. Introduction

Dimethyl ether (DME) has emerged as a promising alternative for standard diesel [1]. It also shows high potential in advanced combustion concepts, e.g. premixed charge compression ignition (PCCI) [2]. For instance, Zhu et al. [3] pointed out that the nitrogen oxide and unburnt hydrocarbon emissions are significantly reduced using DME instead of standard diesel fuel and Park et al. [4] found that DME combustion in diesel engines is nearly soot free. Several fundamental scientific studies on the oxidation of DME have been reported both on the experimental as well as the modelling side [5–11]. The resulting chemical reaction mechanisms can and have been used in detailed kinetic modelling studies. However, these models are still too complex for several purposes. For instance, real time model based control of homogenised low temperature

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combustion for DME fuelled PCCI engines could further improve motor vehicle fuel economy while complying with emissions regulations [12]. Within this context, a potential control parameter could be the ignition delay time. Unfortunately, the time needed for calculating ignition delay times with a kinetic mechanism is orders of magnitude higher than needed for model based control in engines. Here, analytically derived solutions for ignition delay times are very useful. Further, analytical solutions can be used to develop a fundamental understanding or provide information about how different fuels in a fuel blend interact with each other. On the basis of detailed kinetic schemes, it is possible to derive analytical solutions for DME/air mixtures for the low and high temperature regime, which is the purpose of this paper. In detail, the objectives are the following. First a 36-step skeletal mechanism is developed from a detailed model. Then, a four step global mechanism is derived, which will be used subsequently in the analysis. Competing reactions for chain-branching and chain-propagating are identified, which are important for the transition from the low temperature to the intermediate temperature regime. After this, the presentation of the analytical solution in the low temperature regime follows. Finally, an analytical solution adapted to DME on the basis of work by Peters et al. [13] for *n*-heptane in the high temperature regime is presented.

2. Formulation of 36-step short mechanism

The detailed mechanism from Fischer et al. [5], chosen as the basis for the present work, has been widely validated with data obtained from flow reactors and jet stirred reactor experiments for ambient pressure as well as shock tube experiments for pressures of 13 bar and 40 bar. This model has been systematically reduced to 32 species and 49 elementary reactions in [14]. It was compared successfully against experimental data from Pfahl et al. [15], Dagaut et al. [7], and Cook et al. [11] over a wide range of equivalence ratios, pressures and dilution factors. The kinetic model was further reduced in this work in order to present a kinetic model that allows for the derivation of a global mechanism and further analytical analysis. For this purpose, the Directed Relation Graph with Error Propagation method (DRGEP) developed by Pepiot-Desjardins and Pitsch [16] was used as an automatic reduction strategy to reduce the mechanism to a skeletal size retaining the original rate data. The ignition delay calculations were performed using the FlameMaster software package [17]. Prior to the reduction with DRGEP, reaction rate data in the base chemistry were updated with rates from a widely validated mechanism by Narayanaswamy et al. [18] to provide compatibility to different fuel components as well as for the use in fuel blends. Fuel specific rate data were maintained from Fischer et al. [5]. The rate updates did not influence calculated ignition delay times. The final result of the reduction process is a 36-step skeletal mechanism. It will be shown later that altogether twelve steps are relevant for the derivation of the analytical approximations presented in this work. Therefore, these steps are only listed in Table 1, whereas the complete 36-step mechanism is provided as supplemental material. The final model is able to describe first and second stage ignition as well as the rapid transition to the final combustion products. Figure 1 compares the calculated ignition

Table 1
12-Step extraction of the 36-step skeletal mechanism for DME.

Number	Reaction	*A*	*n*	*E*	Refs.
2	$CH_3OCH_3 + O_2 \rightarrow CH_3OCH_2 + HO_2$	4.10E+13	0	44910	[5]
3	$CH_3OCH_3 + HO_2 \rightarrow CH_3OCH_2 + H_2O_2$	1.68E+13	0	17690	[5]
4	$CH_3OCH_3 + OH \rightarrow CH_3OCH_2 + H_2O$	9.35E+05	2.29	−780	[5]
10f	$CH_3OCH_2 + O_2 \rightarrow CH_3OCH_2O_2$	2.00E+12	0	0	[5]
11	$CH_3OCH_2O_2 \rightarrow CH_2OCH_2O_2H$	6.00E+10	0	21580	[5]
12	$CH_2OCH_2O_2H \rightarrow OH + CH_2O + CH_2O$	1.50E+13	0	20760	[5]
13	$CH_2OCH_2O_2H + O_2 \rightarrow O_2CH_2OCH_2O_2H$	7.00E+11	0	0	[5]
14	$O_2CH_2OCH_2O_2H \rightarrow HO_2CH_2OCHO + OH$	4.00E+10	0	18580	[5]
15	$HO_2CH_2OCHO \rightarrow OCH_2OCHO + OH$	2.00E+16	0	40500	[5]
16	$OCH_2OCHO \rightarrow CH_2O + HCO_2$	5.96E+16	−1.5	19620	[5]
35	$H_2O_2\ (+M') \rightarrow OH + OH\ (+M')\quad K_\infty$	1.19E+20	−1.538	52449	[18]
	K_0	2.15E+23	−1.748	50157	[18]
	Troe parameter/7.35E−01 9.40E+01 1.76E+03 5.18E+03/				
36	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.30E+11	0	−1630	[18]
	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	3.66E+14	0	12001	[18]

Rate constants in the form, $k = AT^n \exp(-E/RT)$. A in units of cm^3, mol, sec, E in cal/mol. In the Troe form, F_{cent} is given by $F_{cent} = (1 - \alpha)\exp(-T/T^{***}) + \alpha\exp(-T/T^{*}) + \exp(-T^{**}/T)$. Order of the Troe parameters: $\alpha, T^{***}, T^{*}, T^{**}$. $[M'] = 0.70[AR] + 2.00[CH_4] + 12.00[H_2O] + 1.75[CO] + 3.60[CO_2] + 3.00\ [C_2H_6] + 2.00[H_2]$

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