

## Calculations of Rate Coefficients for the Uni and Bimolecular Reactions of Dimethyl Ether and Improvement of its Combustion Mechanism

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**Abstract:** Great attention has been given to dimethyl ether (DME) since it has been indicated as potential candidate fuel for compression ignition engines. It shows high cetane number ( $> 55$ ) and favorable C/O ratio for combustion. [1] Moreover, it has been shown that DME is smokeless when it burns, causing lower CO and particulate emission [2], the latter observation justified by the lack of carbon-carbon bonds, resulting in low soot formation. From the economical appeal, DME can be cheaply produced from syngas (CO, H<sub>2</sub>), also from coal, natural gas, biomass, and blends of these. Previous studies on the combustion properties highlight the importance of the unimolecular reactions (DME  $\rightarrow$  products) for the initiation of the combustion mechanism at the high temperature range. DME shows six unimolecular steps, namely: dissociation (CH<sub>3</sub>OCH<sub>3</sub>  $\rightarrow$  CH<sub>3</sub>O + CH<sub>3</sub> (R1) and CH<sub>3</sub>OCH<sub>3</sub>  $\rightarrow$  CH<sub>3</sub>OCH<sub>2</sub> + H (R2)), H<sub>2</sub> elimination (E11, CH<sub>3</sub>OCH<sub>3</sub>  $\rightarrow$  CH<sub>3</sub>OCH + H<sub>2</sub> (R3) and E12, CH<sub>3</sub>OCH<sub>3</sub>  $\rightarrow$  CH<sub>2</sub>OCH<sub>2</sub> + H<sub>2</sub> (R4)) and decomposition (CH<sub>3</sub>OCH<sub>3</sub>  $\rightarrow$  CH<sub>2</sub>O + CH<sub>4</sub> (R5) and CH<sub>3</sub>OCH<sub>3</sub>  $\rightarrow$  CH<sub>3</sub>OH + CH<sub>2</sub> (R6)). In turn, bimolecular reactions (DME + X  $\rightarrow$  CH<sub>3</sub>OCH<sub>2</sub> + HX, X = OH (R7), O (R8), CH<sub>3</sub> (R9), HO<sub>2</sub> (R10), O<sub>2</sub> (R11) and H (R12)) are important channels for the mechanism propagation. In special, reaction R11 prevails in the initiation phase, in the low temperature combustion. Despite the relevance of the combustion models for the decision about the implementation of a candidate fuel, the kinetic parameters for the abovementioned reactions have only been crudely estimated. In this work, a contribution for this issue is proposed by the determination of the rate coefficients for these most important reactions, based on a quantum mechanical description at the M06-2X/aug-cc-pVTZ level (with *a posteriori* improvement of the electronic energies from single point calculations at the CCSD(T)/aug-cc-pVTZ level) and variational transition state theory calculations. The reassessment of the combustion mechanism represents another goal of our work. Here, a numerical analysis of the improved combustion mechanism has been simulated using kintecus®, adopting the DVODE numerical method to integrate the coupled ordinary differential equations. The improved mechanism has been proposed adopting the combustion model by Yasunaga and co-workers [3] as a starting point and including our calculated rate parameters. The R1 and R2 unimolecular reactions are barrierless, with dissociation limits predicted as 80.33 and 93.73 kcal mol<sup>-1</sup>. Barrier heights for the unimolecular reactions R2 – R6 are 84.78, 79.31, 88.49 and 83.20 kcal mol<sup>-1</sup>, respectively. The bimolecular, DME + OH



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reaction (R7), is also shown to be important for the consumption of the fuel and proceeds by a hydrogen abstraction mechanism, leading to methoxymethyl radical and  $\text{H}_2\text{O}$ . For such reaction, theoretical calculations have also been performed at the M06-2X/aug-cc-pVTZ level. Concerning the available literature on this bimolecular reaction, new stationary points have been located and connected to reactants and products via reaction paths, whose contribution to the global kinetics has been proved significant. Pre-barrier complexes have been located, stabilized by 0.76, 4.81 and 5.05 kcal mol<sup>-1</sup>. These intermediates are connected to corresponding saddle points, which lie 0.29, -0.34 and 1.57 kcal mol<sup>-1</sup>, respectively, also with respect to reactants. For the other bimolecular reactions the predicted barrier heights at the M06-2X/aug-cc-pVTZ level are (in kcal mol<sup>-1</sup>): 0.4 (R8), 11.6 and 14.1 (R9a and R9b), 14.3 and 13.4 (R10a and R10b), 40.8 and 41.1 (R11a and R11b) and 8.0 (R12). Canonical variational rate coefficients have been calculated for all reaction paths in the range from 500 – 2000 K. For the reactions showing more than one saddle point, individual rate coefficients have been summed up to predict the global rate coefficients. Some kinetic parameters (R7 and R9-R12) have been compared to literature data, showing very good agreement with the previous results. These reactions have finally been included in the DME combustion model and the agreement of the predicted ignition delay times have been improved, as compared to the original combustion model. The proposed kinetic data finally represent a great contribution to the literature, concerning the combustion chemistry of dimethyl ether.

**Key-words:** combustion chemistry, ether combustion, rate coefficients

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**References:**

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