Supporting Information

Low Temperature Reaction Dynamics for the CH_3OH + OH Collisions on a New Full Dimensional Potential Energy Surface

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S1. *ab initio* calculations

In Table 1 the stationary points of the R_{OH} and R_{CH} reactions are compared with several methods. Note that for the methods MRCI-F12 and MRCI-F12 + Q the geometries correspond to those calculated with the CCSD-F12a method and cc-pVDZ-F12 basis set. These results indicate that the CCSD-F12a method yields to an accurate description of the PES near the transition state region. Indeed, if we analyze the multi-reference wave function of the MRCI-F12 method, we see that two configurations dominate, that correspond to the configurations $\cdots 13a^2 14a^1$ and $\cdots 13a^1 14a^2$. Note that these valence orbitals correspond to the degenerate π orbitals of the OH reactant in the $^2\Pi$ state, that are mixed when OH reacts with methanol. Because the second configuration corresponds to an excitation of one electron from one valence orbital to other valence orbital of the Hartree-Fock configuration, the CCSD-F12a method takes into account the main excitations of these configurations and, for this reason, correctly describes this region. As shown in Fig. 1, the energy of the transition state of the CCSD(T)-F12a method is between the MRCI-F12 values with and without Davidson correction.

On the other hand, it is interesting to analyze the energies of the excited states along the IRC. The two first electronic states, 1^2A and 2^2A, are degenerated in the reactants asymptote. In the transition state region of the ground electronic state, the excited electronic states 2^2A and 3^2A show an avoided crossing at about 1.5-2.0 eV. The excitation from one valence orbital to the $15a$ virtual orbital have only a weight less than 5% in the CASSCF reference configurations, and it is only important in the 4^2A electronic state, that shows a ionic character for $s > 1$ Å.

S2. Force Fields used in the fit

A zero-order description of the full potential of the CH_3OH + OH system is built using a Reactive Force Field (RFF), as described recently[2], within the Empirical Valence Bond (EVB) approach[3]. In this approach, the PES is represented by a $N \times N$ matrix, H^{diab}, where N is the number of rearrangement channels considered: in the present case $N=5$, one for the CH_3OH + OH entrance channel, the second corresponds to the product channel CH_3O + H_2O and the three remaining refer to the three CH_2OH + H_2O arrangement channels (one for each hydrogen of the CH_3 group).

The diagonal elements of the matrix are represented as the sum $V_A + V_B + V_{AB}$, where V_A and V_B are the potential of each individual A and B fragments, respectively, and V_{AB} is the interaction between them. The off-diagonal elements couples the different arrangements and are optimized in such a way that the lower eigenvalue of the RFF-EVB matrix matches the *ab initio* energies in the region of the transition states.

Each V_A or V_B potentials are represented by Force Fields of MM3 level, which include all bond stretch, bonds bending and dihedral bendings (common and improper) as well as crossed-bond terms, crossed bending terms and bond-bend product crossed terms[4]. The bond stretch terms are described by Morse type functions, and the crossed terms have been multiplied by a tanh damping function to kill them when the bond distances becomes large to avoid undesirable artifacts in different arrangements. All V_A were parametrized fitting more than 1000 *ab initio* points obtained by a normal mode sampling considering 6 quanta of excitation in each vibrational mode. This is necessary to avoid undesirable features introduced by the crossing terms at the relatively high vibrational energy available in the products due to the high exothermicity of the reaction studied.

The interaction between fragments, V_{AB}, are represented by the sum of all possible crossed-pairs between the atoms of A and B fragments. Each pairwise interaction is described by Morse type functions or repulsive exponential functions. In addition, the dominant electrostatic interaction term in this arrangement, namely, the dipole-dipole interaction, have been explicitly included to get a good description of the long range interaction

$$V_{lr} = \frac{R^2 \mathbf{d}_{OH} \mathbf{d}_{CH_3OH} - 3(\mathbf{d}_{OH}\mathbf{R})(\mathbf{d}_{CH_3OH}\mathbf{R})}{4\pi\varepsilon_0 R^5} \tag{1}$$

where $\mathbf{R}$ is the vector between the two centers of mass. To match the *ab initio* potential, the dipoles of CH_3OH and OH have been described by punctual effective charges on each atom that have been parametrized to match the *ab initio* dipole moment along a normal mode trajectory sampling.

The non-diagonal terms introducing the couplings among the different channels are described by

$$V_{eff} = A \cdot \exp(-\alpha \cdot \Delta E^2)^q \cdot D_1 \cdot D_2 \cdot D_3$$

where A is the effective coupling intensity. ΔE^2 is the square of the energy difference of the two coupled arrangements, and q and α are the damping parameters used to modulate the coupling intensity as a function of ΔE. D_1 and D_2 are distance-like damping functions acting on the reaction coordinate $s = r_1 - r_2$ and $-s = r_2 - r_1$

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Reaction R_{CH}		
Method	V_{TS}/eV	ΔV/eV
CCSD(T)-F12a/jun-cc-pVTZ[a]	0.063	−0.949
CCSD(T)-F12a/cc-pVDZ-F12	0.093	−0.940
MRCI-F12/cc-pVDZ-F12	0.209	−0.786
MRCI-F12+Q/cc-pVDZ-F12	0.066	−0.920
MB FIT	0.089	−1.041
Experimental		−0.946 ± 0.026

Reaction R_{OH}			
Method	$V_{Complex}$/eV	V_{TS}/eV	ΔV/eV
CCSD(T)-F12a/jun-cc-pVTZ[a]	−0.281	0.173	−0.534
CCSD(T)-F12a/cc-pVDZ-F12	−0.280	0.270	−0.534
MRCI-F12/cc-pVDZ-F12	−0.260	0.337	−0.530
MRCI-F12+Q/cc-pVDZ-F12	−0.277	0.230	−0.575
MB FIT	−0.335	0.289	−0.520
Experimental			−0.539 ± 0.033

[a] See reference [1]

with r_1 the distance of the XH breaking bond of methanol (X=C,O) and r_2 the OH forming bond of water. D_3 is an additional angle-like damping function which depends on the CHO angles exclusively, and aim to avoid interferences between the couplings of the different arrangements associated Only the couplings between the $CH_3OH + OH$ and the two products channels are considered here, while the coupling between $CH_2OH + H_2O$ and $CH_3O + H_2O$ channels are neglected.

S3. Many body term

The H^{MB} terms are expanded as polynomials in Rydberg variables expressed in terms of all the internuclear distances[5]. The Reactive Force Field used takes into account the permutation symmetry of the three hydrogen of the CH_3 of methanol. Hence, the many body term used has been developed to be invariant with respect to the permutation of these hydrogens. The polynomials are symmetrized using the (unnormalized) Young operator corresponding to the totally symmetric irreducible representation of the S_3 permutation group of three objects,

$$w^{[3]} = \sum_P^{3!} P \tag{2}$$

where P are the 3! permutations of the three hydrogen. The application of this projector to the product of the Rydberg variables, $\rho_{\alpha\beta} = R_{\alpha\beta} e^{-\beta_{\alpha\beta} R_{\alpha\beta}}$, where $R_{\alpha\beta}$ is the distance between nuclei α and β, gives the symmetry adapted functions (SAF) permutationally invariant with respect to the interchange of the three equivalent hydrogen nuclei,

$$\rho_r^{SAF} = w^{[3]} \prod_{\alpha>\beta} \rho_{\alpha\beta}^{i_{\alpha\beta}} \tag{3}$$

where $i_{\alpha\beta}$ are the powers of the Rydberg variables, and $r = \{i_{\alpha\beta}\}$. Only 3 of the 5 hydrogen atoms of $CH_3OH + OH$ are considered to be permutationally invariant, corresponding to the three hydrogen of the CH_3.

The functional form for the eight-body potential in terms of the SAF polynomial takes the form

$$H^{MB}(\{R_{\alpha\beta}\}) = \sum_r c_r \rho_r^{SAF} \tag{4}$$

For 8 atoms the lowest order of the polynomial, $\sum_{\alpha>\beta} i_{\alpha\beta} = 7$, gives about 10^6 SAF. To obtain a good fit with a smaller number of polynomials, we have to select the SAF's that best reproduce the interaction zone. To do this, we have calculated the value of the polynomials in the regions of greatest interaction, such as the minima in the input and output channels and the two transition states. For the final fit we have selected the 2000 SAF functions with the highest weight in those regions. The non-linear exponents $\{\beta_{\alpha\beta}\}$ of the Rydberg variables have been set at a value of 1 to avoid conflicts in the long range region, where the 8 atoms many body term must vanish.

S4. Properties of the analytical fit of the PES

In the fit of the MB term about 200 000 *ab initio* points have been calculated with the CCSD(T)-F12a method, of which approximately 180 000 have an energy lower than 5 eV with respect to the $CH_3OH + OH$ reactants energy (here after considering as zero of energy). The points have been calculated in different forms. First, several regular grids in the reactants and products channels were calculated to characterize them at the equilibrium geometry of the fragments. Second, these regular grids are complemented by calculating points chosen along classical trajectories obtained using different versions of the fit. The kinetic energy of these test trajectories was 1 eV plus the Zero Point Energy (ZPE) allowing to explore all region of the configuration space at energies well above those of interest in this work. This systematic procedure allows to locate the spurious minima than can be introduced by the fitting method. Once spurious minima are detected, *ab initio* calculations were performed and these new points were introduced in a new fit. This procedure was repeated iteratively until no spurious minima were found running more than 10^4 trajectories. Similarly, trajectories at low kinetic energies, $\approx$ 1meV, were made to locate artificial barriers. Finally, to reproduce accurately the transition state region, the intrinsic reaction coordinate for the two reactions (R_{CH} and R_{OH}) where calculated for each of the versions of the fit, adding the calculated CCSD(T)-F12a points to the new fits. In addition, normal modes in the region of the transition state were calculated, and *ab initio* points were calculated as a function of each normal coordinate. The IRC and normal modes points were

2

Points	Energy range	Error RFF	Error RFF + MB
123	IRC R_{CH}	143	66
96	IRC R_{OH}	249	78
49104	$E < 0.0$ eV	108	84
172464	$E < 2.0$ eV	188	130
186209	$E < 5.0$ eV	283	208

Table 2 Analysis of the errors in the RFF and RFF + MB fits, in meV. The number of points in each energy interval considered is also shown

The root-mean-square errors of the RFF and RFF + MB fit are listed in Table 2. The errors of the fit in the IRC are a half of the RFF for the R_{CH} reaction, and one third for the R_{OH} reaction.

S5. QCT calculations

The Quassi-Classical calculations have been done as in Ref.[2,6] with an extension of the miQCT code[7,8] applied to N atoms.

Two kind of calculations are performed:

- The reactive cross section, $\sigma(E)$, is calculated as[9]

$$\sigma(E) = \pi b_{max}^2 P_r(E) \quad \text{with} \quad P_r(E) = \frac{N_r}{N_{tot}}, \quad (5)$$

  at fixed collision energies with the two reactants initially in their ground rotational and vibrational energy. In this expression, N_t is the maximum number of trajectories with initial impact parameter lower than b_{max}, the maximum impact parameter for which reaction takes place, and N_r is the number of trajectories leading to products. For each energy about 10^5 trajectories were run.

- The thermal reaction rate constants, $K(T)$, is calculated as

$$K(T) = q_e \sqrt{\frac{k_B T}{\mu \pi}} \pi b_{max}^2 P_r(T), \quad (6)$$

  where μ is the reduced mass of the $CH_3OH + OH$ system, and $P_r(T)$ is the reaction probability at a fixed temperature. The electronic term $q_e = [1 + \exp(-200.279/T)]^{-1}$ is introduced to consider that only the ground spin-orbit state of OH($^2\Pi$) reacts. The spin-orbit states split into $F_1(^2\Pi_{1/2})$ and $F_2(^2\Pi_{3/2})$ states, with an energy separation of 200.3 K. 10^7 trajectories are propagated for each temperature, using a Boltzmann distribution over the relative translational energy and the rotational states of the two reactants, keeping their vibrations in the ground state.

The initial conditions were sampled using a Monte Carlo method. The internal vibrational degrees of freedom of each fragment are described using an adiabatic switching method[10–12]. In this method, a random selection of initial conditions is done according to analytical normal modes, and then the harmonic potential is adiabatically switched to the real one. Since the energy spreading is rather high, we select a particular trajectory with the closest energy to the anharmonic ground state eigenvalue of each fragment, which is propagated for 100000 steps. OH and CH_3OH are initially set at zero angular momentum, by using the method

domly selected. Finally, the initial impact parameter is randomly set in the interval $[0, B]$, with B being set according to a capture model[14] as

$$B = \sqrt{3} \left(\frac{A}{2E} \right)^{1/3}, \quad (7)$$

for a dipole-dipole interaction, Eq. (1), varying as $-A/R^3$ for long distances R between the center-of mass of the two reactants (with $A = 4 d_{OH} d_{CH_3OH}$ corresponding to the optimal orientation between the permanent dipoles of the two reactants). The maximum impact parameter found for the lower energy is of 60 a.u. For this reason the initial distance between reactants is set to 125 a.u., and the trajectories are ended when any distance becomes longer than 135 a.u. Trajectories were propagated with a time step of 0.1 fs and a conservation of energy better than 0.001 meV is imposed.

For low energies the collision time is very long, of several hundreds of nanoseconds for many long trajectories, and most of the time is spent in the approximation between the two reactants. To consider the formation of the collisional complex, we estimate the collision complex lifetime as the average over all trajectories of the individual time spent at short distances, $\tau_{complex}$. This individual $\tau_{complex}$ is calculated as the time difference between the first and last time that the distance between reactants or products center-of-masses is equal to 10 a.u.

Notes and references

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4