A short reaction mechanism for the combustion of dimethyl-ether

Juan C. Prince [a],*, Forman A. Williams [b]

[a] Departamento de Metal-Mecánica, Instituto Tecnológico de Veracruz, Veracruz 91860, Mexico
[b] Department of Mechanical and Aerospace Engineering, University of California at San Diego, La Jolla, CA 92093-0411, USA

ABSTRACT

Fourteen chemical-kinetic steps are identified, and their associated reaction-rate parameters are given, that enable an existing short chemical-kinetic mechanism (the San Diego mechanism) to be expanded to include the ignition and combustion of dimethyl-ether, over a range of conditions that includes both low-temperature and high-temperature chemistry, as well as both high and low pressures, extending to normal atmospheric pressure. This entails introducing five additional chemical species. Tests of predictions against measured ignition delays, laminar burning velocities, and flow-reactor and jet-stirred-reactor data are reported, that support the success of the mechanism. The results therefore can be useful in combustion computations, especially when larger mechanisms are too time-consuming to be accommodated.

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1. Introduction

Dimethyl-ether (DME: CH_3OCH_3) is an attractive alternative to conventional diesel fuel for compression-ignition (CI) engines because it auto-ignites favorably and burns with little soot formation [1,2]. The main property of DME relevant to its engine compatibility is its high cetane number (CN>55), resulting in low auto-ignition temperatures along with its rapid vaporization. In addition, DME is an oxygenated hydrocarbon, with a low carbon-to-hydrogen ratio and the absence of a C–C bond, leading to very low emissions of particle matter (PM) during CI combustion. The main disadvantages of using DME in CI-powered vehicles are related to its viscosity, which is lower than that of diesel fuel, enhancing both leakage from fuel-supply systems and surface wear of moving parts within fuel-injection systems. An additional disadvantage of DME is its lower combustion enthalpy, compared with that of diesel, thereby requiring a larger injected volume to deliver the same amount of energy as that provided by diesel. Direct and indirect methods can be used to produce DME [3,4]; direct synthetic methods make it directly from natural gas, while indirect synthetic methods generate it through a dehydration reaction after synthetic production of methanol.

Since DME is considered a clean alternative to diesel fuel, with notably low PM, for example, a combustion model to predict its ignition delays, flame propagation, and emission properties is critical to designing practical combustion devices for using this fuel optimally. Also, as a simple oxygenated fuel, DME provides a useful reference compound for comparison with other more complex oxygenated fuels, such as biofuels. In addition, having a low-temperature combustion (LTC) path, DME exhibits a negative-temperature-coefficient (NTC) phenomenon and two-stage ignition. This is of great interest in CI engines, where the LTC mode, combined with the other favorable DME properties, ultimately may enable cleaner and more efficient engines to be designed.

Several DME oxidation mechanisms, reported in the literature [5–11], have been tested against data from numerous types of experiments [5,12–19], including pressure-flow reactors, jet-stirred reactors, shock tubes, rapid-compression machines, and direct sampling from flames. These chemical mechanisms have also been used for modeling additional combustion processes, mainly in flames or for ignition at high-pressure conditions [20–29]. Some recent flow-reactor experiments at atmospheric conditions [30–33], which provide new insight into the DME ignition delay, are, however, not modeled accurately by the above mechanisms. New reactions and rate parameters have to be used to update these chemical models [32,34] to better describe these recent experimental data.

Because the mechanisms in these publications are too complex for several practical purposes, a need exists for deriving reduced mechanisms that can be validated against the wider range of experimental data that extends to atmospheric conditions. The present paper addresses this need by taking as a base mechanism the so-called San Diego mechanism (http://combustion.ucsd.edu), which has been designed to be a short mechanism, for use in applications in which larger mechanisms become impractical [35,36].

* Corresponding author. fax: +52 2999385764.
  E-mail address: jcpa@itver.edu.mx, jcpa1000@gmail.com (J.C. Prince).

2. The reaction mechanism

The approach to be adopted here takes into account recent chemical-kinetic studies of DME combustion processes, especially flow-reactor experiments under atmospheric conditions. It also makes use of applicable steady-state approximations and lumping procedures for reducing the size of the mechanism. In addressing DME oxidation at atmospheric conditions, literature on elementary reaction rates relevant to this condition [37–48] was reviewed. In order to obtain a simplified mechanism, consistent with the philosophy of the base mechanism, only those reactions that affect the ignition delay time over the range of conditions of interest were retained.

The base mechanism consists of C_1–C_3 chemistry [36], tested for a wide range of parameters. In developing a short DME sub-mechanism, different detailed mechanisms were consulted [5–11]. For the sake of consistency, wherever possible the reactions rates and thermodynamic data were based on one recent, widely used detailed chemical model [9]. This model was reduced and updated with new rate parameters recommended in more recent literature for matching flow-reactor experiments at atmospheric conditions.

Table 1 shows our final selection of the DME sub-mechanism and its rate parameters, which are added to the San Diego mechanism. Basically, 14 new reactions are added that involve 5 new species (CH_3OCH_3, CH_3OCH_2, $CH_3OCH_2O_2$, $CH_2OCHOOH$, and HO_2CH_2OCHO). These species have, respectively, been termed DME, methoxy-methyl, methoxy-methyl-peroxy, hydroperoxy-methyl-methoxy, and a hydroperoxymethyl formate. Just as with the LTC of normal alkanes, such as heptane, which has recently been added to the mechanism [49,50], a carbonyl that is not a radical but that also is not very stable initiates the low-temperature branching path.

In obtaining the desired degree of reduction, the radical formed after the second O_2 addition, which appears in the other mechanisms and which might be termed hydroperoxy-methoxy-methyl-peroxy, was eliminated by introducing its steady-state approximation, which is obeyed quite accurately. In addition, vertical lumping procedures were used for expressing the products of the carbonyl decomposition and of the bimolecular hydroperoxy-methoxy-methyl reaction (step 10). This last step was selected in favor of the competing reaction of this radical with the hydroperoxyl radical to obtain better agreement with the results in [30,33], a choice that also is consistent with the claim [43] that the attack by hydroperoxyl is generally of lesser importance. The lumping selections correspond to introducing steady-state approximations for smaller radicals initially formed in the reactions, thereby making it unnecessary to introduce the chemistry of formic acid and methyl formate. The exclusion of that chemistry, which, of course, prevents any consideration of participation of these two compounds, saves adding about 20 additional elementary steps, which we consider to be warranted, in view of the objective of achieving the greatest possible reduction.

The mechanism in Table 1 can be described as follows: the first six steps in the table are all necessary to describe properly the initial breakdown of DME over the full range of conditions of interest. The uni-molecular decomposition shown in the first step is known to be important even at flow-reactor temperatures, for example [9]; for this step, an improved rate and the newly determined pressure falloff from [44] were used. For the other five initial steps, all H abstractions, the rate parameters were taken from [9], except for steps 3 and 5, whose parameters were updated both from [44], to match better results of flow-reactor measurements at atmospheric conditions, as proposed in [32]. The abstraction of H atoms by OH, CH_3, and H in steps 3, 4, and 5 is very important for shock-tube and flow-reactor ignition delays. In addition, if good results are to be obtained for low-temperature chemistry, then the H-atom abstraction by HO_2, appearing in reaction 6, must be included to increase the reactivity of the system at temperatures above 700 K properly.

The methoxy-methyl radical, produced by the H abstraction, can decompose through β-scission to form formaldehyde and a methyl radical (step 7), or it may react with oxygen, either ultimately breaking up to generate a hydroxyl radical and two molecules of formaldehyde (step 8) or simply experiencing addition to form methoxy-methyl-peroxy (step 9), which begins the low-temperature chemistry. The rate parameters for reactions 7 and 9 are taken from [9], but reaction 8 is a new channel, not found in [9], proposed in [41,42] and used in [32], mainly to obtain better agreement with experimental data at atmospheric conditions; the rate constant of [41] for 10 bar was chosen here because it appeared to be the best compromise, consistent with the decision not to introduce the complication of using different rate expressions for different pressures.

Subsequent to this first O_2 addition, isomerization (step 11) carries on the low-temperature path, but comparisons with results of experiments at atmospheric pressure clearly show, on the basis of our present investigation, that the bimolecular removal of this intermediate (step 10) must be included if agreement is to be obtained with measurements of ignition processes at atmospheric pressure [37,41,42]. For this reaction the rate parameters are taken from the supplementary material provided with [34], with vertical lumping introduced to eliminate intermediates that play no other role. The

Table 1

The elementary reactions of the DME sub-mechanism with the specific reaction rate constants $k = BT^\alpha \exp(-E/RT)$; units are moles, cubic centimeters, seconds, kilocalories, K.

R#	Reaction	B_n	α_n	E_n
1	$CH_3OCH_3 \leftrightarrow CH_3 + CH_3O$	2.33E + 19	− 0.66	84.139
	Low pressure limit	1.72E + 59	− 11.40	93.296
	Troe: 1.0 1.0E − 30 880			
	H_2/3.0/ H_2O/9.0/ CH_4/3.0/ CO/2.25/ CO_2/3.0/			
	C_2H_6/4.5/ AR/1.0/ N_2/1.50/ CH_3OCH_3/5/			
2	$CH_3OCH_3 + O_2 \leftrightarrow CH_3OCH_2 + HO_2$	4.10E + 13	0.00	44.910
3	$CH_3OCH_3 + OH \leftrightarrow CH_3OCH_2 + H_2O$	1.95E + 07	1.90	− 0.366
4	$CH_3OCH_3 + CH_3 \leftrightarrow CH_3OCH_2 + CH_4$	2.68E + 01	3.78	9.632
5	$CH_3OCH_3 + H \leftrightarrow CH_3OCH_2 + H_2$	3.94E + 00	4.10	1.780
6	$CH_3OCH_3 + HO_2 \leftrightarrow CH_3OCH_2 + H_2O_2$	2.00E + 13	0.00	16.500
7	$CH_3OCH_2 \leftrightarrow CH_2O + CH_3$	1.20E + 13	0.00	25.750
8	$CH_3OCH_2 + O_2 \leftrightarrow OH + 2CH_2O$	9.53E + 10	0.40	3.416
9	$CH_3OCH_2 + O_2 \leftrightarrow CH_3OCH_2O_2$	2.00E + 12	0.00	0.000
10	$2CH_3OCH_2O_2 \leftrightarrow O_2 + 2CH_3O + 2CH_2O$	1.31E + 14	− 1.10	− 0.366
11	$CH_3OCH_2O_2 \leftrightarrow CH_2OCH_2OOH$	2.20E + 09	0.00	15.846
12	$CH_2OCH_2OOH \leftrightarrow OH + 2CH_2O$	1.50E + 13	0.00	20.500
13	$CH_2OCH_2OOH + O_2 \leftrightarrow OH + HO_2CH_2OCHO$	2.86E + 16	− 1.48	1.873
14	$HO_2CH_2OCHO \leftrightarrow OH + CH_2O + CO_2 + H$	5.00E + 16	0.00	43.000