

Supporting Information for:

Dynamics and kinetics of the Si(¹D)+H₂/D₂ reactions on a new global ab initio potential energy surface

Jianwei Cao,^a Yanan Wu,^{ab} Haitao Ma,^a Zhitao Shen^c and Wensheng Bian^{*ab}

^a Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China.

^c Henan Key Laboratory of Photovoltaic Materials, Henan University, Kaifeng 475004, China

E-mail: bian@iccas.ac.cn

Phone: +86 (0)10 62566307. Fax: +86 (0)10 62563167

Contents

| | |
|--------------------|----|
| Table S1 | S2 |
| Supplementary text | S3 |
| References | S4 |

Table S1. Initial state-specific rate coefficient k for the $\text{Si}(^1\text{D})+\text{H}_2$ ($v=0, j$) reaction at 1500 K.

| $\text{Si}(^1\text{D})+\text{H}_2$ ($v=0, j$) | $10^{12}k(\text{cm}^3 \text{s}^{-1})$ | | |
|---|---------------------------------------|------|------|
| | QCT | QD | RPMD |
| $j = 0$ | 0.72 ± 0.06 | 0.37 | |
| $j = 1$ | 0.94 ± 0.07 | | |
| $j = 2$ | 1.08 ± 0.08 | | |
| $j = 3$ | 1.31 ± 0.08 | | |
| $j = 4$ | 2.09 ± 0.09 | | |
| $j = 5$ | 3.64 ± 0.11 | | |
| thermal | | | 6.00 |

Supplementary text

1. Electronic degeneracy factor

The electronic degeneracy factor $g_e(T)$ is calculated using its analytic form

$$g_e(T) = \frac{q[\text{Si}(^1\text{D})\text{H}_2]}{q[\text{Si}(^1\text{D})]q[\text{H}_2]} = \frac{1 + \exp[-E/RT]}{5 \times 1},$$

with $E = 44.05 \text{ kcal mol}^{-1} = 184129 \text{ J mol}^{-1}$, $R = 8.31 \text{ J mol}^{-1}\text{K}^{-1}$. Therefore, the degeneracy factor has a value of 1/5 in the studied temperature range.

2. Multi-configuration time-dependent Hartree (MCTDH) calculations

To determine the ro-vibrational energy levels of SiH_2 ($\tilde{X}^1\text{A}_1$), a quantum mechanics Hamiltonian in valence coordinates (r_1, r_2, θ) are used,¹ where $r_{1,2}$ is the distance between Si and H atoms, and θ is the angle between r_1 and r_2 . The block improved relaxation scheme^{2,3} implemented in the MCTDH program package⁴ is applied to obtain the eigenvalues and eigenstates. The Hamiltonian is discretized in a direct product discrete variable representation (DVR), and the PES is transformed to a product form using the potfit algorithm^{5,6} implemented in the MCTDH package.⁴ For the radial degrees of freedom, r_1 and r_2 , we use sine DVR, and for the angle variable, θ , Legendre DVR is used. To achieve convergence, the primitive basis (DVR) size is chosen as $N_{r_1}=N_{r_2}=100$ and $N_\theta=120$, whereas $n_{r_1}=n_{r_2}=20$ and $n_\theta=40$ are selected for the single-particle functions (SPFs). The DVR ranges adopted in the calculations are $1.9 \leq r_1 \leq 3.9 \text{ bohr}$, $1.9 \leq r_2 \leq 3.9 \text{ bohr}$, and $0 \leq \theta \leq \pi$. With these basis sets, the calculated energy levels of interest are converged to better than 0.05 cm^{-1} . The assignments are made by analysis of the wavefunctions.

3. Quasiclassical trajectory (QCT) calculations

The QCT method has been described adequately in literature.⁷⁻⁹ Here, we only give some details related to the present calculations. All the present QCT calculations are performed using a modified version of the VENUS96^{10,11} code customized to incorporate our PES. For all the trajectories, the integration time step is 0.01 fs, which guarantees a conservation of the total energy better than 1 in 10^6 . The trajectories are initiated at the $\text{Si}+\text{H}_2$ asymptote with a separation of 9.0 Å between the two species and are terminated when the parting fragments reach the same separation, which is sufficiently large so that the interaction between the fragments is negligible.

Batches of 18000–30000 trajectories with initial H_2 molecule set on different rotational states are calculated with b being sampled from $b=b_{\text{max}}\beta^{1/2}$ at 1500 K, and the value of b_{max} is set to 2.0 Å, the relative translational energy is randomly selected to mimic the Boltzmann distribution 1500 K.

The state-specific rate coefficient versus T can be obtained by

$$k_{vj}(T) = g_e \left(\frac{8k_B T}{\pi\mu} \right)^{1/2} \int_0^\infty \sigma(E_{rel}) P(E_{rel}) dE_{rel} = g_e \left(\frac{8k_B T}{\pi\mu} \right)^{1/2} \pi b_{\max}^2 \frac{N_r}{N_t}$$

where N_r is the reactive trajectory number, N_t is the total trajectory number, $g_e = 0.2$ is the electronic degeneracy factor, k_B is the Boltzmann constant, μ is the reduced mass of the reactant species. The corresponding error is given by $\Delta k = k [(N_t - N_r)/(N_r N_t)]^{1/2}$.

References

- (1) F. Gatti, C. Iung, and X. Chapuisat, *J. Mol. Struct. THEOCHEM*, 1998, 430, 201–208.
- (2) H.-D. Meyer, U. Manthe, and L. S. Cederbaum, *Chem. Phys. Lett.*, 1990, 165, 73.
- (3) M. Beck, A. Jäckle, G. Worth, H.-D. Meyer, *Phys. Rep.*, 2000, 324, 1.
- (4) G. A. Worth, M. H. Beck, A. Jäckle, H.-D. Meyer, the MCTDH package, version 8.2, University of Heidelberg, Heidelberg, Germany, 2000; H.-D. Meyer, the mctdh package, version 8.3, 2002; version 8.4, 2007, see <http://mctdh.uni-hd.de>.
- (5) A. Jäckle and H.-D. Meyer, *J. Chem. Phys.*, 1996, 104, 7974.
- (6) A. Jäckle and H.-D. Meyer, *J. Chem. Phys.*, 1998, 109, 3772.
- (7) F. J. Aoiz, L. Bañares, V. J. Herrero, *J. Chem. Soc., Faraday Trans.*, 1998, 94, 2483–2500.
- (8) T. D. Sewell, D. L. Thompson, *Int. J. Mod. Phys. B*, 1997, 11, 1067–1112.
- (9) G. H. Peslherbe, H. Wang, W. L. Hase, *Adv. Chem. Phys.*, 1999, 105, 171–201.
- (10) W. L. Hase, R. J. Duchovic, X. Hu, A. Komornicki, K. F. Lim, D.-H. Lu, G. H. Peslherbe, K. N. Swamy, S. R. V. Linde and A. J. C. Varandas, *QCPE Bull.*, 1996, 16, 671.
- (11) X. Hu, W. L. Hase and T. Pirraglia, *J. Comput. Chem.*, 1991, 12, 1014–1024.