

Supporting Information for

**Combined Valence Bond-Molecular Mechanics Potential Energy
Surface and Direct Dynamics Study of Rate Constants and Kinetic
Isotope Effects for the H + C₂H₆ Reaction**

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1. Canonical Variational Theory

The CVT rate constant can be written as

$$\begin{aligned}
 k^{\text{CVT}}(T) &= \min_s k^{\text{GT}}(T, s) \\
 &= \sigma \frac{k_{\text{B}}T}{h} \frac{Q^{\text{GT}}(T, s_*^{\text{CVT}})}{\Phi^{\text{R}}(T)} e^{-V_{\text{MEP}}^{\text{CVT}}/k_{\text{B}}T}, \quad (\text{S-1})
 \end{aligned}$$

where $k^{\text{GT}}(T, s)$ is the quasiclassical rate constant for temperature T with a GTS located at s , where s denotes a point along the MEP, σ is the symmetry factor which accounts for the reaction-path multiplicity, k_{B} is Boltzmann's constant, h is Planck's constant, $Q^{\text{GT}}(T, s_*^{\text{CVT}})$ is the internal quantum mechanical partition function computed without symmetry numbers for a generalized transition state at a value $s = s_*^{\text{CVT}}$ of the reaction coordinates with $V_{\text{MEP}}^{\text{CVT}}$ as the local zero of the energy, and Φ^{R} is the reactant quantum partition function per unit volume computed without symmetry numbers with respect to the overall zero of energy taken as the equilibrium potential of reactants infinitely apart for bimolecular reactions. In this context "quasiclassical" denotes a hybrid treatment in which the reaction coordinate is classical and all the vibrational degrees of freedom are quantized.

2. Factorization Analysis of the KIEs

In order to analyze the KIEs for the $\text{H} + \text{C}_2\text{H}_6/\text{X} + \text{C}_2\text{Y}_6$ reactions (where X, Y = H, D or D, D or D, H), we present a factorization analysis of the KIEs similar to that

employed previously.^{24,140–152} Each KIE can be expressed as

$$\eta^{\text{CVT/SCT}}(T) = k_{\text{H}+\text{C}_2\text{H}_6} / k_{\text{X}+\text{C}_2\text{Y}_6} = \frac{\kappa_{\text{H}+\text{C}_2\text{H}_6}^{\text{SCT}} Q_{\text{C}_2\text{H}_7}^{\text{GT}} \Phi_{\text{X}+\text{C}_2\text{Y}_6}^{\text{R}} e^{-V_{\text{MEP}}(s_*^{\text{CVT}}(\text{C}_2\text{H}_7)/k_{\text{B}}T)}}{\kappa_{\text{X}+\text{C}_2\text{Y}_6}^{\text{SCT}} Q_{\text{C}_2\text{Y}_6\text{X}}^{\text{GT}} \Phi_{\text{H}+\text{C}_2\text{H}_6}^{\text{R}} e^{-V_{\text{MEP}}(s_*^{\text{CVT}}(\text{C}_2\text{Y}_6\text{X})/k_{\text{B}}T)}} \quad (\text{S-2})$$

$\eta^{\text{CVT/SCT}}(T)$ can be further factored into a translational partition function contribution (η_{trans}), a rotational partition function contribution (η_{rot}), a vibrational partition function contribution (η_{vib}), a potential energy contribution (η_{pot}), and a tunneling contribution (η_{tun}). Equation (20) yields

$$\eta^{\text{CVT/SCT}}(T) = \eta_{\text{trans}} \eta_{\text{rot}} \eta_{\text{vib}} \eta_{\text{pot}} \eta_{\text{tun}} \quad (\text{S-3})$$

where

$$\eta_{\text{trans}} = \Phi_{\text{trans}}^{\text{R}}(\text{X} + \text{C}_2\text{Y}_6) / \Phi_{\text{trans}}^{\text{R}}(\text{H} + \text{C}_2\text{H}_6) \quad (\text{S-4})$$

$$\eta_{\text{rot}} = \frac{Q_{\text{rot}}^{\text{GT}}(\text{C}_2\text{H}_7) Q_{\text{rot}}^{\text{R}}(\text{X} + \text{C}_2\text{Y}_6)}{Q_{\text{rot}}^{\text{GT}}(\text{C}_2\text{Y}_6\text{X}) Q_{\text{rot}}^{\text{R}}(\text{H} + \text{C}_2\text{H}_6)} \quad (\text{S-5})$$

$$\eta_{\text{vib}} = \frac{Q_{\text{vib}}^{\text{GT}}(\text{C}_2\text{H}_7) Q_{\text{vib}}^{\text{R}}(\text{X} + \text{C}_2\text{Y}_6)}{Q_{\text{vib}}^{\text{GT}}(\text{C}_2\text{Y}_6\text{X}) Q_{\text{vib}}^{\text{R}}(\text{H} + \text{C}_2\text{H}_6)} \quad (\text{S-6})$$

$$\eta_{\text{pot}} = \exp\{-[V_{\text{MEP}}(s_*^{\text{CVT}}(\text{C}_2\text{H}_7)) - V_{\text{MEP}}(s_*^{\text{CVT}}(\text{C}_2\text{Y}_6\text{X}))]/k_{\text{B}}T\} \quad (\text{S-7})$$

$$\eta_{\text{tun}} = \kappa_{\text{H}+\text{C}_2\text{H}_6}^{\text{SCT}} / \kappa_{\text{X}+\text{C}_2\text{Y}_6}^{\text{SCT}} \quad (\text{S-8})$$

Detailed analysis of the vibrational contribution of Eq. (S-6) can be performed by using

$$\eta_{\text{vib}} = \eta_{\text{vib,low}} \eta_{\text{vib,mid}} \eta_{\text{vib,high}} \quad (\text{S-9})$$

where the mode classification is based on the magnitude of the vibrational frequency for the reaction (R1). The low/mid border is taken as 350 cm^{-1} and mid/high border is taken as 2000 cm^{-1} .

3. APPENDIX A

The functional forms of the relevant MM3 equations are summarized as follows:

3.1. Stretch terms

The bond stretch term was calculated using a fourth order polynomial

$$V_{\text{MM3}}^{\text{S}}(k_{\text{s}}, r_0, r) = C_1^{\text{S}} k_{\text{s}} (r - r_0) [1 + C_2^{\text{S}} (r - r_0) + C_3^{\text{S}} (r - r_0)^2], \quad (\text{A1})$$

where k_{s} is the bond stretch force constant, and r_0 is the equilibrium bond distance.

3.2. Bending terms

The angle bending term for a given bond angle θ is given as:

$$V_{\text{MM3}}^{\theta}(k_{\theta}, \theta_0, \theta) = C_1^{\theta} k_{\theta} (\theta - \theta_0) [1 + C_2^{\theta} (\theta - \theta_0) + C_3^{\theta} (\theta - \theta_0)^2 + C_4^{\theta} (\theta - \theta_0)^3 + C_5^{\theta} (\theta - \theta_0)^4], \quad (\text{A2})$$

where k_{θ} and θ_0 are the bending force constant and the equilibrium bond angle, respectively.

3.3. Torsion terms

The torsional term is a cosine function of the torsion angle φ :

$$V_{\text{MM3}}^{\varphi}(\varphi) = (V_3 / 3)(1 + \cos 3\varphi), \quad (\text{A3})$$

where the parameter V_3 controls the torsional barrier height.

3.4. Stretch-bend cross terms

The stretch-bend interaction between two bonds of lengths r and r' is given in terms of the bond angle θ between them as:

$$V_{\text{MM3}}^{\text{S}\theta}(k_{\text{s}\theta}, r_0, r'_0, \theta_0, r, r', \theta) = C^{\text{S}\theta} k_{\text{s}\theta} [(r - r_0) + (r - r'_0)] (\theta - \theta_0), \quad (\text{A4})$$

where $k_{\text{s}\theta}$ is the force constant, and r_0 and r'_0 are the equilibrium bond distances.

3.5. Torsion-stretch cross terms

The interaction between the torsion angle φ and the C-C bond in the H-C-C-H torsional term is given by the torsion-stretch term:

$$V_{\text{MM3}}^{\text{S}\varphi}(k_{\text{S}\varphi}, r_0, r, \varphi) = C^{\text{S}\varphi} (k_{\text{S}\varphi} / 2)(r - r_0)(1 + \cos 3\varphi), \quad (\text{A5})$$

where $k_{\text{S}\varphi}$ is the force constant, and r_0 is the equilibrium bond distance.

3.6. Bend-bend cross terms

The bend-bend cross term between two bond angles with a common central atom is given by the following equation:

$$V_{\text{MM3}}^{\theta\theta'}(k_{\theta\theta'}, \theta_0, \theta'_0, \theta, \theta') = C^{\theta\theta'} k_{\theta\theta'} (\theta - \theta_0)(\theta - \theta'_0), \quad (\text{A6})$$

where $k_{\theta\theta'}$ is the force constant, and θ_0 and θ'_0 are the two equilibrium bond angles.

3.7. Van der Waals terms

MM3 includes van der Waals interactions for nonbonded atoms (but excluding interactions between geminal atoms, which are called 1,3 interactions). These are given as:

$$V_{\text{MM3}}^{\text{V}}(\varepsilon, r_{\text{v}}^0, r_{\text{v}}) = \varepsilon [C_1^{\text{V}} (r_{\text{v}}^0 / r_{\text{v}})^6 + C_2^{\text{V}} e^{-12(r_{\text{v}} / r_{\text{v}}^0)}], \quad (\text{A7})$$

where the parameter ε is an energy scale factor for each atom pair, and r_{v}^0 is the reference distance. The van der Waals interaction in aliphatic hydrocarbons requires special attention.^{63,66} In both the MM2 and MM3 force fields the van der Waals interaction of an H atom in aliphatic hydrocarbons is not centered on the hydrogen atom but at a point closer to the carbon atom along the C-H bond. As described in Ref. 66 the centers for van der Waals interaction in MM3 force field are located at 92.3% of the calculated C-H bond distance.

The set of parameters in Eqs. (A1)–(A7) that do not depend on the character of the chemical system (for example C_1^{S} , C_2^{S}) are listed in Table S3.

4. APPENDIX B

The total MM energy is a sum over stretches, bends, bend-bend interactions, and torsion interactions. In the present case the MM system is so small that it has no torsions. Then

$$V_{\text{MM}} = V_{\text{MM}}^{\text{stretch}} + V_{\text{MM}}^{\text{bend}} + V_{\text{MM}}^{\text{bnd-bnd}}. \quad (\text{B1})$$

There are three stretch terms in the MM part corresponding to the three C₂-H_{*i*} stretch with *i* = 3, 4, 5. The total MM stretch energy is given as:

$$V_{\text{MM}}^{\text{stretch}} = \sum_{i=3}^5 V_{\text{MM3}}^{\text{s}}(k_{\text{CH}}, r_{\text{CH}}^0, r_{\text{C}_2\text{H}_i}). \quad (\text{B2})$$

There are three bend interactions corresponding to the three H-C-H bends. The total MM bending energy is given as:

$$V_{\text{MM}}^{\text{bend}} = \sum_{i=3}^5 \sum_{j=i+1}^5 V_{\text{MM3}}^{\theta}(k_{\text{HCH}}^{\theta}, \theta_{\text{HCH}}^0, \theta_{\text{H}_i\text{C}_2\text{H}_j}). \quad (\text{B3})$$

There are three H-C-H bend-bend interactions. The total MM bend-bend energy is given as:

$$\begin{aligned} V_{\text{MM}}^{\text{bnd-bnd}} = & V_{\text{MM3}}^{\theta\theta'}(k_{\text{HCH}}^{\theta\theta'}, \theta_{\text{HCH}}^0, \theta_{\text{HCH}}^0, \theta_{\text{H}_3\text{C}_2\text{H}_4}, \theta_{\text{H}_3\text{C}_2\text{H}_5}) \\ & + V_{\text{MM3}}^{\theta\theta'}(k_{\text{HCH}}^{\theta\theta'}, \theta_{\text{HCH}}^0, \theta_{\text{HCH}}^0, \theta_{\text{H}_3\text{C}_2\text{H}_4}, \theta_{\text{H}_4\text{C}_2\text{H}_5}) \\ & + V_{\text{MM3}}^{\theta\theta'}(k_{\text{HCH}}^{\theta\theta'}, \theta_{\text{HCH}}^0, \theta_{\text{HCH}}^0, \theta_{\text{H}_3\text{C}_2\text{H}_5}, \theta_{\text{H}_4\text{C}_2\text{H}_5}) \end{aligned} \quad (\text{B4})$$

5. APPENDIX C

The total VB/MM energy is divided into seven components: stretches, bends, torsions, stretch-bend, stretch-torsion, bend-bend, and van der Waals interactions:

$$\begin{aligned} V_{\text{VB/MM}} = & V_{\text{VB/MM}}^{\text{stretch}} + V_{\text{VB/MM}}^{\text{bend}} + V_{\text{VB/MM}}^{\text{torsion}} + V_{\text{VB/MM}}^{\text{str-bnd}} \\ & + V_{\text{VB/MM}}^{\text{tor-str}} + V_{\text{VB/MM}}^{\text{bnd-bnd}} + V_{\text{VB/MM}}^{\text{vdw}} \end{aligned} \quad (\text{C1})$$

5.1. Stretch terms

The C₁-C₂ stretch term is:

$$V_{\text{VB/MM}}^{\text{stretch}} = V_{\text{MM3}}^{\text{s}}(k_{\text{CC, VB/MM}}, r_{\text{CC, VB/MM}}^0, r_{\text{CC}}). \quad (\text{C2})$$

5.2. Bending terms

There are six bending interactions corresponding to the six C-C-H bends in the VB/MM term. The total VB/MM bending energy is given as:

$$V_{\text{VB/MM}}^{\text{bend}} = \sum_{i=3}^5 V_{\text{MM3}}^{\theta} (k_{\text{CCH,R}}^{\theta}, \theta_{\text{CCH,R}}^0, \theta_{\text{C}_1\text{C}_2\text{H}_i}) + \sum_{i=6}^8 V_{\text{MM3}}^{\theta} (k_{\text{CCH,VB/MM}}^{\theta}, \theta_{\text{CCH,VB/MM}}^0, \theta_{\text{C}_1\text{C}_2\text{H}_i}) T_1(r_{\text{C}_1\text{H}_i}), \quad (\text{C3})$$

The presence of the switching term $T_1(r_{\text{C}_1\text{H}_i})$ ensures that as the reaction proceeds from reactants to products the bending term of the hydrogen being abstracted vanishes at the product geometry.

5.3. Torsion terms

There are nine torsional interactions, and the total VB/MM torsional energy is:

$$V_{\text{VB/MM}}^{\text{torsion}} = \sum_{i=6}^8 \sum_{j=3}^5 V_{\text{MM3}}^{\varphi} (\varphi_{\text{H}_i\text{C}_1\text{C}_2\text{H}_j}) T_1(r_{\text{C}_1\text{H}_i}), \quad (\text{C4})$$

where $\varphi_{\text{H}_i\text{C}_1\text{C}_2\text{H}_j}$ is the torsion angle between $\text{H}_i\text{-C}_1\text{-C}_2\text{-H}_j$ along the C-C bond.

5.4. Stretch-bend cross terms

There are six C-C-H stretch-bend interactions, and the total VB/MM stretch-bend energy is:

$$V_{\text{VB/MM}}^{\text{str-bnd}} = \sum_{i=6}^8 V_{\text{MM3}}^{s\theta} (k_{\text{CCH}}^{s\theta}, r_{\text{CC,VB/MM}}^0, r_{\text{CH}}^0, \theta_{\text{CCH,VB/MM}}^0, r_{\text{C}_1\text{C}_2}, r_{\text{C}_1\text{H}_i}, \theta_{\text{C}_2\text{C}_1\text{H}_i}) T_1(r_{\text{C}_1\text{H}_i}) + \sum_{i=3}^5 V_{\text{MM3}}^{s\theta} (k_{\text{CCH}}^{s\theta}, r_{\text{CC,R}}^0, r_{\text{CH}}^0, \theta_{\text{CCH,R}}^0, r_{\text{C}_1\text{C}_2}, r_{\text{C}_2\text{H}_i}, \theta_{\text{C}_1\text{C}_2\text{H}_i}). \quad (\text{C5})$$

5.5. Torsion-stretch cross terms

There are nine torsion-stretch interactions, and the total VB/MM torsion-stretch energy is:

$$V_{\text{VB/MM}}^{\text{tor-str}} = \sum_{i=6}^8 \sum_{j=3}^5 V_{\text{MM3}}^{s\varphi} (k_{\text{CC}}^{s\varphi}, r_{\text{CC,R}}^0, r_{\text{C}_1\text{C}_2}, \varphi_{\text{H}_i\text{C}_1\text{C}_2\text{H}_j}) T_1(r_{\text{C}_1\text{H}_i}). \quad (\text{C6})$$

5.6. Bend-bend cross terms

There are three H-C-H and six C-C-H bend-bend interactions. The total VB/MM bend-bend energy is given as:

$$\begin{aligned}
 & V_{\text{VB/MM}}^{\text{bnd-bnd}} \\
 &= \sum_{i=6}^8 \sum_{j=i+1}^8 V_{\text{MM3}}^{\theta\theta'} (k_{\text{CCH}}^{\theta\theta'}, \theta_{\text{CCH,VB/MM}}^0, \theta_{\text{CCH,VB/MM}}^0, \theta_{\text{C}_2\text{C}_1\text{H}_i}, \theta_{\text{C}_2\text{C}_1\text{H}_j}) T_1(r_{\text{C}_1\text{H}_i}) T_1(r_{\text{C}_1\text{H}_j}) \\
 &+ \sum_{i=3}^5 \sum_{j=i+1}^5 V_{\text{MM3}}^{\theta\theta'} (k_{\text{CCH}}^{\theta\theta'}, \theta_{\text{CCH,R}}^0, \theta_{\text{CCH,R}}^0, \theta_{\text{C}_1\text{C}_2\text{H}_i}, \theta_{\text{C}_1\text{C}_2\text{H}_j}). \tag{C7}
 \end{aligned}$$

5.7. Van der Waals terms

In the present work, nine van der Waals interactions of the form $\text{H}_i\text{-H}_j$ with $(i = 3, 4, 5; j = 6, 7, 8)$ were included:

$$V_{\text{VB/MM}}^{\text{vdw}} = \sum_{i=3}^5 \sum_{j=6}^8 V_{\text{MM3}}^{\text{v}} (\epsilon_{\text{HH}}, r_{\text{v,HH}}^0, r_{\text{v,H}_i\text{H}_j}). \tag{C8}$$

As described in Sec. II.B all van der Waals interactions involving H_9 and C_2 are set equal to zero for the present parameterization.

6. APPENDIX D

The three-body LEPS function is

$$\begin{aligned}
 V_{\text{JG}}^{\text{str}}(r_{\text{AB}}, r_{\text{AC}}, r_{\text{BC}}) &= Q_{\text{AB}} + Q_{\text{AC}} + Q_{\text{BC}} \\
 &- \sqrt{\frac{(J_{\text{AB}} - J_{\text{BC}})^2 + (J_{\text{BC}} - J_{\text{AC}})^2 + (J_{\text{AC}} - J_{\text{AB}})^2}{2}}, \tag{D1}
 \end{aligned}$$

where Q_{AB} and J_{AB} are the Coulomb and resonance terms that are obtained from the singlet and the triplet energies:

$$Q_{\text{AB}}(r_{\text{AB}}) = \frac{{}^1E_{\text{AB}} + {}^3E_{\text{AB}}}{2}, \tag{D2}$$

$$J_{AB}(r_{AB}) = \frac{{}^1E_{AB} - {}^3E_{AB}}{2}. \quad (D3)$$

The singlet and the triplet energies were represented by the Morse and anti-Morse potentials are:

$${}^1E_{AB}(r_{AB}) = {}^1D_{AB} [e^{-2\alpha_{AB}(r_{AB} - r_{AB}^0)} - 2e^{-\alpha_{AB}(r_{AB} - r_{AB}^0)}], \quad (D4)$$

$${}^3E_{AB}(r_{AB}) = {}^3D_{AB} [e^{-2\alpha_{AB}(r_{AB} - r_{AB}^0)} + 2e^{-\alpha_{AB}(r_{AB} - r_{AB}^0)}]. \quad (D5)$$

The Morse parameter α_{CH} for the C-H bond was changed smoothly from the reactant to the product value using

$$\alpha_{CH} = a_{CH} + b_{CH} \left(\frac{\tanh[c_{CH}(u_{av} - u^0)]}{2} \right), \quad (D6)$$

where

$$u_{av} = \frac{1}{4} \sum_{i=1}^4 u_i. \quad (D7)$$

The bending term is divided into two parts, the out-of-plane term and an in-plane harmonic term. The out-of-plane bend term is given as:

$$V_{JG}^{op} = \sum_{i=1}^3 f_{\Delta i} \sum_{\substack{j=1 \\ j \neq i}}^3 \Delta_{ij}^2 + \sum_{i=1}^3 h_{\Delta i} \sum_{\substack{j=1 \\ j \neq i}}^3 \Delta_{ij}^4, \quad (D8)$$

where

$$f_{\Delta i} = [1 - S_3(u_i)] f_{\Delta}^{CH_3}, \quad (D9)$$

$$h_{\Delta i} = [1 - S_3(u_i)] h_{\Delta}^{CH_3}. \quad (D10)$$

$$S_3 = 1 - \tanh[\alpha_3(u_i - u^0)(u_i - \beta_3)^2], \quad (D11)$$

$$\Delta_{ij} = \cos^{-1} \left[\frac{(\mathbf{u}_k - \mathbf{u}_j) \times (\mathbf{u}_l - \mathbf{u}_j) \cdot \mathbf{u}_i}{\|(\mathbf{u}_k - \mathbf{u}_j) \times (\mathbf{u}_l - \mathbf{u}_j)\| \cdot \|\mathbf{u}_i\|} \right] - \gamma_{ij}^0. \quad (D12)$$

The reference angle γ_{ij}^0 changes smoothly from reactant to product and is defined as

$$\begin{aligned} \gamma_{ij}^0 = & \tau + (\tau - \pi/2)[S_{\varphi}(u_i)S_{\varphi}(u_j) - 1], \\ & + (\tau - 2\pi/3)[S_{\theta}(u_k)S_{\theta}(u_l) - 1] \end{aligned} \quad (D13)$$

$$S_{\varphi}(u_i) = 1 - \tanh\{A_{\varphi}(u_i - u_i^0)e^{B_{\varphi}(u_i - C_{\varphi})^3}\}, \quad (\text{D14})$$

$$S_{\theta}(u_i) = 1 - \tanh\{A_{\theta}(u_i - u_i^0)e^{B_{\theta}(u_i - C_{\theta})^3}\}. \quad (\text{D15})$$

The harmonic in-plane bending term is written in terms of the bond angle γ_{ij} which is defined as the angle between the bonds represented by the bond vectors \mathbf{u}_i and \mathbf{u}_j :

$$V_{\text{JG}}^{\text{ip}} = \frac{1}{2} \sum_{i=1}^3 \sum_{j=i+1}^3 k_{ij}^0 k_i k_j (\gamma_{ij} - \gamma_{ij}^0)^2, \quad (\text{D16})$$

where

$$k_i = A_1 e^{-A_2(u_i - u_i^0)^2}, \quad (\text{D17})$$

$$A_1 = 1 - e^{-a_1 r_{\text{HH},i}^2}, \quad (\text{D18})$$

$$A_2 = a_2 + a_3 e^{-a_4 (r_{\text{HH},i} - r_{\text{HH}}^0)^2}, \quad (\text{D19})$$

$$k_{ij}^0 = k^{\text{CH}_4} + k^{\text{CH}_3} [S_1(u_i)S_1(u_j) - 1] + (k^{\text{CH}_4} - k^{\text{CH}_3}) [S_2(u_k)S_2(u_l) - 1], \quad (\text{D20})$$

$$S_1(u_i) = 1 - \tanh[\alpha_1(u_i - u_i^0)(u_i - \beta_1)^8], \quad (\text{D21})$$

$$S_2(u_i) = 1 - \tanh[\alpha_2(u_i - u_i^0)(u_i - \beta_2)^6]. \quad (\text{D22})$$

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Table S1. Parameters used in the MM terms. Distances are in Å, angles are in degrees, and energies are in kcal/mol.

Parameter	Value	Parameter	Value
r_{CH}^0	1.085	$\theta_{\text{CCH,R}}^0$	113.9
k_{CH}	4.740	$\theta_{\text{CCH,P}}^0$	120.0
$r_{\text{CC,R}}^0$	1.500	$k_{\text{CCH,R}}^\theta$	0.590
$r_{\text{CC,P}}^0$	1.471	$k_{\text{CCH,P}}^\theta$	0.592
w_1	22.00	k_{HCH}^θ	0.550
w_2	1.354	V_3	0.238
$k_{\text{CC,R}}$	4.489	$k_{\text{CCH}}^{s\theta}$	0.080
$k_{\text{CC,P}}$	4.493	$k_{\text{CC}}^{s\varphi}$	0.059
w_3	10.00	$k_{\text{HCH}}^{\theta\theta'}$	0.00
w_4	2.144	$k_{\text{CCH}}^{\theta\theta'}$	0.090
θ_{HCH}^0	107.5	ε_{HH}	0.020
k_{HCH}^θ	0.550	$r_{\text{v,HH}}^0$	1.620

Table S2. List of parameters used in the reactive terms. Distances are in Å, angles are in degrees, and energies are in kcal/mol.

Parameter	Value	Parameter	Value	Parameter	Value
u_R^0	1.085	c_{CH}	6.614	B_φ	0.4006
u_P^0	1.075	λ_1	-1178.8900	C_φ	1.921
$r_{HH,R}^0$	0.70	λ_2	32.8065	A_θ	0.9078
$r_{HH,P}^0$	0.7359	λ_3	10.3118	B_θ	0.3548
$r_{C_1H_9}^0$	1.40	λ_4	-159.8465	C_θ	1.8915
\bar{u}^0	1.17320	λ_5	17.3383	a_1	3.2139
w_5	10.0	λ_6	1280.3678	a_2	1.5999
${}^1D_{HH,R}$	109.458	χ	0.25	a_3	2.1659
${}^1D_{HH,P}$	112.468	d_1	1.94923	a_4	11.5699
${}^3D_{HH}$	39.664	d_2	1.01386	k^{CH_4}	0.5377
${}^1D_{CH}$	112.230	d_3	2.79027	k^{CH_3}	0.4077
${}^3D_{CH}$	38.8337	d_4	1.48154	α_1	1.533×10^{-7}
${}^1D_{C_1H_9}$	26.409	d_5	2.36975	β_1	-4.669
${}^3D_{C_1H_9}$	20.063	d_6	1.902065	α_2	1.0147×10^{-7}
α_{HH}	1.9457	$f_\Delta^{CH_3}$	0.09575	β_2	-12.3638
$\alpha_{C_1H_9}$	1.853	$h_\Delta^{CH_3}$	0.1915	α_3	0.1419
a_{CH}	1.713	τ	1.910633	β_3	-0.3068
b_{CH}	0.135	A_φ	0.5287		

Table S3. Parameters used to define the MM3 equations.^a

Parameter	Value	Parameter	Value
C_1^s	71.94	C_5^θ	$9.0 \times 10^{-10} \text{ deg}^{-4}$
C_2^s	-2.55 \AA^{-1}	$C^{s\theta}$	2.51118
C_3^s	1.4875 \AA^{-2}	$C^{s\varphi}$	11.995
C_1^θ	0.021914	$C^{\theta\theta'}$	-0.021914
C_2^θ	-0.014 deg^{-1}	C_1^v	-2.25
C_3^θ	$5.6 \times 10^{-5} \text{ deg}^{-2}$	C_2^v	1.84×10^5
C_4^θ	$-7.0 \times 10^{-7} \text{ deg}^{-3}$		

^aThe parameters in the table are constants and are independent of the character of the chemical system.

Table S4. Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) calculated by the TST/W method using MPW54/6-31+G(d,p) electronic structure level.^a

T (K)	H + C ₂ H ₆	H + C ₂ D ₆	D + C ₂ D ₆	D + C ₂ H ₆
200	8.27E-21	2.09E-22	9.85E-22	3.94E-20
260	1.75E-18	9.89E-20	2.92E-19	5.29E-18
281	6.66E-18	4.63E-19	1.22E-18	1.80E-17
300	1.90E-17	1.56E-18	3.78E-18	4.72E-17
320	5.04E-17	4.83E-18	1.08E-17	1.16E-16
360	2.58E-16	3.22E-17	6.31E-17	5.21E-16
400	9.65E-16	1.49E-16	2.65E-16	1.76E-15
420	1.71E-15	2.90E-16	4.93E-16	2.99E-15
467	5.45E-15	1.12E-15	1.75E-15	8.81E-15
480	7.24E-15	1.56E-15	2.39E-15	1.15E-14
491	9.11E-15	2.04E-15	3.07E-15	1.42E-14
511	1.35E-14	3.22E-15	4.73E-15	2.06E-14
520	1.60E-14	3.91E-15	5.69E-15	2.41E-14
534	2.06E-14	5.24E-15	7.50E-15	3.05E-14
586	4.77E-14	1.39E-14	1.88E-14	6.71E-14
600	5.85E-14	1.76E-14	2.35E-14	8.12E-14
612	6.92E-14	2.13E-14	2.83E-14	9.52E-14
630	8.81E-14	2.81E-14	3.70E-14	1.20E-13
637	9.65E-14	3.12E-14	4.08E-14	1.30E-13
662	1.32E-13	4.47E-14	5.74E-14	1.75E-13
680	1.63E-13	5.69E-14	7.23E-14	2.14E-13
693	1.88E-13	6.73E-14	8.48E-14	2.46E-13
700	2.03E-13	7.35E-14	9.23E-14	2.64E-13
729	2.76E-13	1.04E-13	1.29E-13	3.53E-13
748	3.33E-13	1.29E-13	1.58E-13	4.23E-13
776	4.34E-13	1.75E-13	2.11E-13	5.44E-13
796	5.19E-13	2.14E-13	2.57E-13	6.45E-13
800	5.37E-13	2.23E-13	2.67E-13	6.67E-13
826	6.69E-13	2.85E-13	3.39E-13	8.22E-13
880	1.02E-12	4.59E-13	5.35E-13	1.23E-12
1000	2.26E-12	1.12E-12	1.27E-12	2.64E-12
1300	9.48E-12	5.44E-12	5.89E-12	1.06E-11
1500	1.88E-11	1.14E-11	1.22E-11	2.08E-11
2000	6.27E-11	4.13E-11	4.31E-11	6.76E-11

^aTST/W means conventional TST with the one dimensional Wigner tunneling contribution using MPW54/6-31+G(d,p).

Table S5. Rate constants ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for $\text{H} + \text{C}_2\text{H}_6$ reaction calculated by the TST/W method using CVBMM potential energy surface.

T (K)	TST/W
200	7.59E-21
300	1.70E-17
400	8.25E-16
467	4.55E-15
491	7.55E-15
534	1.68E-14
586	3.85E-14
600	4.71E-14
612	5.55E-14
637	7.71E-14
693	1.49E-13
748	2.62E-13
776	3.40E-13
796	4.06E-13
826	5.22E-13
1000	1.75E-12
1500	1.48E-11
2000	5.14E-11

Figure S1. V_{MEP} for the four reactions as a function of reaction coordinate s obtained using the MPW54/6-31+G(d,p) level with the HR approximation.

