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Computational Kinetics by Variational Transition State Theory with Semiclassical Multidimensional Tunneling: Direct Dynamics Rate Constants for the Abstraction of H from CH₃OH by Triplet Oxygen Atoms

Rubén Meana-Pañeda^{#a,b}, Xuefei Xu^{#a,c}, He Ma^{#a}, and Donald G. Truhlar^{a,*}

^aDepartment of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States

^bLaboratory of Computational Biology, National Heart, Lung and Blood Institute, National Institutes of Health, Bethesda, MD 20892, United States

^cCenter for Combustion Energy and Department of Thermal Engineering, Tsinghua University, Beijing 100084, PR China

[#] These authors contributed equally to this work.

Abstract

Rate constants and the product branching ratio for hydrogen abstraction from CH₃OH by O(³P) were computed with multi-structural variational transition state theory including microcanonically optimized multi-dimensional tunneling. Benchmark calculations of the forward and reverse classical barrier heights and the reaction energetics have been carried out by using coupled cluster theory and multireference calculations to select the most reliable density functional method for direct dynamics computations of the rate constants. The dynamics calculations included the anharmonicity of the zero-point energies and partition functions, with specific-reaction-parameter scaling factors for reactants and transition states, and multi-structural torsional anharmonicity was included for the torsion around the C-O bond in methanol and in the transition states. The resulting rate constants are presented over a wider range than they are available from experiment, but in the temperature range where experiments are available, they agree well with experimental values, which is encouraging for their reliability over the wider temperature range and for future computations of oxygen atom reaction rates. In contrast to a previous computational prediction, the branching ratio predicted by the present work shows that the formation of CH₂OH + OH is the dominant channel over the whole range of temperature from 250 K to 2000 K.

TOC Graphic

*Corresponding Author truhlar@umn.edu.

Supporting Information.

Cartesian coordinates and absolute energies for reactants, products and transition structures of R1 and R2 are provided in supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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1. Introduction

Methanol is used as a fuel for internal combustion engines, an additive in gasoline, and a reducing agent for fuel cells.^{1,2} A large amount of research has been conducted to develop a comprehensive mechanism for methanol combustion including the kinetics of methanol's elementary reactions.^{3,4,5,6,7,8}

The present article considers the reactions between methanol and atomic oxygen O(³P):

Production of $\text{CH}_3\bullet + \text{HO}_2$, which has a much higher activation energy, is not considered in this work. Several experimental studies of the kinetics of R1 and R2 have been reported.^{9,10,11,12,13,14,15,16,17} The experimental total rate constants k_{1+2} are plotted as functions of temperature in Figure 1. Lu *et al.*¹⁵ used a diaphragmless shock tube with atomic resonance absorption detection of O atoms and evaluated the rate constants in the temperature range of 835-1777 K; the other experiments were conducted under 1006 K, where our studies indicate that only reaction R1 contributes non-negligibly. Most of these results are similar, but rate constants measured by LeFevre *et al.*¹⁰ and Basevich *et al.*¹¹ are significantly higher, and those measured by Avramenko *et al.*⁹ are significantly lower.

Computational studies of these reactions are scarce. Tsang¹⁸ carried out transition state theory computations with a potential energy surface (PES) modeled by the bond-energy-bond-order approximation empirically adjusted to experimental activation energies; obtaining the non-Arrhenius formula $k_{1+2} = 6.44 \times 10^{-19} T^{2.5} \exp(-1550/T)$ from 300 K to 1100 K, which later was extended to 2000 K by Herron¹⁹ by using the formula $k_{1+2} = 3.99 \times 10^{-19} T^{2.5} \exp(-1550/T)$ in the temperature range of 1000-2000 K. Lu *et al.*¹⁵

used canonical variational transition state theory with small curvature tunneling (CVT/SCT) to compute rate constants based on a PES calculated by coupled cluster calculations (CCSD(T)/6-311+(3df,2p)//B3LYP/6-311+G(3df,2p)). They predicted that R2 becomes important at high temperature and outweighs R1 above 1700 K. One concern with their calculations is that B3LYP is known to underestimate reaction barrier heights^{20,21} and in fact gives a negative barrier height for R1; thus the transition state geometry is unreliable. Another concern is that they used the single-structural harmonic-oscillator (SS-HO) approximation to evaluate partition functions for reactants or transition states, while in this work it is shown that neither multi-structural torsional anharmonicity nor anharmonicity of high-frequency modes are negligible. A subsequent calculation by Alves *et al.*²² used more accurate geometries and a correction for core-valence (CV) correlation. They obtained a higher barrier height for R1 and R2, but a similar total rate constant, perhaps by cancellation of errors due to also having improved frequencies and that they used the wrong symmetry number for reaction R1. One goal for the present paper is to reduce the uncertainties by using a more accurate PES, better evaluation of zero point energies, and an improved treatment of torsional anharmonicity.

Section 2 summarizes the methodology used in this paper. Section 3 gives results and discussion. Section 4 is a summary.

2. Methods

2.1. Best estimates for reaction energies

The classical reaction energy, V , is defined as the equilibrium potential energy of the products minus the equilibrium potential energy of reactant, may be obtained from experimental enthalpies of reaction at 0 K, by subtracting the change in vibrational zero point energy (ZPE). For comparison to our theoretical predictions, experimental enthalpies of reaction are obtained from experimental heats of formation of products and reactants; these are listed in Table 1, where $\Delta_f H_0^\circ$ for CH₂OH, CH₃O and OH radical come from the IUPAC critical evaluation project led by Ruscic²³, $\Delta_f H_0^\circ$ for the other species come from references 24 and 25.

Alecu *et al.*²⁶ proposed that the ratio of the sum of the fundamental frequencies to the ZPE may be approximated as a constant, $\alpha^{F/ZPE} = 0.974$, for a wide variety of molecules, and therefore, we estimate ZPEs for CH₃OH and OH from experimental fundamental frequencies by

$$\text{ZPE} \approx \frac{hc}{2\alpha^{F/ZPE}} \sum_m \bar{\nu}_m \quad (1)$$

where h is Planck's constant, c is the speed of light, and $\bar{\nu}_m$ is the fundamental frequency of mode m in wave numbers. The uncertainty of the ZPE evaluated by eq 1 is estimated to be $\pm 2\%$.

CH₂OH and CH₃O need special treatment. As indicated by Marenich and Boggs,^{27,28} CH₂OH has considerable structural flexibility and highly anharmonic vibrations, and CH₃O has a strong Jahn-Teller effect and spin-vibronic interaction. Marenich and Boggs constructed a sophisticated rovibrational Hamiltonian for CH₂OH and obtained its ZPE as the lowest eigenenergy of the rovibrational Hamiltonian. For CH₃O, they developed a model accounting for spin-orbit coupling, Jahn-Teller interaction, and anharmonic effects, and they evaluated the spin-vibronic-zero-point-energy from the model. Their ZPE values for CH₂OH and CH₃O are adopted here.

Combining the ZPEs and $\Delta_f H_0^\circ$ in Table 1 leads to V of -3.50 ± 0.57 kcal/mol for R1, and 5.84 ± 0.77 kcal/mol for R2. These values serve as the best experimentally based estimates of the classical energies of reaction.

2.2. Best estimates for barrier heights

The transition states for reactions R1 and R2 each have a low-energy electronically excited state. The overall barrier is determined by the ground electronic state, and we consider that first. Electronic structure calculations yield estimates for the difference between the potential energy at the highest-energy point on the minimum energy path (MEP) and at the equilibrium geometry of reactants; this will be called the forward classical barrier height $V_{\text{for}}^\ddagger$. A similar calculation employing products yields the reverse classical barrier height $V_{\text{rev}}^\ddagger$. Since experimental kinetic data such as Arrhenius energies of activation do not translate simply into barrier heights, we performed high-level single-point wave function calculations for reactants, products and transition states for R1 and R2 to estimate classical barrier heights. The best estimate energies used for this purpose were taken as

$$E(\text{CCSDT}(2)_Q/\text{CBS}) = E(\text{CCSDT}(2)_Q/\text{jun-cc-pVDZ}) + E(\text{CCSD}(\text{T})\text{-F12b}/\text{aug-cc-pVTZ}) - E(\text{CCSD}(\text{T})/\text{jun-cc-pVDZ})$$

(2)

where CCSDT(2)_Q²⁹ denotes coupled cluster theory with single, double, and triple excitations and a second-order estimate for connected quadruple excitations, jun-cc-pVDZ^{30,31} and aug-cc-pVTZ³² are basis sets, and CCSD(T)-F12b denotes coupled cluster theory with single and double excitations, a quasiperturbative treatment of connected triple excitations,³³ and the addition of explicitly correlated basis functions by the F12b method.³⁴ Geometries of all species are optimized by Kohn-Sham (KS) theory with the M08-HX exchange-correlation functional³⁵ and the MG3S basis set.³⁶ These geometries are shown in Figure 2, where transition states for R1 and R2 are denoted by TS1 and TS2, respectively. Correlation of core electrons was not included (it would largely be cancelled out when evaluating relative energies). The notation “CBS” on the left-hand side of eq 2 denotes that the last two terms of the equation are expected to correct the first term for basis set incompleteness.

Based on work presented elsewhere,³⁷ we expect that eq 2 should be reliable within about a half of a kcal/mol. The classical energies of reaction calculated in this way are -3.54 kcal/mol for R1 and 5.91 kcal/mol for R2; these agree with the experimentally based estimates (given above) within the experimental error bars. Therefore, we take the CCSDT(2)_Q/CBS classical energies of reaction and classical barrier heights as our best estimates for testing affordable model chemistries for possible use in the kinetics calculations. In these tests (details are in sections 2.3–2.5), all energies were calculated using the same set of geometries, namely the M08-HX/MG3S geometries, as were used to obtain these best estimates of the reaction energies and barrier heights.

An important complication in the reaction of O(³P) atoms is that the transition state has a low-energy excited state associated with an alternate orientation of the singly occupied spectator *p* orbital of the oxygen atom. For reactions with linear transition states, the two states become a degenerate Π state,³⁸ for C_{3v} transition states, the two states are a degenerate *E* state,^{39,40} for planar transition states without a threefold or higher axis they have *A'* and *A''* symmetries,^{41,42,43,44,45} and for structures belonging to the C_1 point group, such as in the reactions studied here, they both have the same *A* symmetry.^{46,47} The calculations in this article include the contribution of the excited state for both the R1 reaction and the R2 reaction.

2.3. Basis sets, geometries, and software

The calculations discussed in Section 2.2 use either a one-electron basis set or a combination of a one-electron basis set with the F12a or F12b schemes^{34,48} for including explicitly correlated basis functions in CCSD(T) calculations. The one-electron basis sets tested are cc-pVTZ⁴⁹, maug-cc-pVTZ⁵⁰, jul-cc-pVTZ^{30,31}, and aug-cc-pVTZ³², and the convergence with respect to basis sets were examined. The F12 schemes are designed to converge relatively quickly to the complete basis set limit (CBS).

All calculations in section 2.3–2.5 (except the B1 diagnostics) were carried out using a single set of geometries, namely the M08-HX/MG3S geometries used to obtain the best estimates of the barrier heights.

All density functional theory calculations were performed using the *Gaussian 09*⁵¹ program with the *MN-GFM* module⁵². All CCSD(T)-F12a and CCSD(T)-F12b calculations and CASPT2 calculations were carried out by *Molpro 2010*⁵³. CCSD(T), CCSDT, and CCSDT(2)_Q calculations were performed with *NWChem* program⁵⁴. In all CCSD(T)-F12a, CCSD(T)-F12b, CCSD(T), CCSDT, and CCSDT(2)_Q calculations, the core orbitals are frozen.

2.4. Kohn-Sham model chemistries

We tested 37 model chemistries based on KS density functional theory. A KS model chemistry is defined as a combination of an exchange-correlation functional and a one-electron basis set. The principal aim is to determine the most accurate KS-based model chemistry to be employed in kinetics when calculating energies and frequencies along the MEPs.

In testing KS methods, we considered a series of Minnesota functionals including M06⁵⁵, M06-L⁵⁶, M06-2X⁵⁵, M08-HX³⁵, M08-SO³⁵, M11⁵⁷, M11-L⁵⁸, SOGGA11-X⁵⁹, MN12-L⁶⁰, MN12-SX⁶¹, PW6B95⁶², PW6B95-D3(0)^{62,63}, PW6B95-D3(BJ)^{62,64}, PWB6K⁶², GAM⁶⁵, MGGAMS0, MGGAMS1, MGGA MS2, MGGA MS2h, and OreLYP; we also tested the popular B3LYP^{66,67,68} functional and the B97-3⁶⁹ functional. The goal of these tests is not to test all possible functionals to determine a best functional (such tests should be made on broad databases, not on a single reaction), but rather to find one functional that would be suitable for direct dynamics calculations on the reactions of interest here.

For all exchange-correlation functionals we report results for the MG3S basis set³⁶, which is usually adequate for barrier height evaluation in KS calculations.³¹ For M06-2X, M08-HX and M08-SO, which show relatively high accuracy in predicting barrier heights^{70,71,72}, we further tested a hierarchy of basis sets.

A pruned grid with 99 radial shells and 974 angular points in each shell is used for numerical integration in all KS calculations.

2.5. Coupled cluster model chemistries

For coupled cluster theory, a model chemistry consists of a combination of excitation level and basis set.

In several recent studies of reaction kinetics in biofuel combustion,^{73,74,75} CCSD(T)-F12a and CCSD(T)-F12b results were considered the best estimate for barrier heights and reaction energies when higher-level model chemistries were too expensive to be performed. Here we tested the validity of CCSD(T)-F12 methods for describing R1 and R2. The CCSD(T)-F12a and CCSD(T)-F12b calculations were unrestricted and based on restricted open-shell Hartree-Fock (ROHF) wave functions. We also present some results with CCSD(T) without F12, with CCSDT, and with CCSDT(2)_Q; these were spin-unrestricted and based on unrestricted Hartree-Fock (UHF) wave functions.

2.6. Multi-reference diagnostics and multi-reference computations

To determine the extent of multireference character of the reagents and triplet transition states, we calculated three multi-reference diagnostics for all species in R1 and R2. The diagnostic considered are the generalized B1 diagnostic (henceforth just called B1), the T1 diagnostic, and the %TAE diagnostic. The rationale and details of these diagnostics can be found elsewhere.^{76,77,78} All diagnostics involve electronic energies (including nuclear repulsion), that is, classical potential energies.

The B1 diagnostic is defined as the difference between a bond energy, reaction energy, or barrier height calculated with the BLYP exchange correlation functional and one calculated by the B1LYP exchange-correlation functional at the BLYP geometries (divided by the number n of bonds broken, but in the present cases all n are unity). A B1 diagnostic value that is higher than 10 kcal/mol indicates the system has significant multi-reference character or at least that it is a difficult case.

The T1 diagnostic is defined as the Euclidian norm of T_1 amplitudes vector in a coupled cluster singles and doubles (CCSD) wave function. It has been proposed that a T1 diagnostic larger than 0.02 for a closed-shell system or 0.045 for open shell system⁷⁹ suggests the need for a multi-reference treatment.

The %TAE diagnostic used in this work is the %TAE[(T)] diagnostic, which is defined as the percentage of total atomization energy recovered from adding the quasiperturbative connected triples contribution to a coupled cluster singles and doubles (CCSD) calculation of an atomization energy (AE):

$$\%TAE[(T)] = \frac{AE[CCSD(T)] - AE[CCSD]}{AE[CCSD(T)]} \quad (3)$$

A %TAE value less than 2% indicates the system is dominated by dynamical correlation, a %TAE value in the range of 2-10% implies mild-to-moderate static correlation, and a %TAE value greater than 10% suggests severe static correlation.

As shown in section 3.1.2, the diagnostics demonstrate that the transition state of reaction R2 has mild static correlation. Therefore, we performed calculations on the species involved in reaction R2 by complete active space second-order perturbation theory (CASPT2) based on complete active space self-consistent field (CASSCF) wave functions using the aug-cc-pVTZ basis set.

Five active spaces of various sizes are tested in this work for the energy of reaction and classical barrier height of reaction R2; they are labeled as (n,m) , where n is the number of active electrons, and m is the number of active orbitals. The first four active spaces are chosen based on the correlated participating orbitals (CPO) scheme that has been proposed for defining multireference model chemistries for thermochemical kinetics.⁸⁰ The choice of orbitals to be included in the active space in a CPO calculation is motivated by generalized valence bond⁸¹ (GVB) theory. In the CPO scheme, only the orbitals that participate most strongly in bond breaking and bond forming are considered. The smallest active space is of size (4,4), and it includes the three electrons and two orbitals participating in the breaking of CH₃O–H bond and in the forming of new O–H bond plus the other singly occupied orbital and a correlating orbital for the doubly occupied orbital. This (4,4) active space corresponds to the nominal CPO (*nom*-CPO)⁸⁰ active space. The next standard CPO active space is the moderate CPO (*mod*-CPO) one. It has size (10,10), and it adds the three p orbitals geminal to bonds that are broken or formed plus a correlating orbital for each of them. Correlating orbitals occupy approximately the same space as the orbitals they correlate. We label the oxygen atom of the reactant as O and the oxygen atom of the methanol as O', and we note that we treat the $\sigma(\text{CO}')$ bond orbital as one of the participating “p” orbitals geminal to bonds that are broken or formed, and the correlating unoccupied orbital of $\sigma(\text{CO}')$ is $\sigma^*(\text{CO}')$. The (6,6) and (8,8) active spaces are intermediate between nominal and moderate. Due to the inclusion of a correlating function for one of the p orbitals of the oxygen atom in the CPO active space, the (6,6), (8,8), and (10,10) active spaces lead to nondegenerate components of the P state of the O atom in the reactant region, where the P state should be

threefold degenerate since these calculations neglect spin-orbit splitting. Therefore, we also examined a modified CPO scheme where we removed the correlating p orbital of O atom from the *mod*-CPO active space to have a more balanced active space, whose size is (10,9).

A level shift of 0.3 hartree is used in all CASPT2 calculations for removal of intruder states⁸². When computing the reactants and products of R2, the two molecules involved were separated by more than 10 Å.

The compositions of the various active spaces examined for calculations on reaction R2 are summarized in Table 2, which is keyed to Figures 3-5, which show the active orbitals at the three stationary points. The orbitals in the figures are labeled based on their main molecular bonding characters. The bottom four orbitals are doubly occupied in the dominant configuration; the middle two orbitals are singly occupied; and the top four orbitals are virtual orbitals.

The calculation of the low-lying excited state energy for the transition states was carried out by MS-CASPT2⁸³ with the reference wave function being a two-state state-averaged CASSCF⁸⁴ calculation with 8 electrons in 6 orbitals using the aug-cc-pVTZ basis set. The active space includes the two σ bonding orbitals and the two σ antibonding orbitals for the breaking and forming bonds and two lone pair orbitals of the reactant O atom.

2.7. Dynamics

Multi-structural^{85,86,87} canonical variational transition state theory^{88,89,90,91} with microcanonical optimized multidimensional tunneling^{92,93} (MS-CVT/ μ OMT) was employed to compute the rate constants for R1 and R2 in the temperature range 250-2000 K. The dynamics calculations were carried out with direct dynamics using an implicit potential energy surface defined by the M08-SO/maug-cc-pVTZ density functional method that is validated above. For bimolecular reaction, the MS-CVT/ μ OMT rate constant is given by:

$$k^{\text{MS-CVT}/\mu\text{OMT}} = \frac{k_B T}{h} k \Gamma \frac{Q_{\text{elec}}^{\ddagger} Q_{\text{con-rovib}}^{\text{MS-T}, \ddagger}}{2 \prod_{i=1}^2 Q_{\text{elec}}^{R_i} Q_{\text{con-rovib}}^{\text{MS-T}, R_i}} \exp(-V^{\ddagger}/k_B T) \quad (4)$$

$$\Phi_{\text{trans}}^{\text{rel}}$$

where k_B is Boltzmann's constant, T is the temperature, h is Planck's constant, $V^{\ddagger}$ is the classical barrier height, and κ is the tunneling transmission coefficient accounting for quantum tunneling and nonclassical reflection. In the μ OMT scheme both small-curvature tunneling^{94,95,96,97} and large curvature tunneling (LCG4⁹⁸ in this work) are evaluated, and the larger of the two approximations is used at each tunneling energy. Γ is a factor accounting for the variational effect (i.e., the decrease of the calculated rate constant (without tunneling) due to variational optimization of the transition state as compared to placing the transition state at the saddle point). The factors $Q_{\text{elec}}^{R_i}$ and $Q_{\text{elec}}^{\ddagger}$ are electronic partition functions for reactant i ($i = 1, 2$) and the saddle point; $\Phi_{\text{trans}}^{\text{rel}}$ is the relative

translational partition function; and $Q_{\text{con-rovib}}^{\text{MS-T}, R_i}$ and $Q_{\text{con-rovib}}^{\text{MS-T}, \ddagger}$ (whose details can be found in ref. 86) are multi-structural conformational-rovibrational partition functions including torsional anharmonicity for the reactants and saddle point respectively.

The electronic partition function of the reactants is computed from the energies of the $^3\text{P}_{0,1,2}$ states of oxygen atom. The electronic partition function of the transition state is

$$Q_{\text{elec}}^{\ddagger} = 3 \sum_{\alpha=0}^1 e^{-\left(\epsilon_{\alpha}^{\ddagger} - \epsilon_0^{\ddagger}\right)/RT} \quad (4a)$$

Where $\epsilon_{\alpha}^{\ddagger}$ is the electronic energy of state α of the transition state.

In practical calculations, we first evaluate conformational-rovibrational partition functions ($Q_{\text{con-rovib}}^{\text{SS-HO}}$) by using the single-structural harmonic-oscillator (SS-HO) approximation, and then multi-structural partition functions including torsional anharmonicity ($Q_{\text{con-rovib}}^{\text{MS-T}}$) is obtained by multiplying SS-HO partition functions to a multi-structural torsional anharmonicity factor $F^{\text{MS-T}}$:

$$F^{\text{MS-T}, X} = \frac{Q_{\text{con-rovib}}^{\text{MS-T}, X}}{Q_{\text{con-rovib}}^{\text{SS-HO}, X}} \quad (5)$$

where X denotes methanol or transition state. The $F^{\text{MS-T}, X}$ factor embodies the effect of multi-structural torsional anharmonicity for species X . If there is only one distinguishable structure, it represents the effect of torsional potential anharmonicity, which can either increase or decrease the partition function. When there is more than one structure it also includes multiple-structure anharmonicity, which always increases the partition function.

In the MS-T method, we consider that the two enantiomers of TS1 can be interconverted by internal rotation, i.e., the internal rotation symmetry number (note that this is different from the overall rotational symmetry number) of TS1 is 2 (that is, in the MS-T approach TS1 has a Voronoi M value of 2) and one of the reactants (methanol) has a symmetry number of internal rotation of 3 ($M=3$ in the notation we have used in the MS-T papers).

Computations of rate constants under SS-HO approximation were carried out with the *POLYRATE*⁹⁹ and *GAUSSRATE*¹⁰⁰ programs; evaluation of $F^{\text{MS-T}, X}$ factors for reactants and transition states were performed by *MSTor* program¹⁰¹.

3. Calculations, results, and discussion

3.1. Testing of model chemistries for methanol reactions R1 and R2

3.1.1. Single-reference computations.—The results of model chemistry testing calculations are summarized in Table 3. First consider CCSDT and CCSDT(2)_Q calculations, which give highly accurate reaction energies with < 0.1 kcal/mol deviations from experimental values. The difference between CCSDT and CCSDT(2)_Q results is only 0.14 kcal/mol on average, indicating the convergence of coupled cluster method. Therefore CCSDT(2)_Q results may reasonably serve as the best estimates (BE) for barrier heights and reaction energies. For all other model chemistries, the mean unsigned deviation (MUD) with respect to BE were calculated and act as the indicator for accuracy.

CCSD(T)-F12a and CCSD(T)-F12b calculations give similar results and both achieved sub kcal/mol MUEs. For CCSD(T)-F12, we assume based on past experience that triple zeta is sufficiently accurate for our purposes when combined with F12, based on past experience but the question remains about the extent of the need for diffuse functions. We conclude from the tests carried out here that the convergence of the F12a scheme with respect to diffuse functions is achieved for the present work when the basis set reaches the jul level, based on the observation that when basis set is enlarged from jul-cc-pVTZ to aug-cc-pVTZ, all energy quantities differs by no more than 0.13 kcal/mol. The convergence for CCSD(T)-F12b is not achieved until the basis set reaches aug-cc-pVTZ, as the energy difference between CCSD(T)-F12b/jul-cc-pVTZ and CCSD(T)-F12b/aug-cc-pVTZ is on average 0.31 kcal/mol. However, we can infer that CCSD(T)-F12b/aug-cc-pVTZ has already converged to CBS limit (which is the basic assumption when we made basis set correction to CCSDT(2)_Q) by comparing the results with CCSD(T)-F12a/jul-cc-pVTZ or CCSD(T)-F12a/aug-cc-pVTZ values: the average energy discrepancy is only 0.07 kcal/mol.

Among various KS methods, M08-HX and M08-SO functionals show remarkable accuracy with MUEs of less than 1.04 kcal/mol with all basis sets, even with unaugmented cc-pVTZ. There is no evident improvement by using basis sets larger than the minimally augmented basis sets MG3S or maug-cc-pVTZ, which is consistent with previous work.³¹ Functionals other than M08-HX and M08-SO failed to give sub-kcal MUEs, especially the popular and widely-used B3LYP functional, which gave −1.2 kcal/mol forward barrier height for R1 (8.5 kcal/mol lower than BE), and 3.5 kcal/mol for R2 (10.1 kcal/mol lower than BE). Within all 26 KS model chemistries tested, M08-SO/maug-cc-pVTZ was the most accurate one with 0.58 kcal/mol MUD(6), and therefore it will be adopted in subsequent kinetics computation.

3.1.2. Multi-reference diagnostics and multi-reference computation.—Table 4 lists the B1 diagnostic of 9 quantities for R1 and R2 including classical barrier heights, classical reaction energies, and equilibrium dissociation energies of bonds to be formed or broken. The B1 diagnostics of three bond dissociation energies are all significantly lower than 10 kcal/mol, indicating that the stable species in R1 and R2 are single-reference systems. The B1 diagnostic of barrier heights of R2 are around 10 kcal/mol, which implies mild multi-reference property for TS2.

The values of T1 and %TAE diagnostics are presented in Table 5. The conclusions made by T1 and by %TAE diagnostic are similar: all stable species show no multi-reference character. For TS1 and TS2, the T1 and %TAE diagnostic values are just below the criterion for mild-to-moderate static correlation. Combined with B1 diagnostic, we infer that the transition state of R2 possesses borderline multi-reference character.

As shown in Table 3, the CASPT2 calculations with the nominal CPO space (4,4) (denoted as *nom*-CASPT2) and CASPT2 calculations with *mod*-CPO space (10,10) (denoted as *mod*-CASPT2) give very similar barriers and reaction energy for R2 reaction to each other, and the mean unsigned deviations from BE are 1.16 kcal/mol for *nom*-CASPT2 and 1.21 kcal/mol for *mod*-CASPT2, respectively. With the intermediate active spaces (6,6) and (8,8), the mean unsigned deviations from BE are decreased to 0.72 and 0.58 kcal/mol, respectively. The better performances of CASPT2 calculations with (6,6) and (8,8) active spaces could be a result of cancellation of errors, or it could be a result of better balance in the active space; achieving a well balanced active space in CASSCF calculations is one of the well known problems that makes it hard to define a good model chemistry of the complete active-space type. When we removed the correlating function ($p'_x(\text{O})$), as shown in Figs. 3-5) of one of the p orbitals of O atom from the *mod*-CPO space, we obtained better agreement with the best estimates, as shown for the (10,9) entry in Table 3; in particular, the mean unsigned deviation from BE of CASPT2(10,9) is only 0.47 kcal/mol.

3.2. Kinetics of R1 and R2

3.2.1. SRP Scaling Factor.—In order to better evaluate zero point energies and partition functions, we calculated specific-reaction-parameter (SRP) zero-point-energy (ZPE) scaling factors for methanol, for TS1, and for TS2.

The ZPE scaling factor (λ_{ZPE}) is defined as the ratio of the best-estimate ZPE to the ZPE computed by a given model chemistry with the harmonic approximation. Generically optimized scaling factors are available (or can be easily determined²⁶) for individual model chemistries, as derived by fitting to a database. However, these databases (or example, the F38/06 database^{26,55}) contain only stable molecules, and the generic values are more applicable to stable species than to transition states. In this work we computed SRP ZPE scaling factors for methanol and the transition structures based on the assumption that λ_{ZPE} can be separated into two parts⁷³:

$$\lambda_{\text{ZPE}} = \lambda_{\text{Harm}} \lambda_{\text{Anh}} \quad (6)$$

where λ_{Harm} , defined as the ratio between true harmonic frequencies and computed harmonic frequencies with a specific model chemistry (see ref 26 for details), is species-independent; while λ_{Anh} , the ratio between real ZPE and real harmonic ZPE, is model-chemistry-independent. Approximately λ_{Harm} can be viewed as the correction for inaccuracy of electronic model chemistry, whereas λ_{Anh} is the correction for anharmonicity of potential energy surface and therefore should be determined species-specifically. Species-specific anharmonic ZPEs are calculated by the hybrid degeneracy-corrected second-order

vibrational perturbation theory^{102,103,104} (HDCVPT) based on MPW1K/6-31+G(d,p)¹⁰⁵ calculations. Table 6 shows the SRP λ_{Anh} and the associated SRP λ_{ZPE} .

The universal λ_{ZPE} obtained by M08-SO/maug-cc-pVTZ calculations²⁶ is 0.983, and we found it is reasonably accurate for methanol as the SRP λ_{ZPE} of methanol is 0.982. However, for transition structures the discrepancy between universal and SRP λ_{ZPE} is evident. The SRP λ_{ZPE} values for TS1 and TS2 are respectively 0.016 and 0.008 smaller than universal values. For TS1, the error of ZPE caused by using universal scaling factor is as large as 0.5 kcal/mol and may significantly influence kinetics results.

3.2.2. Tunneling.—Figure 6 shows the tunneling coefficient κ^{uOMT} for R1 and R2. At high temperatures, κ^{uOMT} for both R1 and R2 asymptotically decrease to 1, indicating the classical limit for nuclear motion in the reaction coordinate. In low temperatures, κ^{uOMT} for R1 and R2 show significant discrepancy. At 250 K, the κ^{uOMT} for R2 reaches 17 due to strong tunneling effect of hydrogen atom, while for R1 κ^{uOMT} is only 1.87. The low value for R1 can be explained by the shape of $V_{\text{a}}^{\text{G}}(s)$ (adiabatic ground-state energy) curve with respect to reaction coordinate, see Figure 7.

Examination of the normal mode frequencies along the MEP demonstrated that the plateau in the $V_{\text{a}}^{\text{G}}(s)$ curve is caused by a C–H bending mode which undergoes a drastic frequency decrease when the system travels through the plateau region to transition state. As shown in Figure 8, from $s=-0.306$ Å to -0.108 Å the frequency of the C–H bending mode decreased by 354 cm^{-1} , accordingly ZPE contribution from the mode decreased by 0.51 kcal/mol. Since at the same time V^{MEP} increased only by 0.78 kcal/mol, the increase is largely cancelled out by the ZPE drop. The frequency decrease of a reactive mode is a common motif in hydrogen atom transfer reactions¹⁰⁶ and is mainly caused by weakening of a force constant transverse to the reaction coordinate.

3.2.3. Torsional Anharmonicity.—Figure 9 shows the multi-structural torsional anharmonicity factor $F^{\text{MS-T}}$ for methanol and the transition states. (The values calculated at the transition structures are also used at generalized transition states, and $F^{\text{MS-T}}$ for the oxygen atom is unity.) Since we only calculate the forward reaction, we do not consider $F^{\text{MS-T}}$ for products.

For methanol and TS2, which are single-structure molecules, the multi-structural torsional anharmonicity (MS-T) correction reduces to a torsional potential anharmonicity correction. The $F^{\text{MS-T}}$ for methanol is close to 1 under all temperatures considered, indicating the torsion around C–O bond in methanol can be reasonably approximated by a normal mode harmonic vibration. When the temperature is increased, $F^{\text{MS-T}}$ gradually decreases. For TS2, $F^{\text{MS-T}}$ is quite low, which is due to the small effective torsional barrier (0.16 kcal/mol) for the torsion around C–O bond. The smallness of the torsional barrier is explained by the large distance between hydrogen atom in methyl group and hydrogen in hydroxyl group. For TS1, the situation is different. TS1 has two enantiomeric structures contributing equally to the partition function; therefore the $F^{\text{MS-T}}$ for TS1 is significantly larger than 1. Note that the factor of two for two enantiomers can be included in conventional TST by using an

appropriate symmetry factor; the symmetry factor to account for a chiral transition structure is two.⁸⁹

3.2.4 Excited state.—We calculated the excitation energy of the transition structures for reaction R1 and R2. The MS-CASPT2 calculations give a vertical excitation energy of 0.38 and 2.28 kcal/mol for reactions R1 and R2, respectively. We analyzed the change in the vertical excitation energy with respect to the geometry by carrying out MS-CASPT single point calculations along the 1-2-3-6 and 1-2-3-4 torsion angles (see Figure 2) for TS1 and TS2, respectively. None of these scans significantly lowers the excitation energy of TS1 or TS2. Therefore we used the vertical excitations energies to compute the electronic partition function as described in equation 4a.

3.2.5 Rate Constants.—Figure 10 shows the MS-CVT/ μ OMT rate constants of R1 and R2 as calculated two ways - with the universal vibrational frequency scaling factor and with the SRP scaling factors. A comparison between the computational and experimental values of the total rate constant k_{1+2} can be found in Figure 1, where the computational results based on SRP scaling factor agree well with experimental values at all temperatures where experiments are available. The small deviation of computational results from the experimental values is partly due to the fact that experimental results are fitted to the Arrhenius formula and behave as straight lines in the graph. Regarding the previous theoretical studies, the present study is, to the best of our knowledge, the only one that includes the effect of the low-energy electronically excited state in the values of the thermal rate constants for both R1 and R2 reactions.

It also should be noted that the values of the rate constants reported by Alves et al. have an error factor of 1.5 because they used a reaction symmetry number of 3 for reaction R1 instead of 2. As shown in Figure 2 the reactant and transition structure TS1 both have a symmetry C_1 , which means their rotational symmetry numbers are 1, but TS1 is chiral, and both structures lead to products, so in the harmonic-oscillator approximation that they used the rate constant for R1 has overall symmetry number of 2^{107} (not 3). This can be handled by using an overall symmetry number of two or by counting each of the two enantiomeric structures of the transition state, each with a symmetry number of one.

Rate constants based on SRP scaling factors were used for all fits. For R2, the correction from SRP scaling factor is not evident due to the fact that the difference between the SRP scaling factor and the universal scaling factor for TS2 is smaller than for TS1.

The rate constants k_1 and k_2 are fitted by the non-Arrhenius formula proposed in previous studies.^{73,75} For R1, which is an exothermic reaction, equation (7) is used to fit the temperature dependence of the rate constant:

$$k = A \left(\frac{T + T_0}{300} \right)^n \exp \left(- \frac{E(T + T_0)}{R(T^2 + T_0^2)} \right) \quad (7)$$

This gives the result:

$$k_1 = 2.931 \times 10^{-13} \left(\frac{T + 119.065}{300} \right)^{2.791} \exp \left(-\frac{1.923(T + 119.065)}{R(T^2 + 1476.474)} \right) \quad (8)$$

For R2, which has a positive enthalpy of reaction at 0 K, a slightly different formula is used to recover the correct limiting behavior at low temperatures:

$$k = A \left(\frac{T}{300} \right)^n \exp \left(-\frac{E(T + T_0)}{R(T^2 + T_0^2)} \right) \quad (9)$$

The resultant rate constant expression is:

$$k_2 = 1.192 \times 10^{-14} \left(\frac{T}{300} \right)^{3.338} \exp \left(-\frac{3.918(T + 136.741)}{R(T^2 + 18698.101)} \right) \quad (10)$$

In eq 8 and eq 10, rate constants have units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and R is the ideal gas constant in units of $\text{kcal} \cdot \text{mol}^{-1} \text{ K}^{-1}$. The value of the total rate constant k_{1+2} at 775 K computed by using the non-Arrhenius formulas is $1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which agrees reasonably well with the single-temperature flash photolysis measurement value of $9.6 \pm 0.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by Carr et al.¹⁷

Branching ratios of R1 and R2 were computed and are shown in Table 7. At 775 K the calculated branching fraction of R1 is 0.990 which is slightly larger than the top of the error bar on the measured value of 0.92 ± 0.05 reported by Carr et al.;¹⁷ theory and experiment agree that reaction R1 dominates at this temperature, as expected from the relative bond energies of the bonds being broken in R1 and R2. The data in Table 7 indicate that R1 is the dominant channel over the whole temperature range considered (250–2000 K), with a branching fraction higher than 90% even at 2000 K; this disagrees with Lu *et al.*'s work¹⁵ which had predicted that R2 would become the dominant branch above 1700 K. The source of the difference in branching ratio between this work and that of Lu *et al.* may be understood from Table 8, which compares transition structure properties from their work,¹⁵ from this work, and from the work of Alves et al.²² The table gives transition structure geometries, imaginary frequencies, and forward barrier heights calculated in the three studies. In the following discussion we will use B3LYP to denote the B3LYP/6-311+G(3df, 2p) computation of Lu et al., BB1K to denote the BB1K/aug-cc-pVTZ computation in Alves et al.'s work, and M08-SO to denote the M08-SO/maug-cc-pVTZ computation of the present study.

For TS1, the geometry and imaginary frequency calculated by BB1K lie between the B3LYP and M08-SO results. But in terms of imaginary frequency, the BB1K value ($1370i$) is much closer to M08-SO ($1487i$) than is the B3LYP value ($426i$). As discussed in the section on

testing and validation, B3LYP fails drastically in predicting the forward barrier height for R1, for which it yields -1.2 kcal/mol. However, when a CCSD(T) single-point calculation is carried out on the B3LYP geometry, the resultant barrier height (6.3 kcal/mol) agrees well with BB1K and M08-SO results (6.4 kcal/mol and 6.2 kcal/mol respectively). In Figure 11, we plotted rate constants computed by the three methods. It can be clearly seen that k_1 computed by CCSD(T)//B3LYP (blue dots) coincides with the M08-SO results that do not include the low-lying excited state of TS1 (denoted in Figure 11 as M08-SO(ground-state)); therefore, the discrepancy between CCSD(T)//B3LYP and M08-SO(ground-state) total rate constants is due to different k_2 values.

For TS2, BB1K once again gives an intermediate geometry and imaginary frequency between B3LYP and M08-SO, but it is more similar to the M08-SO results. For instance, the BB1K and M08-SO bond lengths for O1-H2 are respectively 1.169 Å and 1.170 Å, while B3LYP gives 1.209 Å; the difference between BB1K and M08-SO bond lengths for the H2-O3 bond (0.020 Å) is slightly smaller than difference between BB1K and B3LYP (0.022 Å); as for imaginary frequency, the B3LYP result ($1313i\text{ cm}^{-1}$) is significantly lower than either the BB1K ($2083i\text{ cm}^{-1}$) or M08-SO ($2281i\text{ cm}^{-1}$) result. As in the case of TS1, BB1K and M08-SO yield similar barrier heights (13.1 kcal/mol and 13.0 kcal/mol respectively), while B3LYP drastically underestimates the barrier (only 3.4 kcal/mol). However, in this case, a CCSD(T) single-point calculation does *not* correct the poor agreement of B3LYP results with the BB1K and M08-SO calculations; the CCSD(T) single-point barrier height is 10.6 kcal/mol, about 2.5 kcal/mol lower than BB1K and M08-SO. This is the main reason why k_2 calculated by Lu *et al.* is orders of magnitude larger than M08-SO results and even dominates the reaction at high temperatures. Another cause is their neglect of the torsional anharmonicity effect, which is shown here to have negative effect on k_2 ($k_2^{\text{MS-T}}(\text{TS2}) \ll 1$).

4. Summary

In this work, we first compiled accurate thermochemical data for species in R1 and R2. Classical reaction energies were derived and served as reference values for a systematic testing of various model chemistries: both those based on Kohn-Sham (KS) density functional theory and those based on wave function theory. This testing led to M08-SO/maug-cc-pVTZ as the most accurate KS-type model chemistry for describing R1 and R2; therefore, M08-SO/maug-cc-pVTZ was employed in kinetics computations.

To better evaluate zero-point energies along minimum energy path (MEP) and partition functions for transition states, we calculated the specific-reaction-parameter (SRP) scaling factors for species in R1 and R2. Finally, kinetics of R1 and R2 were studied by canonical variational transition state theory with microcanonical optimized multidimensional tunneling (CVT/ μ OMT). Multi-structural torsional anharmonicity corrections were considered and were demonstrated to change the partition functions of transition states by a factor of up to 1.6.

The final rate constants agree very well with experimental values in all experimentally studied temperature ranges. We also calculated the branching ratio of the two reaction products, which is available experimentally at only one temperature; we found that R1 is the

dominant channel over the whole range of temperature from 250 K to 2000 K. The prediction by previous work that R2 will be dominant at high temperatures is questionable due to their unreliable optimization of TS2 by the B3LYP functional and subsequent underestimation of the R2 barrier height. Neglect of multi-structural torsional anharmonicity also contributes to their R2-biased branching ratio.

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Figure 1. Arrhenius plot of experimental and theoretical results for total (R1+R2) thermal rate constants. The CVT/μOMT calculations in this figure are our final values including the SRP scaling factor and the contribution of the excited potential energy surface (see text).

Figure 2. Geometries of the stationary points for reactions R1 and R2 by using M08-HX/MG3S model chemistry, where the important distances are in Å. TS1 and TS2 are the transition state geometries for reactions R1 and R2, respectively.

Figure 3.

The active orbitals in the (10,10) active space of TS2. In the dominant configuration, (a-d) are doubly occupied orbitals, (e) and (f) are singly occupied orbitals, and (g-j) are unoccupied (virtual) orbitals. The z axis coincides with the bond that breaks or forms; x and y axes are perpendicular to z axis.

Figure 4.

The active orbitals in (10,10) active space of R2 reactants. (a-d) are doubly occupied orbitals, (e) and (f) are singly occupied orbitals, and (g-j) are unoccupied orbitals. The red cross stands for the reactant O atom. The y axis for O1 is perpendicular to the bond that breaks. For x, y, and z labeled for O atom, they are random because the two reactants are placed randomly with 10 Å separation.

Figure 5.

The active orbitals in (10,10) active space of products of R2 reaction. (a-d) are doubly occupied orbitals, (e) and (f) are singly occupied orbitals, and (g-j) are unoccupied orbitals. The z axis coincides with the bond that breaks or forms; the x and y axes are perpendicular to z axis.

Figure 6.
Tunneling coefficients $K^{\mu_{OMT}}$ for R1 and R2.

Figure 7. V^{MEP} and V_a^G with respect to reaction coordinate s for R1. Red line in V_a^G graph presents the LCG4 representative tunneling energy at 298 K.

Figure 8.

The C–H bending mode that causes the flat region from $s \approx -0.1$ to $s \approx -0.3$ in the V_a^{G} curve.

Figure 9.

Multi-structural torsional anharmonicity factors $F^{\text{MS-T}}$ for methanol and for the transition structures of reactions R1 and R2.

Figure 10.
Computational rate constants for R1 and R2 based on universal and SRP scaling factors for vibrational frequencies.

Figure 11.

Rate constants from ref. 15 (CCSD(T)), ref. 22 (BB1K), and present work including the first electronically excited state of the TS (M08-SO) and also without including it (M08-SO(ground-state)). For the BB1K method, Alves *et al.* did not calculate the branching ratio, and therefore only total rate constants are plotted (cyan line) for their work. For the M08-SO and M08-SO(ground-state) rate constants, k_2 is negligible compared with k_1 , so k_1 and k_{1+2} behave as a single curve (black) in the graph.

Table 1.

Experimental enthalpies of formation and zero-point energies for reactants and products of R1 and R2 (kcal/mol).

Species	CH ₃ OH	O(³ P)	CH ₂ OH	CH ₃ O	OH
$\Delta_f H_0^\circ$	-45.44 ± 0.14^a	58.98 ± 0.02^b	-2.56 ± 0.17^c	6.79 ± 0.50^c	8.87 ± 0.07^c
ZPE	31.85 ± 0.51^d	0	22.59 ± 0.02^e	22.60 ± 0.22^f	5.52 ± 0.09^d

^a taken from ref 24;

^b taken from ref 25;

^c taken from ref 23;

^d calculated from equation 1;

^e taken from ref 27;

^f F taken from ref 28.

Table 2.

Orbitals in the employed active spaces in CASPT2 calculations for the reactants (denoted R2), transition state (denoted TS2), and products (denoted P2) of reaction R2.^a

	R2	TS2	P2
(4,4), i.e., <i>nom</i>	$d^2e^1f^1g^0$	$d^2e^1f^1g^0$	$d^2e^1f^1g^0$
(6,6)	$(4,4)+b^2i^0$	$(4,4)+b^2i^0$	$(4,4)+c^2h^0$
(8,8)	$(6,6)+c^2h^0$	$(6,6)+a^2j^0$	$(6,6)+a^2j^0$
(10,10), i.e., <i>mod</i>	$(8,8)+a^2j^0$	$(8,8)+c^2h^0$	$(8,8)+b^2i^0$
(10,9)	$(10,10)-j^0$	$(10,10)-j^0$	$(10,10)-j^0$

^aThe superscripts on the orbitals denote the occupancy in the dominant configuration. The orbitals (a-j) refer to Figures 3–5.

Table 3.

Forward and reverse barrier heights and reaction energies (kcal/mol)^a

Method	Basis set	R1 $V_{\text{for}}^{\ddagger}$	R1 $V_{\text{rev}}^{\ddagger}$	R2 $V_{\text{for}}^{\ddagger}$	R2 $V_{\text{rev}}^{\ddagger}$	R2 V	MUD(3) ^b	MUD(6) ^b
B3LYP	MG3S	-1.17	6.08	-7.25	3.53	3.87	-0.34	6.70
M08-HX	cc-pVTZ	5.49	10.29	-4.80	13.34	8.60	4.74	0.77
	MG3S	5.37	10.05	-4.68	13.24	8.54	4.70	0.80
	maug-cc-pVTZ	5.61	10.23	-4.62	13.41	8.54	4.87	0.69
	jun-cc-pVTZ	5.75	9.47	-3.73	12.68	7.41	5.27	0.60
	jul-cc-pVTZ	5.49	10.26	-4.78	13.33	8.56	4.77	0.75
	aug-cc-pVTZ	5.40	10.21	-4.81	13.24	8.51	4.73	0.78
M08-SO	cc-pVTZ	6.13	10.03	-3.90	12.89	7.75	5.13	0.51
	MG3S	5.88	9.98	-4.10	12.57	7.50	5.08	0.67
	maug-cc-pVTZ	6.21	9.98	-3.77	12.95	7.70	5.25	0.43
	jun-cc-pVTZ	6.35	9.25	-2.90	12.18	6.46	5.72	0.93
	jul-cc-pVTZ	6.11	10.01	-3.89	12.87	7.72	5.14	0.50
	aug-cc-pVTZ	6.07	9.98	-3.91	12.82	7.70	5.13	0.52
M06-2X	cc-pVTZ	1.02	8.32	-7.30	7.04	5.74	1.30	4.36
	MG3S	4.63	8.18	-3.55	10.52	5.73	4.79	2.04
	maug-cc-pVTZ	1.02	8.32	-7.30	7.04	5.74	1.30	4.36
	jun-cc-pVTZ	4.71	7.66	-2.95	9.91	4.65	5.26	2.45
	jul-cc-pVTZ	4.50	8.33	-3.83	10.55	5.78	4.77	2.02
	aug-cc-pVTZ	4.43	8.30	-3.87	10.50	5.76	4.74	2.05
SOGGA11-X	MG3S	4.09	7.30	-3.21	10.24	8.13	2.12	2.52
M06-L	MG3S	-0.92	2.58	-3.50	2.71	2.39	0.32	7.25
M06	MG3S	3.14	7.32	-4.17	8.30	4.72	3.58	3.52
M11-L	MG3S	3.22	9.68	-6.46	9.14	9.56	-0.43	4.22
M11	MG3S	4.51	9.29	-4.78	12.75	7.60	5.14	0.56
MN12-L	MG3S	3.90	8.38	-4.47	9.33	8.24	1.09	3.21
MN12-SX	MG3S	4.51	9.50	-4.99	10.23	8.04	2.19	2.47
B97-3	MG3S	1.37	7.18	-5.81	7.33	6.47	0.86	4.17

Method	Basis set	R1 $V_{\text{for}}^{\ddagger}$	R1 $V_{\text{rev}}^{\ddagger}$	R1 V	R2 $V_{\text{for}}^{\ddagger}$	R2 $V_{\text{rev}}^{\ddagger}$	R2 V	MUD(3) ^b	MUD(6) ^b
GAM	MG3S	-3.57	1.00	-4.57	0.76	-2.00	2.76	8.55	7.88
MGGAMS0	MG3S	-3.38	4.44	-7.82	-1.25	5.77	-7.02	9.89	8.49
MGGAMS1	MG3S	-2.87	4.62	-7.50	-0.48	5.67	-6.15	9.37	8.06
MGGA_MS2	MG3S	-3.49	4.33	-7.82	-1.33	5.07	-6.40	9.94	8.55
MGGA_MS2h	MG3S	-0.56	5.86	-6.42	2.25	7.08	-4.83	7.55	6.38
OreLYP	MG3S	-4.39	2.95	-7.34	-1.26	-0.94	-0.32	9.89	8.83
PW6B95	MG3S	1.34	6.15	-4.81	6.90	4.87	2.04	4.45	4.19
PW6B95-D3(0)	MG3S	1.03	5.72	-4.69	6.62	4.45	2.17	4.64	4.39
PW6B95-D3(BJ)	MG3S	1.10	5.85	2.10	6.67	4.57	2.10	4.61	5.08
PWB6K	MG3S	6.73	8.31	4.50	13.36	8.85	4.50	0.93	2.29
CCSD(T) ^c	6-311G(3df,2p)	6.3	11.8	-5.5	10.6	8.2	2.4	2.33	1.83
CCSD(T) ^d	CBS+CV	7.6	11.3	-3.7	14.4	8.4	6.0	0.55	0.46
CCSD(T)	F12a-cc-pVTZ	8.59	11.03	-2.44	14.38	7.61	6.77	0.58	0.74
	F12a-maug-cc-pVTZ	8.25	11.40	-3.15	14.76	8.35	6.41	0.79	0.73
	F12a-jul-cc-pVTZ	7.85	11.19	-3.34	14.43	8.36	6.07	0.57	0.49
	F12a-aug-cc-pVTZ	7.72	11.18	-3.46	14.36	8.35	6.01	0.52	0.42
	F12b-cc-pVTZ	8.56	10.83	-2.27	14.41	7.57	6.83	0.62	0.75
	F12b-maug-cc-pVTZ	8.23	11.21	-2.98	14.81	8.34	6.47	0.82	0.74
	F12b-jul-cc-pVTZ	8.18	11.02	-2.84	14.82	8.33	6.50	0.83	0.49
	F12b-aug-cc-pVTZ	7.69	10.99	-3.30	14.39	8.30	6.09	0.54	0.42
CCSDT	CBS	7.42	10.88	-3.46	13.87	7.98	5.89	0.20	0.16
nom-CASPT2	aug-cc-pVTZ	-	-	-	14.37	6.74	7.64	1.16	-
CASPT2(6,6)	aug-cc-pVTZ	-	-	-	13.96	8.76	5.20	0.72	-
CASPT2(8,8)	aug-cc-pVTZ	-	-	-	14.45	7.69	6.77	0.58	-
mod-CASPT2	aug-cc-pVTZ	-	-	-	14.55	6.84	7.72	1.21	-
CASPT2(10,9)	aug-cc-pVTZ	-	-	-	13.14	6.97	6.17	0.47	-
Experiment	[Section 2.1]	-	-	-3.50	-	-	5.84	-	-

Method	Basis set	R1 $V_{\ddagger}^{\text{for}}$	R1 $V_{\ddagger}^{\text{rev}}$	R1 V	R2 $V_{\ddagger}^{\text{for}}$	R2 $V_{\ddagger}^{\text{rev}}$	R2 V	MUD(3) ^b	MUD(6) ^b
CCSDT(2)Q	CBS [eq 2]	7.24	10.75	-3.50	13.58	7.68	5.90	0.00	0.00

^a All computations except those from previous work (*c* and *d*) are based on geometries optimized by M08-HX/MG3S.

^b MUD(6) is the mean unsigned deviation of the four classical barrier heights and two classical reaction energies from the best estimates, which are the results of the CCSDT(2)Q/CBS calculations. MUD(3) is the deviation of two classical barrier heights and the classical reaction energy of R2 reaction from the results of the CCSDT(2)Q/CBS calculations.

^c from Lu *et al.* at B3LYP/6-311+G(3df,2p) geometries

^d from Alves *et al.* at BB1K/aug-cc-pVQZ geometries

Table 4.

B1 Diagnostic (kcal/mol) for methanol reactions R1 and R2

	BLYP/MG3S	B1LYP/MG3S	B1 diagnostic
$D(\text{HOCH}_2 - \text{H})$	98.76	99.54	0.79
$D(\text{CH}_3\text{O} - \text{H})$	106.01	105.80	0.21
$D(\text{O}-\text{H})$	109.53	105.50	4.04
R1 forward barrier	-1.77	2.42	4.19
R1 reverse barrier	9.01	8.38	0.63
R1 energy of reaction	-10.78	-5.95	4.82
R2 forward barrier	-6.22	5.83	12.05
R2 reverse barrier	-2.70	5.52	8.22
R2 energy of reaction	-3.52	0.30	3.82

All calculations are based on BLYP geometries, except for saddle point of R2, which cannot be correctly optimized using BLYP, so it is optimized with B1LYP.

Table 5.

T1 diagnostic and %TAE diagnostic for species in methanol reactions R1 and R2

	CH ₃ OH	O	TS1	TS2	CH ₂ OH	CH ₃ O	OH
T1	0.010	0.007	0.035	0.035	0.017	0.021	0.009
%TAE	1.22%	-	1.73%	1.87%	1.42%	1.24%	1.33%

T1 diagnostics are calculated from CCSD/aug-cc-pVTZ single-point energy calculations; %TAE values are based on CCSD/cc-pVTZ and CCSD(T)/cc-pVTZ evaluations of the atomization energy. All geometries for this table are optimized by M08-HX/MG3S.

Table 6.

Zero point energies and specific-reaction parameterized (SRP) scaling factors for species in R1, R2 (kcal/mol)

	CH ₃ OH	TS1	TS2
ZPE(Harm)	33.270	30.186	28.626
ZPE(Anh)	32.781	29.269	28.005
$\lambda_{\text{Anh}}(\text{SRP})$	0.985	0.970	0.978
$\lambda_{\text{ZPE}}(\text{SRP})$	0.982	0.967	0.975

Both harmonic and anharmonic ZPE are calculated on MPW1K/6-31+G(d,p) level, anharmonic ZPE are obtained using HDCVPT2 method. $\lambda_{\text{ZPE}}(\text{SRP})$ is calculated by multiplying $\lambda_{\text{Anh}}(\text{SRP})$ by harmonic scaling factor on M08-SO/maug-cc-pVTZ level (0.997).

Table 7.Rate constants and branching ratio of R1 and R2 as functions of temperature ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

Temperature (K)	Rate constants for R1			Rate constants for R2		
	Universal scaling factor	SRP scaling factor	Branching ratio(%)	Universal scaling factor	SRP scaling factor	Branching ratio(%)
250	1.97E-15	4.91E-15	99.99	3.47E-19	5.31E-19	0.01
298	6.84E-15	1.48E-14	99.97	2.89E-18	4.13E-18	0.03
350	1.92E-14	3.73E-14	99.94	1.68E-17	2.28E-17	0.06
400	4.20E-14	7.59E-14	99.89	6.40E-17	8.39E-17	0.11
500	1.39E-13	2.27E-13	99.74	4.82E-16	6.01E-16	0.26
600	3.36E-13	5.16E-13	99.51	2.10E-15	2.53E-15	0.49
700	6.74E-13	9.91E-13	99.23	6.51E-15	7.72E-15	0.77
750	9.09E-13	1.31E-12	99.07	1.05E-14	1.24E-14	0.93
800	1.19E-12	1.70E-12	98.90	1.62E-14	1.89E-14	1.10
850	1.53E-12	2.16E-12	98.73	2.40E-14	2.78E-14	1.27
900	1.93E-12	2.69E-12	98.55	3.44E-14	3.97E-14	1.45
1000	2.93E-12	4.01E-12	98.18	6.49E-14	7.44E-14	1.82
1100	4.21E-12	5.67E-12	97.80	1.12E-13	1.28E-13	2.20
1200	5.79E-12	7.72E-12	97.42	1.81E-13	2.05E-13	2.58
1300	7.71E-12	1.02E-11	97.04	2.75E-13	3.11E-13	2.96
1400	9.98E-12	1.31E-11	96.67	4.00E-13	4.50E-13	3.33
1500	1.26E-11	1.64E-11	96.31	5.61E-13	6.29E-13	3.69
1800	2.27E-11	2.92E-11	95.28	1.29E-12	1.44E-12	4.72
2000	3.15E-11	4.01E-11	94.67	2.03E-12	2.26E-12	5.33

Rate constants calculated by MS-CVT/ μ OMT based on M08-SO/maug-cc-pVTZ. Either universal ZPE scaling factor or SRP ZPE scaling factors were used. Branching ratios were calculated from SRP ZPE scaling factor results.

Table 8.

Comparison of transition state geometries (bond lengths in Å, angles in degrees), imaginary frequencies (cm⁻¹) and barrier heights (kcal/mol) computed in different works^a

Properties	B3LYP	BB1K	M08-SO
	/6-311+G(3df,2p) ^b	/aug-cc-pVTZ ^c	/maug-cc-pVTZ ^d
TS1	1O – 2H	1.375	1.285
	2H – 3C	1.207	1.243
	∠2H – 3C – 6O	111.0	109.9
	f_i	426 <i>i</i>	1370 <i>i</i>
	$V_{\text{for}}^\ddagger$	6.4	6.2
TS2	1O – 2H	1.209	1.169
	2H – 3O	1.115	1.137
	∠1O – 2H – 3O	161.2	160.6
	∠2H – 3O – 4C	116.8	114.6
	$\tau(2\text{H} - 3\text{O} - 4\text{C} - 6\text{H})$	-62.7	-62.8
	f_i	1313 <i>i</i>	2083 <i>i</i>
	$V_{\text{for}}^\ddagger$	13.1	13.0

^a numbering of atoms is shown in Figure 2

^b used in Lu et al.'s work;

^c used in Alves et al.'s work;

^d used in this work.

^e values in parenthesis are CCSD(T) energies on B3LYP/6-311+G(3df,2p) geometries.