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Detailed kinetic modeling of dimethoxymethane. Part I: *Ab initio* thermochemistry and kinetics predictions for key reactions

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ABSTRACT

Despite the great interest in oxygenated methyl ethers as diesel fuel additives and as fuels themselves, the influence of their methylenedioxy group(s) (O–CH_2–O) has never been quantified using *ab initio* methods. In this study we elucidate the kinetics and thermochemistry of dimethoxymethane using high-level *ab initio* (CCSD(T)/aug-cc-pV(D+T)Z//B2PLYPD3BJ/6-311++g(d,p)) and statistical mechanics methods. We model torsional modes as hindered rotors which has a large influence on the description of the thermal behavior. Rate constants for hydrogen abstraction by $\dot{H}$ and $\dot{C}H_3$ are computed and show that abstraction from the methylenedioxy group is favored over abstraction from the terminal methyl groups. β-scission and isomerization of the radicals are computed using master equations. The effect of rovibrationally excited radicals from preceding hydrogen abstraction reactions on subsequent hot β-scission is computed and has large influence on the decomposition of the formed dimethylether radical. The quantification of the effect of the dominant methylenedioxy group using *ab initio* methods can guide modeling of oxygenated methyl ethers that contain that group several times.

1. Introduction

Dimethoxymethane (DMM) is the smallest member of the family of oxygenated methyl ethers (OMEs). OMEs (CH_3–O–(CH_2–O)$_n$–CH_3) are beneficial additives for diesel fuels: they reduce soot [1–3], noise [4] and increase the efficiency by altering viscosity, lubricity, and cetane number [5]. In particular, their positive influence on the soot-NO_x tradeoff [6,7] makes them attractive in the context of current pollutant challenges. DMM has been tested as a fuel itself [8,9]. Its production pathways have been studied in recent years [1] and it can be produced from renewable feedstocks [10,11], biomass [12], and CO_2 [13].

To understand and simulate (*e.g.* with CFD) combustion and pollutant formation, detailed chemical models are needed [14]. The first detailed chemical kinetic model for DMM was developed in 2001 by Daly et al. from jet-stirred reactor experiments [15]. In 2010, Dias et al. performed mass spectrometry studies for DMM-flames and proposed a 90-species model [16]. Experiments for high-pressure oxidation [17] and atmospheric flames [18] contribute to the recent model of Marrodán et al. [18]. Most hydrogen abstraction and β-scission rate constants are taken from the study of Dias et al. [16], which in turn have been taken from analogies to similar compounds, *e.g.* dimethylether (DME) or diethylether (DEE). Nevertheless, the methylenedioxy group (O–CH_2–O) that is characteristic for OMEs is not contained in these substances. Neither is the O–(CH–O)–O group (that occurs in DMM intermediates) known to be formed from DME or DEE intermediates. Molecules that contain groups that are (so far) uninvestigated—*e.g.* because the molecules are new, expensive, dangerous or unstable—can still be investigated *in silico* using *ab initio* methods. So far, no *ab initio* calculations have been conducted for the methylenedioxy group or for DMM itself.

In this work, we elucidate the origin and fate of DMM radicals using *ab initio* calculations. We compute enthalpies, entropies, and heat capacities for DMM, the primary radicals ($\dot{R}1$: $\dot{C}H_2$–O–CH_2–O–CH_3 and $\dot{R}3$: CH_3–O–$\dot{C}H$–O–CH_3), $R\dot{O}_2$ and $\dot{Q}O_2H$ species. We compute rate constants for hydrogen abstraction by $\dot{H}$ and $\dot{C}H_3$ because oxidation and pyrolysis conditions are found to be sensitive to these reactions in recent flow reactor measurements [18]. The hydrogen abstraction products are initially rovibrationally excited.

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If subsequent reactions as *e.g.* β-scission take place before collisions thermalize these excited molecules, the corresponding reaction rates differ from rates obtained assuming the reactants to be in a Boltzmann distribution. We therefore not only compute thermal isomerization and β-scission, but we also compute branching ratios for the so called hot β-scission of rovibrationally excited radicals. Altogether, these insights help in the quantification of the impact of the O–CH_2–O group onto the combustion kinetics of OMEs.

2. Methods

All electronic structure calculations in this study have been performed with the Gaussian09 software, revision d01 [19]. Geometries and vibrational harmonic frequencies have been obtained at the B2PLYPD3BJ/6-311++g(d,p) level for the following reasons: first, harmonic frequencies from B2PLYP have proven to outperform the widely used B3LYP frequencies [20] (used *e.g.* in the CBS-QB3 and the G4 compound methods). The mean unsigned error (MUE) in wavenumbers for B3LYP/N07D[1] on the F38 benchmark set amounts to 34 cm^{-1} [22] and for B2PLYP/N07D to 23 cm^{-1} [20]. Second, in addition to the fact that one must use the same method for the geometries that one uses for the frequencies, bond lengths from B2PLYP show a mean absolute error (MAD) of 0.003 Å while the (MAD) for B3LYP is twice as large [23]. Third, the addition of the empirical 3-parameter dispersion with Becke–Johnson damping (D3BJ) has been shown to improve reaction energies [24]. We therefore assume that this method is a higher-quality model for chemical reactions and thus we include it in our DFT calculations.

We compute single-point CCSD(T) energies for the geometries from the aforementioned B2PLYPD3BJ/6-311g++(d,p) level using an extrapolation of single-point energies [25] according to:

$$E_X = \frac{a}{X^3} + E_{\mathrm{CBS}} \tag{1}$$

We use the basis sets aug-cc-pVDZ with $X = 2$ and aug-cc-pVTZ with $X = 3$ to obtain both parameters of Eq. (1). This scheme yields a MUE of 0.57 kcal/mol on the DBH24/08 database of reaction barrier heights [26]. The single-reference approach is adequate for our systems because the T1-diagnostics yields maximum values of 0.023 that is well below the threshold of 0.04 [27].

We compute partition functions Q for the isobaric-isothermal ensemble (N, p, T) using the python package TAMkin [28] to derive thermal energies and entropies. In addition to the rigid rotor harmonic oscillator (RRHO) model for the stiffer stretching and bending modes, we use a one-dimensional hindered rotor model for all torsional modes. The potential energy profiles are obtained from the method used for the geometries (B2PLYPD3BJ/6-311g++(d,p)). When a lower minimum is found during the dihedral angle scan, all scans for that molecule are restarted from that lowest-energy structure. Fourier series are fitted to represent the computed potential energies as a function of the corresponding dihedral angle. The number of Fourier functions is varied to yield a good compromise between deviation from the computed points and unphysical oscillations in the fitting function. The resulting potential energy function is used in a one-dimensional Schrodinger equation to compute the eigenenergies of the torsional mode. The corresponding partition function is obtained from accurate eigenvalue summation. The potential energy scans, the fitted Fourier function and the lowest energy eigenvalues for all torsional modes are depicted in the Supporting Information. We use 1000 and 2000 eigenfunctions—yielding 1000 respectively 2000 energy levels— to check whether the partition function changes at high temperature when higher energy levels are included. The increase of the number of energy levels hardly has an effect even at 4000 K. Since the hindered rotor partition function has been determined for an internal coordinate, not for a normal coordinate, the frequency that needs to be replaced is computed from the curvature at the minimum of the scan following the recommendation of Ghysels et al. [28].

Several torsional modes can influence each other (coupling), rendering the validity of the superposition of one-dimensional hindered rotor models questionable. Coupling will have a large effect when oxygen atoms are involved that may form intramolecular hydrogen bonds during the rotation [29]. Treating coupled degrees of freedom can be very tedious; complete coupled treatments are currently limited to seven-atomic systems [30]. Approximations still require the determination of all possible conformations. In the case of *n*-butanol this leads to 262 transition state conformations for a single abstraction channel [31]. The superposition of one-dimensional hindered rotors is shown to yield errors below 1% in the entropy [32,33] for larger alkanes. For dimers and tetramers of alcohols, where hydrogen bonds play a key role, the superposition of one-dimensional hindered rotation yields excellent reproduction of experimental enthalpies and entropies when one corrects for the topological symmetry of the coupled topological symmetry of the coupled potential energy surface (PES) [34]. In this study we therefore use the superposition of one-dimensional hindered rotors as a feasible means to include a large part of torsional anharmonicity.

Thermochemical values are calculated from the isobaric-isothermal (N, p, T) partition functions Q and the well-known statistical thermodynamic relations $H = RT^2 \partial \ln(Q)/\partial T$, $C_p = \partial H/\partial T$ and $S = R\ln(Q) + H/T$ again using the TAMkin python package [28]. DeTar [35] investigated the accuracy of heat capacity and entropy values obtained from *ab initio* calculations for several alkanes and found that the deviations from experimental data are mostly less than 0.5 cal/(mol K) for heat capacities and less than 0.6 cal/(mol K) for entropies.

Reaction rate constants for hydrogen abstraction are calculated using conventional transition state theory (cTST). Since the potential energy barriers and the imaginary frequencies are rather high, we expect the change of potential energy along the reaction coordinate to dominate the free energy curve and therefore variational effects to be small. Tunneling is taken into account *via* the zero-curvature Eckart approach. Eckart tunneling was shown to outperform both Wigner and Skodje & Truhlar tunneling methods [36]. Therefore we decided to use this combination of cTST/Eckart-tunneling. Extended Arrhenius forms $k(T) = AT^n \exp(-E_a/T)$ are fitted[2] to reproduce the computed rate constants from 500 K to 2000 K.

Temperature- and pressure-dependent rate constants for the unimolecular isomerization and β-scission of the two DMM radicals and the DME radical[3] are calculated from master equations (MEs) using the MESS software [38]. The microcanonical rate constants are calculated from Rice–Ramsperger–Kassel–Marcus (RRKM) theory including Eckart tunneling. Collisional energy transfer is modeled using the weak collider bath gas argon according to $\langle \Delta E_{\mathrm{down}} \rangle = 200\,\mathrm{cm}^{-1}\,(T/300\ \mathrm{K})^{0.85}$ [39]. The Lennard–Jones collision frequency [39] is calculated from σ = 3.41 Å, 5.85 Å, and 4.94 Å and ε = 81.1 K, 327 K, and 275 K for argon, DMM, and

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[1] The N07D basis set is constructed from addition of a reduced number of diffuse and polarization functions to the 6-31g set and is thus most comparable to the 6-311g++(d,p) basis set [21] used in this study.

[2] We actually fit $\ln k$ which is linear in the three parameters $\ln A$, n, and E_a and weights the rate constant at high temperature similarly to the rate constant at low temperature.

[3] For the DME radical, we used the data from Li et al. [37] obtained at the QCISD(T)/aug-cc-pVTZ//MPW1K/6-31+g(d,p) level of theory.

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