

Stereodynamical Control of Product Branching in Multi-Channel Barrierless Hydrogen Abstraction of CH₃OH by F

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Supporting Information

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S-I. Theory and Calculation Details

It is still a challenge to employ full-dimensional quantum dynamical methods¹ to study the title reaction, which has seven atoms and fifteen degree of freedoms (DOFs). Therefore, the quasi-classical trajectory (QCT) approach was employed with the permutation invariant polynomial-neural network-neural network potential energy surface (PIP-NN PES)² for the title reaction interfaced to the VENUS chemical dynamics program.³ The reactive integral cross section (ICS) of each reaction channel, namely, $\text{HF} + \text{CH}_3\text{O}$ or $\text{HF} + \text{CH}_2\text{OH}$, was computed as follows:

$$\sigma_r(E_c) = \pi b_{\max}^2(E_c) P_r(E_c), \quad (\text{S1})$$

where b_{\max} is the maximum impact parameter. The reaction probability $P_r(E_c)$ of each channel at the specified collision energy E_c is given by the ratio between the number of reactive trajectories (N_r) and total number of trajectories (N_{total}): $P_r(E_c) = N_r/N_{\text{total}}$, with the standard error estimated by

$$\Delta = \sqrt{(N_{\text{total}} - N_r) / N_{\text{total}} N_r}.$$

At the collision energies of 1.0, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 kcal/mol, $5 - 15 \times 10^5$ trajectories each were calculated, making the statistical errors less than 3%. With the methanol in its ro-vibrational ground state, the maximal impact parameter (b_{\max}) was determined using small batches of trajectories with trial values. Then, the impact parameter b of each trajectory was sampled according to $b = b_{\max} \zeta^{1/2}$ with ζ being a random number uniformly distributed between 0.0 and 1.0. The initial separation between F and CH_3OH was set to be 10.0 Å. The termination criteria were chosen to be 10.5 Å for nonreactive processes, and 8 Å for reactive processes, respectively. These initial and termination criteria are sufficiently long so that the interactions between reactants or products are negligible. The spatial orientation and vibrational phases of the initial reactants were determined according to the Monte Carlo approach implemented in VENUS.³ The gradient of the PES with respect to atomic coordinates were calculated numerically. The

combined fourth-order Runge-Kutta and sixth-order Adams-Moulton algorithms were used for the integration of the trajectories with the propagation time step 0.01 fs. Almost all trajectories conserved energy within a chosen criterion (10^{-4} kcal/mol).

The abstraction differential cross section (DCS) for each channel was then calculated according to

$$\frac{d\sigma_r}{d\Omega} = \frac{\sigma_r P_r(\theta)}{2\pi \sin(\theta)} \quad (\text{S2})$$

with the scattering angle θ given by

$$\theta = \cos^{-1} \left(\frac{\vec{v}_i \cdot \vec{v}_f}{|\vec{v}_i| |\vec{v}_f|} \right) \quad (\text{S3})$$

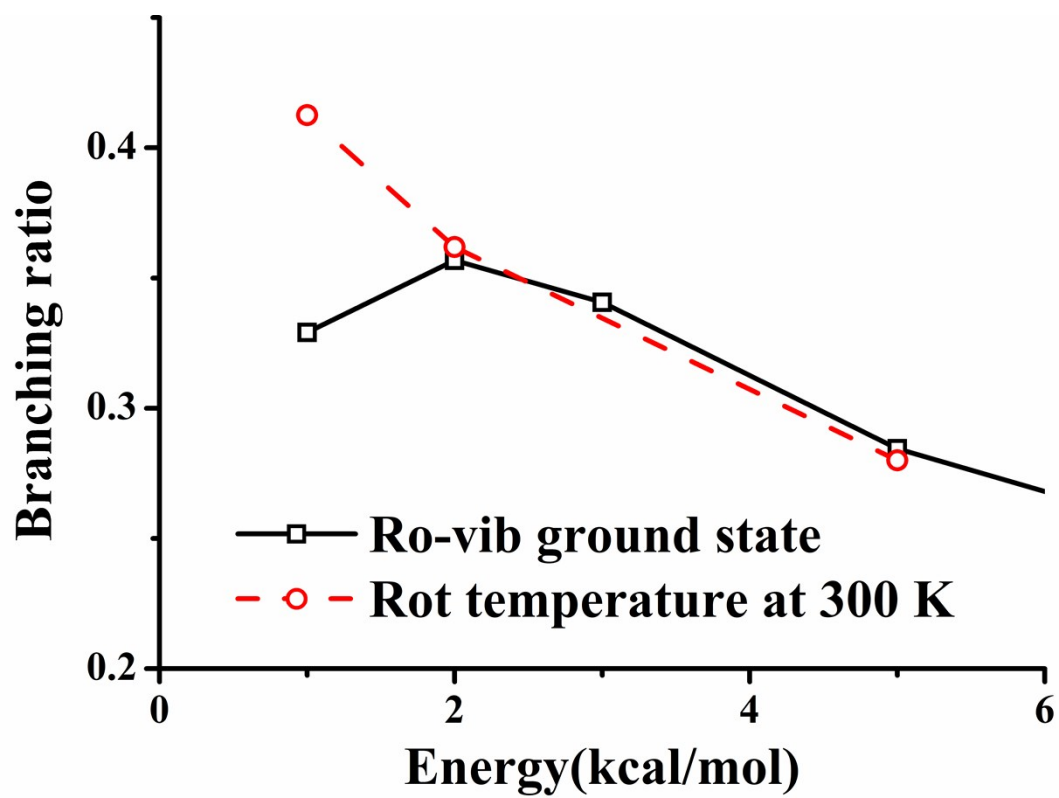
Here, \vec{v}_i and \vec{v}_f denotes the initial and final relative velocity vector, respectively, $\vec{v}_i = \vec{v}_F - \vec{v}_{\text{CH}_3\text{OH}}$, $\vec{v}_f = \vec{v}_{\text{HF}} - \vec{v}_{\text{CH}_3\text{O}}$, or $\vec{v}_f = \vec{v}_{\text{HF}} - \vec{v}_{\text{CH}_2\text{OH}}$. Hence, $\theta=0^\circ$ and $\theta=180^\circ$ corresponds to forward and backward scattering, respectively.

S-II. Promotional effect of methanol rotations

Previously, the QCT predicted thermal branching ratios of the R1 channel were found to be 0.40 – 0.43 at 200 – 1000 K, and agree well with experimental measurements.⁴ In the main text, it has been found that the branching ratios of the R1 channel drop down gradually from 0.36 ($E_c=2$ kcal/mol) to 0.13 ($E_c=30$ kcal/mol). Therefore, we infer that the rotational excitations of the methanol can enhance the reactivity of the R1 channel, thus increasing the branching ratio of this channel, at least for low collision energy scattering. At each of $E_c = 1, 2$, and 5 kcal/mol, $1-2 \times 10^4$ trajectories were carried out. For the methanol molecule, the rotational energy was sampled at 300 K according to the Boltzmann distribution. All other parameters were chosen to be the same described above. As shown in Figure S1, the rotational excitations of methanol significantly

increase the branching ratio of the R1 channel at $E_c = 1$ kcal/mol. With the collision energy increased to 2 and 5 kcal/mol, the rotational excitations of the methanol molecule have a marginal effect on the branching ratio of the R1 channel.

Figure S1. The promotional effect of the methanol rotations on the branching ratio of the R1 channel.



References:

1. D. H. Zhang and H. Guo, *Annu. Rev. Phys. Chem.*, 2016, **67**, 135-158.
2. M. L. Weichman, J. A. DeVine, M. C. Babin, J. Li, L. Guo, J. Ma, H. Guo and D. M. Neumark, *Nat. Chem.*, 2017, **9**, 950-955.
3. X. Hu, W. L. Hase and T. Pirraglia, *J. Comp. Chem.*, 1991, **12**, 1014-1024.
4. D.-D. Lu, C.-J. Xie, J. Li and H. Guo, *Chin. J. Chem. Phys.*, 2019, **32**, 84-88.