

Supplementary Information

Title: Full-dimensional analytical potential energy surface describing the gas-phase Cl + C₂H₆ reaction and kinetics study of rate constants and kinetic isotope effects

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Potential energy surface

The new PES was developed in a two-step process: first, the analytical functional form was proposed, which depends on adjustable parameters, and then they were fitted to the previous ab initio calculations. Next these steps are developed in detail.

a) Analytical functional form

On the basis of our previous experience with symmetrically substituted polyatomic reactions of type $A + CX_4 \rightarrow XA + CX_3$, where the central atom, carbon, is bonded to four equivalent substituents, X, and A represents the attacking atom; the new surface for reactions of type $A + C_2X_6 \rightarrow XA + C_2X_5$ is formulated in similar physically intuitive terms: stretching (str), valence bending (bending), and out-of-plane bending (op), as previously, and two additional terms to include a) the C-C stretching mode, and b) the torsion (tor) about the C-C bond. Therefore, the surface is basically a valence-bond (VB) potential augmented with molecular mechanics (MM) terms, VB-MM surface. Although obviously all six hydrogen atoms are equivalent, for the sake of clarity in the discussion we differentiate between them as i, j, k , for the hydrogen atoms on the C₁ carbon, and l, m, n , for the hydrogen atoms on the C₂ atom, A being the attacking atom, chlorine atom in the title reaction. This nomenclature will allow us to differentiate clearly the CH₃ group from the CH₂ group in the ethyl radical.

The potential energy for a given geometry, V , has the general form

$$V = V_{str} + V_{CC} + V_{bending} + V_{op} + V_{tor} \quad (S1)$$

V_{str} is the stretching term given by,

$$V_{str} = \sum_{i=1}^3 V_3(R_{C_1H_i}, R_{C_1A}, R_{H_iA}) + \sum_{l=4}^6 V_3(R_{C_2H_l}, R_{C_2A}, R_{H_lA}) \quad (S2)$$

where

H_i stands for one of the six ethane hydrogens. The V_3 terms represent the London-Eyring-Polanyi (LEP) functional form, given by,

$$\begin{aligned} & V_3(R_{C_1H_i}, R_{C_1A}, R_{H_iA}) \\ &= (V_{Q,C_1H_i} + V_{Q,C_1A} + V_{Q,H_iA}) + \left[-\frac{(V_{J,C_1H_i} - V_{J,C_1A})^2 + (V_{J,C_1A} - V_{J,AH_i})^2 + (V_{J,C_1H_i} - V_{J,AH_i})^2}{2} \right] \end{aligned} \quad (S3)$$

and

$$\begin{aligned} & V_3(R_{C_2H_l}, R_{C_2A}, R_{H_lA}) \\ &= (V_{Q,C_2H_l} + V_{Q,C_2A} + V_{Q,H_lA}) + \left[-\frac{(V_{J,C_2H_l} - V_{J,C_2A})^2 + (V_{J,C_2A} - V_{J,AH_l})^2 + (V_{J,C_2H_l} - V_{J,AH_l})^2}{2} \right] \end{aligned} \quad (S4)$$

for the C_1 and C_2 carbon atoms, where V_Q and V_J are the Coulomb and exchange integrals, respectively, given by,

$$V_{Q,C_1H_i} = \frac{E_{C_1H_i}^1 + E_{C_1H_i}^3}{2} \quad (S5)$$

$$V_{J,C_1H_i} = \frac{E_{C_1H_i}^1 - E_{C_1H_i}^3}{2} \quad (S6)$$

$$V_{Q,C_2H_l} = \frac{E_{C_2H_l}^1 + E_{C_2H_l}^3}{2} \quad (S7)$$

$$V_{J,C_2H_l} = \frac{E_{C_2H_l}^1 - E_{C_2H_l}^3}{2} \quad (S8)$$

for the C-H bonds, while for the C-A and A-H bonds are given by

$$V_{Q,C_1A} = \frac{E_{C_1A}^1 + E_{C_1A}^3}{2}$$

(S9)

$$V_{J,C_1A} = \frac{E_{C_1A}^1 - E_{C_1A}^3}{2}$$

(S10)

$$V_{Q,C_2A} = \frac{E_{C_2A}^1 + E_{C_2A}^3}{2}$$

(S11)

$$V_{J,C_2A} = \frac{E_{C_2A}^1 - E_{C_2A}^3}{2}$$

(S12)

$$V_{Q,AH_i} = V_{Q,AH_l} = \frac{E_{AH_i}^1 + E_{AH_i}^3}{2}$$

(S13)

$$V_{J,AH_i} = V_{J,AH_l} = \frac{E_{AH_i}^1 - E_{AH_i}^3}{2}$$

(S14)

Each integral term, V_Q and V_J , involves a singlet curve ($E_{C_1H_i}^1$, $E_{C_2H_i}^1$, $E_{C_1A}^1, E_{C_2A}^1$ and $E_{AH_i}^1$) and a triplet curve ($E_{C_1H_i}^3$, $E_{C_2H_i}^3$, $E_{C_1A}^3, E_{C_2A}^3$ and $E_{AH_i}^3$) for each C-H, C-A and A-H bond. They are given by,

$$E_{C_1H_i}^1 = D_{C_1H_i}^1 * e^{-2\alpha_{C_1H_i} * (R_{C_1H_i} - R_{C_1H_i}^0)} - 2 * e^{-\alpha_{C_1H_i} * (R_{C_1H_i} - R_{C_1H_i}^0)}$$

(S15)

$$E_{C_1H_i}^3 = D_{C_1H_i}^3 * e^{-2\alpha_{C_1H_i} * (R_{C_1H_i} - R_{C_1H_i}^0)} + 2 * e^{-\alpha_{C_1H_i} * (R_{C_1H_i} - R_{C_1H_i}^0)}$$

(S16)

$$E_{C_2H_l}^1 = D_{C_2H_l}^1 * e^{-2\alpha_{C_2H_i} * (R_{C_2H_i} - R_{C_2H_i}^0)} - 2 * e^{-\alpha_{C_2H_i} * (R_{C_2H_i} - R_{C_2H_i}^0)}$$

(S17)

$$E_{C_2H_l}^3 = D_{C_2H_l}^3 * e^{-2\alpha_{C_2H_l} * (R_{C_2H_l} - R_{C_2H_l}^0)} + 2 * e^{-\alpha_{C_2H_l} * (R_{C_2H_l} - R_{C_2H_l}^0)} \quad (S18)$$

$$E_{C_1A}^1 = D_{CA}^1 * e^{-2\alpha_{CA} * (R_{C_1A} - R_{CA}^0)} - 2 * e^{-\alpha_{CA} * (R_{C_1A} - R_{CA}^0)} \quad (S19)$$

$$E_{C_1A}^3 = D_{CA}^3 * e^{-2\alpha_{CA} * (R_{C_1A} - R_{CA}^0)} + 2 * e^{-\alpha_{CA} * (R_{C_1A} - R_{CA}^0)} \quad (S20)$$

$$E_{AH_i}^1 = E_{AH_l}^1 = D_{AH_i}^1 * e^{-2\alpha_{AH_i} * (R_{AH_i} - R_{AH_i}^0)} - 2 * e^{-\alpha_{AH_i} * (R_{AH_i} - R_{AH_i}^0)} \quad (S21)$$

$$E_{AH_i}^3 = E_{AH_l}^3 = D_{AH_i}^3 * e^{-2\alpha_{AH_i} * (R_{AH_i} - R_{AH_i}^0)} + 2 * e^{-\alpha_{AH_i} * (R_{AH_i} - R_{AH_i}^0)} \quad (S22)$$

which depend on 8 adjustable parameters, D^1_{XY} and D^3_{XY} , associated with the singlet and triplet dissociation energies, on 8 R^0_{XY} parameters, associated with the equilibrium bond distances, and 8 α_{XY} Morse parameters, where α_{CA} and α_{AH_i} are kept fixed, while the α_{CH} terms are allowed to relax from reactants to products,

$$\alpha_{C_1H_i} = a_{C_1H_i} + b_{C_1H_i} * \frac{\tanh [c_{C_1H_i} (R_{AV_1} - R_{C_1H_i}^0)] + 1}{2} \quad (S23)$$

$$\alpha_{C_2H_l} = a_{C_2H_l} + b_{C_2H_l} * \frac{\tanh [c_{C_2H_l} (R_{AV_2} - R_{C_2H_l}^0)] + 1}{2} \quad (S24)$$

where $a_{C_1H_i}$, $b_{C_1H_i}$, $c_{C_1H_i}$, $a_{C_2H_l}$, $b_{C_2H_l}$ and $c_{C_2H_l}$ are adjustable parameters, while each average distance, R_{AV} , is,

$$R_{AV_1} = \frac{\sum_{i=1}^3 R_{C_1H_i}}{3} \quad (S25)$$

$$R_{AV_2} = \frac{\sum_{l=4}^6 R_{C_2H_l}}{3} \quad (S26)$$

In order to introduce more flexibility in the functional form, the reference C_1-H_i and C_2-H_l bonds distances (R_{XY}^0) are transformed smoothly and independently from reactant to product using the equations (Ref. 10),

$$R_{C_1H_i}^0 = P_1 R_{C_1H_i,R}^0 + (1 - P_1) * R_{C_1H_i,P}^0 \quad (S27)$$

$$R_{C_2H_l}^0 = P_2 R_{C_2H_l,R}^0 + (1 - P_2) * R_{C_2H_l,P}^0 \quad (S28)$$

where the subscripts R and P refer, respectively, to equilibrium distances in reactants and products, and the terms P_1 and P_2 are,

$$P_1 = \prod_{i=1}^3 T_1(R_{C_1H_i}) \quad (S29)$$

$$P_2 = \prod_{l=4}^6 T_2(R_{C_2H_l}) \quad (S30)$$

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ote that P_1 and P_2 are symmetric with respect to three hydrogen atoms bonded to each carbon and go to zero as one of the hydrogen atoms is abstracted. T_1 and T_2 are geometry-dependent switching functions given by

$$T_1(R_{C_1H_i}) = 1 - \tanh[w_3 * (R_{C_1H_i} - w_4)] \quad (S31)$$

$$T_2(R_{C_2H_l}) = 1 - \tanh[w_5 * (R_{C_2H_l} - w_6)] \quad (S32)$$

where w_3 , w_4 , w_5 and w_6 are adjustable parameters. Eqs. (S27-S32) permit the C-H distances in ethane and ethyl radical to relax independently. The C-H distances are equivalent in ethane, but not in the ethyl radical. Hence, Eqs. (S27-S32) permit

differentiation between the C-H distances in the CH₃ group from the C-H distances in the CH₂ group of the ethyl radical. In total, the V_{str} term depends on 26 parameters.

The second term in Eq. (S1), V_{CC} , represents a simple Morse function to describe the C-C stretching motion, and is given by

$$V_{CC} = D_{CC}^1 \left[1 - e^{-a_{CC}(R_{CC} - R_{CC}^0)} \right]^2 \quad (\text{S33})$$

This term depends on three adjustable parameters D_{CC}^1 , a_{CC} and R_{CC}^0 .

The third term $V_{bending}$, representing the harmonic potential is defined as the sum of twelve harmonic potentials,

$$V_{bending} = \frac{1}{2} \sum_{i=1}^3 \sum_{j=i+1}^3 k_{ij}^0 k_i k_j (\theta_{ij} - \theta_{ij}^0)^2 + \sum_{i=1}^3 k_{ic}^0 k_i k_{CC} (\theta_{ic} - \theta_{ic}^0)^2 + \frac{1}{2} \sum_{l=1}^3$$

where the first and third terms refer to the H-C-H angles, while the second and fourth refer to the H-C-C angles. θ_{ij}^0 and θ_{lm}^0 are reference angles defined by the CH bonds in ethane, and $k_{ij}^0, k_{lm}^0, k_{ic}^0, k_{lc}^0, k_i, k_j, k_l, k_m$ and k_{CC} are force constants. In addition, $k_{ij}^0, k_{lm}^0, k_{ic}^0$ and k_{lc}^0 are allowed to relax from ethane to ethyl radical by,

$$k_{ij}^0 = k^{C_2H_6} + k^{C_2H_5} [S_1(R_{C_1H_i}) S_1(R_{C_1H_j}) - 1] + a_k [S_2(R_{C_1H_k}) S_2(R_{CC}) - 1] \quad (\text{S35})$$

$$k_{lm}^0 = k^{C_2H_6} + k^{C_2H_5} [S_1(R_{C_2H_l}) S_1(R_{C_2H_m}) - 1] + a_k [S_2(R_{C_2H_n}) S_2(R_{CC}) - 1] \quad (\text{S36})$$

$$k_{ic}^0 = k^{C_2H_6} + k^{C_2H_5} [S_1(R_{C_1H_i}) S_1(R_{CC}) - 1] + a_k [S_2(R_{C_1H_j}) S_2(R_{CH_k}) - 1] \quad (\text{S37})$$

$$k_{lc}^0 = k^{C_2H_6} + k^{C_2H_5} [S_1(R_{C_2H_l}) S_1(R_{CC}) - 1]$$

$$+ a_k [S_2(R_{C_2H_m}) S_2(R_{C_2H_n}) - 1] \quad (S38)$$

being $k^{C2H6} = k^{C2H5} + a_k$, with k^{C2H5} and a_k as adjustable parameters, and S_1 and S_2 as switching functions,

$$S_1(R_{C_1H_i}) = 1 - \tanh[\alpha_1(R_{C_1H_i} - R_{C_1H_i}^0)(R_{C_1H_i} - \beta_1)^8] \quad (S39)$$

$$S_2(R_{C_1H_i}) = 1 - \tanh[\alpha_2(R_{C_1H_i} - R_{C_1H_i}^0)(R_{C_1H_i} - \beta_2)^6] \quad (S40)$$

$$S_1(R_{C_2H_l}) = 1 - \tanh[\alpha_1(R_{C_2H_l} - R_{C_2H_l}^0)(R_{C_2H_l} - \beta_1)^8] \quad (S41)$$

$$S_2(R_{C_1H_l}) = 1 - \tanh[\alpha_2(R_{C_2H_l} - R_{C_2H_l}^0)(R_{C_2H_l} - \beta_2)^6] \quad (S42)$$

for the H-C-H bending angles, and

$$S_1(R_{CC}) = 1 - \tanh[\alpha_{1CC}(R_{CC} - R_{CC}^0)(R_{CC} - \beta_{1CC})^8] \quad (S43)$$

$$S_2(R_{CC}) = 1 - \tanh[\alpha_{2CC}(R_{CC} - R_{CC}^0)(R_{CC} - \beta_{2CC})^6] \quad (S44)$$

for the H-C-C bending modes, where α_1 , α_2 , β_1 , β_2 , α_{1CC} , α_{2CC} , β_{1CC} and β_{2CC} are adjustable parameters.

The constants force k_i (or j) and k_l (or m) are defined as a function of both R_{CH} , R_{HA} and R_{CC} distances, depending on each carbon atom,

$$k_i = A_1 \exp[-A_2(R_{C_1H_i} - R_{C_1H_i}^0)^2] \quad (S45)$$

$$A_1 = 1 - \exp[-aa_1(R_{H_iA})^2] \quad (S46)$$

$$A_2 = aa_2 + aa_3 \exp[-aa_4(R_{H_iA} - R_{H_iA}^0)^2] \quad (S47)$$

$$k_l = A_1 \exp[-A_2(R_{C_2H_l} - R_{C_2H_l}^0)^2] \quad (S48)$$

$$A_1 = 1 - \exp[-aa_1(R_{H_lA})^2] \quad (S49)$$

$$A_2 = aa_2 + aa_3 \exp[-aa_4(R_{H_lA} - R_{H_lA}^0)^2] \quad (S50)$$

$$k_{CC} = A_{1CC} \exp[-A_{2CC}(R_{CC} - R_{CC}^0)^2] \quad (\text{S51})$$

where six new adjustable parameters are included, namely aa_1 , aa_2 , aa_3 , aa_4 , A_{1CC} and A_{2CC} .

With respect to the reference angles, they are also allowed to relax from ethane, $\tau = 109.5^\circ$, to the ethyl radical configuration,

$$\begin{aligned} \theta_{ij}^0 = \tau + (\tau - \pi/2) & \left[S_\varphi(R_{C_1H_i}) S_\varphi(R_{C_1H_j}) - 1 \right] \\ & + \left(\tau - 2\pi/3 \right) \left[S_\theta(R_{C_1H_k}) S_\theta(R_{CC}) - 1 \right] \end{aligned} \quad (\text{S52})$$

$$\begin{aligned} \theta_{lm}^0 = \tau + (\tau - \pi/2) & \left[S_\varphi(R_{C_2H_l}) S_\varphi(R_{C_2H_m}) - 1 \right] \\ & + \left(\tau - 2\pi/3 \right) \left[S_\theta(R_{C_2H_n}) S_\theta(R_{CC}) - 1 \right] \end{aligned} \quad (\text{S53})$$

$$\begin{aligned} \theta_{ic}^0 = \tau + (\tau - \pi/2) & \left[S_\varphi(R_{C_1H_i}) S_\varphi(R_{CC}) - 1 \right] \\ & + \left(\tau - 2\pi/3 \right) \left[S_\theta(R_{C_1H_j}) S_\theta(R_{C_1H_k}) - 1 \right] \end{aligned} \quad (\text{S54})$$

$$\begin{aligned} \theta_{ic}^0 = \tau + (\tau - \pi/2) & \left[S_\varphi(R_{C_2H_l}) S_\varphi(R_{CC}) - 1 \right] \\ & + \left(\tau - 2\pi/3 \right) \left[S_\theta(R_{C_2H_m}) S_\theta(R_{C_2H_n}) - 1 \right] \end{aligned} \quad (\text{S55})$$

using the following switching functions,

$$S_\varphi(R_{C_1H_i}) = 1 - \tanh\{A_\varphi(R_{C_1H_i} - R_{C_1H_i}^0) \exp[B_\varphi(R_{C_1H_i} - C_\varphi)_3]\} \quad (\text{S56})$$

$$S_\varphi(R_{C_2H_l}) = 1 - \tanh\{A_\varphi(R_{C_2H_l} - R_{C_2H_l}^0) \exp[B_\varphi(R_{C_2H_l} - C_\varphi)_3]\} \quad (\text{S57})$$

$$S_\varphi(R_{CC}) = 1 - \tanh\{A_\varphi(R_{CC} - R_{CC}^0) \exp[B_\varphi(R_{CC} - C_\varphi)_3]\} \quad (\text{S58})$$

$$S_\theta(R_{C_1H_i}) = 1 - \tanh\{A_\theta(R_{C_1H_i} - R_{C_1H_i}^0) \exp[B_\theta(R_{C_1H_i} - C_\theta)_3]\} \quad (\text{S59})$$

$$S_\theta(R_{C_2H_l}) = 1 - \tanh\{A_\theta(R_{C_2H_l} - R_{C_2H_l}^0) \exp[B_\theta(R_{C_2H_l} - C_\theta)_3]\} \quad (\text{S60})$$

$$S_{\theta}(R_{CC}) = 1 - \tanh\{A_{\theta}(R_{CC} - R_{CC}^0)\exp[B_{\theta}(R_{CC} - C_{\theta})^3]\} \quad (\text{S61})$$

In total, the $V_{bending}$ potential needs 22 terms to be fitted in the calibration process.

The next term in Eq. (S1), V_{op} , represents a quadratic-quartic potential whose aim is to describe correctly the out-of-plane motion of the CH_2 group in the ethyl radical,

$$V_{op} = \sum_{i=1}^3 f_{\Delta}^{C1Hi} \sum_{j \neq i}^3 (\Delta_{ij})^2 + \sum_{i=1}^3 h_{\Delta}^{C1Hi} \sum_{j \neq i}^3 (\Delta_{ij})^4 \\ + \sum_{l=4}^6 f_{\Delta}^{C2Hl} \sum_{m \neq l}^6 (\Delta_{lm})^2 + \sum_{l=4}^6 h_{\Delta}^{C2Hl} \sum_{m \neq l}^6 (\Delta_{lm})^4 \quad (\text{S62})$$

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force constants, f_{Δ} and h_{Δ} , are allowed to relax from the reactant, where both CH_3 groups show pyramidal structure, to products, where the CH_3 group shows pyramidal structure, while the CH_2 group shows quasi-planar geometry. We use the following S_3 switching functions, in such way that V_{op} vanishes at the ethane limit,

$$f_{\Delta}^{C1Hi} = [1 - S_3(R_{CC})]S_3(R_{C1Hi})S_3(R_{C1Hj})S_3(R_{C1Hk})f_{\Delta}^{C2H5} \quad (\text{S63})$$

$$f_{\Delta}^{C2Hl} = [1 - S_3(R_{CC})]S_3(R_{C2Hl})S_3(R_{C2Hm})S_3(R_{C2Hn})f_{\Delta}^{C2H5} \quad (\text{S64})$$

$$h_{\Delta}^{C1Hi} = [1 - S_3(R_{CC})]S_3(R_{C1Hi})S_3(R_{C1Hj})S_3(R_{C1Hk})h_{\Delta}^{C2H5} \quad (\text{S65})$$

$$h_{\Delta}^{C2Hl} = [1 - S_3(R_{CC})]S_3(R_{C2Hl})S_3(R_{C2Hm})S_3(R_{C2Hn})h_{\Delta}^{C2H5} \quad (\text{S66})$$

$$S_3(R_{C1Hi}) = 1 - \tanh\left[\alpha_{3S}(R_{C1Hi} - R_{C1Hi}^0)(R_{C1Hi} - \beta_{3S})^2\right] \quad (\text{S67})$$

$$S_3(R_{C2Hl}) = 1 - \tanh\left[\alpha_{3S}(R_{C2Hl} - R_{C2Hl}^0)(R_{C2Hl} - \beta_{3S})^2\right] \quad (\text{S68})$$

$$S_3(R_{CC}) = 1 - \tanh\left[\alpha_{3SCC}(R_{CC} - R_{CC}^0)(R_{CC} - \beta_{3SCC})^2\right] \quad (\text{S69})$$

f_{Δ}^{C2H5} , h_{Δ}^{C2H5} , α_{3S} , β_{3S} , α_{3SCC} and β_{3SCC} being fitting parameters.

The angle measuring the deviation from the reference angle is,

$$\Delta_{ij} = a \cos \left(\frac{(\vec{q}_k - \vec{q}_j) \times (\vec{q}_l - \vec{q}_j) \cdot \vec{r}_i}{\|(\vec{q}_k - \vec{q}_j) \times (\vec{q}_l - \vec{q}_j)\| \|\vec{r}_i\|} \right) - \theta_{ij}^0 \quad (\text{S70})$$

with $(q_k - q_j)$ and $(q_l - q_j)$ being two vectors between three hydrogens on each carbon and \mathbf{r}_i the vector between the carbon and each of the hydrogens directly bonded to it. Therefore, the first term to the right of (S70) represents the angle between the CH_i bond and a vector perpendicular to the plane described by the three hydrogen atoms on each carbon. The reference angles θ_{ij}^0 , are defined in Eqs. (S52-S55). Thus, the V_{op} term depends on 6 fitting parameters.

Finally, to include the motion about the C-C bond, we include a torsional term, V_{tor} , given as a cosine function of the torsional angle γ ,

$$V_{\text{tor}} = \sum_{i=1}^3 \sum_{l=1}^3 \frac{v_3}{3} \left[1 + \cos(3\gamma_{H_i C_1 C_2 H_l}) \right] t_1(i) t_2(l) \quad (\text{S71})$$

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$$t_1(i) = \frac{1}{2} \left[1 - \tanh(w_1(R_{C_1 H_i} - w_2)) \right] \quad (\text{S72})$$

$$t_2(l) = \frac{1}{2} \left[1 - \tanh(w_1(R_{C_2 H_l} - w_2)) \right] \quad (\text{S73})$$

This new term depends on 3 adjustable parameters, where v_3 is associated with the torsional barrier height.

The new PES, therefore, depends on 60 parameters, 26, 3, 22, 6 and 3, respectively to describe the stretching, the V_{cc} , the valence bending, the out-of-plane bending and the V_{tor} potentials. These 60 parameters give great flexibility to the functional form. Note that this surface is symmetric with respect to the permutation of the three hydrogen atoms on each CH_3 group.

b) Fitting process

The second step in the development of the PES is the fitting of the 60 parameters to the high-level ab initio calculations used as input. We began this process by using the popular least-squares approach,

$$R = \sum_x |E(x) - F(x, p)|^2 \quad (\text{S74})$$

where $E(x)$ and $F(x, p)$ are, respectively, the ab initio energy at each point (x) used as input and the analytical function depending on the 60 parameters (p). However, in previous studies by our group (see for instance the recent Refs. 2 and 4) we showed that because this problem is ill-conditioned, the least-squares method is unsuccessful when all parameters are simultaneously introduced. In addition, this method presents a series of inherent problems, for example, that the final result depends on the initial set of parameters, or that different sets of parameters are obtained, all equally probable, which represent difficulties in the process. In order to circumvent these problems, we used a divide-and-conquer approach, which is an iterative step-by-step process, widely developed in previous works^{2,4} and to avoid repetitions here we present only a summary. In the first step, the geometric, vibrational and energetic properties of reactants and products are fitted to the ab initio input data, using the following parameters: $R^0_{\text{C1H,R}}$, $R^0_{\text{C1H,P}}$, $R^0_{\text{C2H,R}}$, $R^0_{\text{C2H,P}}$, D^1_{C1H} , D^1_{C2H} , a_{C1H} , b_{C1H} , a_{C2H} , b_{C2H} , w_3 , w_4 , w_5 , w_6 , R^0_{AH} , D^1_{AH} , R^0_{CC} , D^1_{CC} , α_{AH} , α_{CC} . In the second one, we focus attention on the description of the saddle point (barrier height and imaginary vibrational frequency, which describe the topology in this zone and the fall to the reactant and product asymptotes). The following parameters are used in this step: D^3_{C1H} , D^3_{C2H} , D^3_{AH} , D^3_{CC} , c_{C1H} , c_{C2H} . The correct description of the intermediate complexes in the entrance and exit channels is addressed in the third step, which is a great challenge because of the small energy differences in the reactant channel. Finally, in the four step the reaction path or minimum energy path (MEP), and the reaction valley are fitted to the ab initio input information [where 60 points (energy, gradient and Hessian) were calculated describing the MEP]. Note that in this case the ab initio Hessian calculations are computationally very expensive, because at the CCSD(T) level used the second derivatives of the energy are numerical. With 9 atoms we have 27 coordinates and 729 (27x27) energy calculations per point. In total, this represents about 44,000 energy calculations, taking into account the 60 points on the MEP. In these two last steps we used the parameters related with the switching functions,

Eqs. (S35-S51): α_i , β_i , aa_1 , aa_2 , aa_3 , aa_4 ; Eqs. (S52-S61): A_ϕ , B_ϕ , A_9 , B_9 ; Eqs. (S63-S69): f_Δ^{C2H5} , h_Δ^{C2H5} , α_{3sCC} , β_{3sCC} ; and finally, Eqs. (S71-S73): w_1 , w_2 , w_3 , w_4 , v_3 .

As previously noted, this four-step process is iterative, and is repeated until convergence with the ab initio input data. Obviously this represents a long and tedious task. Once the fitting process was concluded, we obtained the final set of 60 parameters defining the new PES-2017 surface. The best set of parameters is listed in Table S1, while Figure S1 plots a 2D representation of the new PES-2017 surface, where the breaking C-H and forming H-Cl bonds are represented in function of the energy. Finally, note that the new potential energy surface can be obtained upon request from the authors, prior to its publication in the POTLIB library (Ref. 3).

Table S1. Final fitting parameters for the PES-2017 surface describing the

Parameter	Value
V_{str} parameters	
$R^{\circ}_{\text{C1H,R}}$	1.08897 Å
$R^{\circ}_{\text{C1H,P}}$	1.07577 Å
D^1_{C1H}	109.23000 kcal mol ⁻¹
D^3_{C1H}	26.00400 kcal mol ⁻¹
a_{C1H}	1.65300 Å ⁻¹
b_{C1H}	0.12500 Å ⁻¹
c_{C1H}	3.51404 Å ⁻¹
$R^{\circ}_{\text{C2H,R}}$	1.08897 Å
$R^{\circ}_{\text{C2H,P}}$	1.07577 Å
w3	1.00000 Å ⁻¹
w4	1.08897 Å
w5	1.00000 Å ⁻¹
w6	1.08897 Å
D^1_{C2H}	109.23000 kcal mol ⁻¹
D^3_{C2H}	26.00400 kcal mol ⁻¹
a_{C2H}	1.65300 Å ⁻¹
b_{C2H}	0.12500 Å ⁻¹
c_{C2H}	3.51404 Å ⁻¹
R°_{AH}	1.27191 Å
D^1_{AH}	107.85800 kcal mol ⁻¹
D^3_{AH}	28.56400 kcal mol ⁻¹
α_{AH}	1.85570 Å ⁻¹
R°_{CA}	1.95397 Å
D^1_{CA}	46.60900 kcal mol ⁻¹
D^3_{CA}	14.90000 kcal mol ⁻¹
α_{CA}	1.2290285 Å ⁻¹

V _{CC} parameters	
R ^o _{CC}	1.50007 Å
D ¹ _{CC}	117.94900 kcal mol ⁻¹
α _{CC}	1.93400 Å ⁻¹
V _{bending} parameters	
k ^{C2H5}	0.2977000 mdyne Å rad ⁻²
a _k	0.3060000 mdyne Å rad ⁻²
α ₁	2.5313681 Å ⁻¹
β ₁	1.088625 Å
α ₂	2.0147402 Å ⁻¹
β ₂	1.088980 Å
α _{1CC}	2.5313681 Å ⁻¹
β _{1CC}	1.550070 Å
α _{2CC}	2.0147402 Å ⁻¹
β _{2CC}	1.550070 Å
aa ₁	0.300952 Å ⁻²
aa ₂	0.499963 Å ⁻²
aa ₃	6.465953 Å ⁻²
aa ₄	1.569977 Å ⁻²
A _φ	1.0087903 Å ⁻¹
B _φ	1.2006638 Å ⁻³
C _φ	1.0889937 Å
A _θ	1.2078714 Å ⁻¹
B _θ	0.3548859 Å ⁻³
C _θ	1.8915497 Å
A _{1CC}	0.90007 mdyne Å rad ⁻²
A _{2CC}	0.94900 Å ⁻¹

V_{op} parameters	
α_{3s}	1.8419147 \AA^{-1}
β_{3s}	1.0889300 \AA
$f_{\Delta}^{\text{C}2\text{H}5}$	0.1357500 mdyne \AA rad ⁻²
$h_{\Delta}^{\text{C}2\text{H}5}$	0.2615000 mdyne \AA rad ⁻⁴
$\alpha_{3\text{CC}}$	0.531368 \AA^{-1}
$\beta_{3\text{CC}}$	1.550070 \AA
V_{tor} parameters	
v_3	13.730000 kcal mol ⁻¹
w_1	9.3548859 \AA^{-1}
w_2	0.913970 \AA

Figure S1. 2D representation of the PES-2017 surface for the breaking C-H and forming H-Cl bonds. Distances in Å and energy in kcal mol⁻¹.

