



Understanding and modeling the hydrogen-abstraction from dimethyl ether by the methyl radical with torsional anharmonicity



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ABSTRACT

Hybrid density functionals M06-2X and BMK in combination with the MG3S basis set, along with double-hybrid density functional B2PLYP with the TZVP basis set, were employed to better characterize the hydrogen atom transferring from dimethyl ether (DME) to the methyl radical. The distinct orientations of hydrogen atoms (in-plane and out-of-plane ones) in the DME molecule were taken into account. Density functional energetics was validated by comparison with the high-level CBS-QB3, G4, and G4MP2 calculations. Kinetic calculations were performed by means of the conventional transition-state theory (TST), canonical variational TST (CVT), and improved CVT (ICVT) over a wide temperature range 200–2600 K to clarify the available experimental measurements, and tunneling effect and anharmonic torsion were also included. Two transition structures are located with hydrogen-abstraction occurring at the in-plane and out-of-plane hydrogen positions, which are in fact related via the relative motion of the $\text{CH}_3 \cdots \text{H} \cdots \text{CH}_2$ and OCH_3 moieties about the C–O bond. Based on a single reaction pathway, the M06-2X/MG3SICVT rate constants with multidimensional small-curvature tunneling correction and proper treatment of anharmonic torsions compare well with most of the available experimental data. Variational effects on the computed rate constants are found to be negligibly small. Activation energies for the $\text{CH}_3 + \text{DME}$ reaction increase substantially with temperature, and exhibit a nonlinear dependence on the temperature. Therefore, rate constants are fitted to the four-parameter expression $k(T) = 8.59 \times 10^{-16} (T/300)^{5.11} \exp[-19.65(T + 140.90)/R(T^2 + 140.90^2)] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the broad temperature range.

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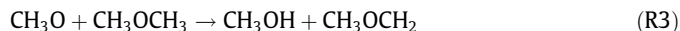
1. Introduction

The simplest of the ethers, dimethyl ether (DME), has diesel engine-compatible properties of high cetane number and low auto-ignition temperature. In addition, the combustion of DME can proceed in an environmentally-friendly way, indeed decreasing the particulate, volatile organic compounds, and NO_x emissions due to its high hydrogen to carbon ratio, the absence of C–C bonds, and high oxygen content [1]. Therefore, DME has been proposed as a possible alternative diesel fuel or potential additive, spurring numerous pyrolysis and combustion studies.

Several previous investigations [2,3] suggested that pyrolysis of DME could be described by a free-radical chain mechanism. At the combustion temperatures, the initiation reaction proceeds primarily via the C–O bond rupture to produce two radical species



The formed methyl (CH_3) and methoxy (CH_3O) radicals are highly active, and readily capture a hydrogen atom from the DME molecule via the propagation reactions (R2) and (R3), respectively, to allow the radical chain reaction to be self-sustaining.



Moreover, in a kinetic modeling study concerning the high-pressure decomposition and oxidation behavior of DME, reaction (R2) was found to be particularly sensitive to the DME consumption and auto-ignition condition [4]. As such, hydrogen-abstraction reaction of DME with the CH_3 radical has been the subject of many investigations. The earlier experimental studies were mostly carried out at low temperatures (below 573 K) with different CH_3 radical sources [5–11]. There appears to be satisfactory mutual agreement among the various determined rate constants presented in Table 1 in the Arrhenius form. Later Pacey et al. performed the investigation of DME pyrolysis in the moderate temperature range of 783–935 K [12], 1005 K [13], and 788–935 K

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Table 1
Kinetic parameters for reaction (R2).

CH ₃ source	T (K)	log(A/cm ³ mol ⁻¹ s ⁻¹)	E _a (kJ mol ⁻¹)	References
Hg photosensitization	472–565	12.0	44	[5]
Dimethylmercury photolysis	373–473	10.8	35.14	[6]
Acetone photolysis	381–471	11.4	40	[7]
Hg photosensitization	473–573	11.9	44	[8]
Acetone photolysis	408–523	11.6	41.84	[9,10]
Azomethane photolysis	373–473	11.3 ± 0.1	39.75 ± 0.84	[11]
DME pyrolysis	783–935	13.5 ± 0.4	63 ± 7	[12]
DME pyrolysis	1005	–	62.76	[13]
DME pyrolysis	788–935	13.3 ± 0.1	60 ± 2	[14]

[14], respectively. Their determined kinetic parameters for the title reaction are also included in Table 1. One can see that the activation barrier was evaluated to be in the neighborhood of 63 kJ mol⁻¹, which was, however, higher than those [5–11] determined at low temperatures by about 20 kJ mol⁻¹. Curran et al. [15,16] extended their experimental work to higher temperature range 800–1300 K and obtained a rate constant expression of $k_2(T) = 2.26 \times 10^{-5} T^{5.35} \exp(-24.31 \text{ kJ}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in non-Arrhenius form for the title reaction which exhibited strong temperature dependence. Subsequent measurement of the rate coefficient has been made up to 900 < T < 1900 K by Hidaka et al. [17] using a shock tube apparatus, and a standard Arrhenius expression for $k_2(T)$ was obtained through kinetic data fitting based on a relatively detailed DME pyrolysis process. The extrapolated values of Curran et al. [15,16] and Hidaka et al. [17] not only perform quite well in reproducing the earlier low-temperature measurements [5–11], but also exhibit good agreement with estimation by Pacey et al. [12,14]. Nevertheless, the rate constants determined by Hidaka et al. [17] are apparently lower than those of Curran et al. [15,16] at temperatures 1100–1300 K. Very recently, Tranter et al. [3,18] experimentally investigated the hydrogen-abstraction reaction particularly at high temperatures of 1100–1700 K in a diaphragmless shock tube with the methyl radical produced by dissociation of 2,3-butanedione to further understand its high-temperature kinetic behavior. Their measured rate constants are larger than the values of Hidaka et al. [17] by up to a factor of 3.84 at 1700 K but only 0.48 at 1100 K, despite the high-temperature model shows improved agreement against that from Curran et al. [15,16], differing by a factor of 0.33 at 1100 K and 0.27 at 1300 K, respectively. From above, there still appears to be some scatter in the measured rate constants for hydrogen-abstraction of DME with the methyl radical at high temperatures, which needs further rigorous investigations.

The only available theoretical study was performed by Wu et al. [19] Their determined rate constant was approximately one third of the experimentally derived low-temperature kinetic data [5–11] and high-temperature measurements [15,16] without taking into account internal rotations and chemically nonequivalent hydrogen orientations in the methyl group of DME, and they identified a single transition state for abstraction occurring at the out-of-plane hydrogen position.

To gain a deeper insight into the reaction fundamental of hydrogen-abstraction from DME by the CH₃ radical and to validate and complement previous experimental investigations, the present work will perform high-level theoretical chemical calculations rigorously to obtain molecular structures and energies of reactants, products, and transition states involved in the title reaction and establish a comprehensive kinetic model at temperatures between 200 and 2600 K covering all the current experimental temperature range based on various versions of transition state theory (TST), which include conventional TST, canonical variational TST (CVT), and improved CVT (ICVT), and tunneling correction and torsional anharmonicity are included.

2. Computational methods

2.1. Electronic energy calculation

Geometries of reactants, products, and transition states pertinent to the title reaction were completely optimized with the hybrid density functional theory (HDFT) of BMK [20] and M06-2X [21] in combination with the MG3S [22] basis set. The BMK/MG3S and M06-2X/MG3S levels have been found to achieve high accuracy thermochemistry and activation barrier of reaction [23]. In addition, “double-hybrid” density functional B2PLYP [24,25] in conjunction with the TZVP [26] basis set has been proven to indeed provide very promising results of molecular structures, harmonic frequencies, and kinetics comparable to those obtained by CCSD (T) calculations and from experiments [25,27], which was also employed to perform the quantum chemical calculations. Singlet state calculations were performed in a spin restricted way, while all open-shell systems were treated unrestrictedly.

The located stationary points were confirmed by analytic vibrational frequencies computed at the same levels as optimizations: minima with all real frequencies and first-order saddle points with only one negative frequency. The intrinsic reaction coordinate (IRC) calculations [28,29] with a step size of 0.03 amu^{1/2} Bohr were performed to provide a approximation for the minimum-energy path (MEP) and to confirm the optimized transition state steepest descent down to the desired reactant and product minima, respectively.

The calculated energetics included zero-point energy (ZPE) correction differences. For systematic errors inherent to the electronic calculations, the BMK/MG3S and M06-2X/MG3S ZPEs were corrected with scaling factors of 0.971 and 0.970 [30], respectively, and the B2PLYP/TZVP ZPEs were scaled by multiplying a factor of 0.9832 which has recently been recommended [31]. The involved energetics were also evaluated by the high-level CBS-QB3 [32], G4 [33], and G4MP2 [34] composite methods to verify the accuracy of HDFT predictions.

2.2. Rate constant calculation

Thermal rate constants with temperature were calculated by conventional TST [35,36], canonical variational TST (CVT) [37], and improved CVT (ICVT) [38,39]. To incorporate the quantum mechanical effects into theoretical kinetic models, the TST, CVT, and ICVT rate constants were improved by a temperature-dependent tunneling coefficient, $\kappa(T)$, which was approximated using multidimensional zero-curvature tunneling (ZCT) [39] and small-curvature tunneling (SCT) [40] methods. For comparison, we also evaluated the tunneling effect by the semiclassical Wigner approximation [41] which assumed that tunneling contributions came only from the transition state region along the reaction coordinate with the neglect of reaction path curvature.

The partition functions Q used in the rate constant calculations were evaluated by assuming separability of electronic,

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