

A few roles of *ab initio* calculations in this paper:

- (1) Determine if there are competing reactions
optimize possible intermediates and transition states connecting them (to determine barriers)

- (2) Assuming no competition, the pressure dependence of the association reaction corresponds to the reverse of the unimolecular dissociation
 - (a) Determine the transition state when the reaction is barrierless on the electronic-only potential energy surface
presumably the transition state exists on the “adiabatic” potential, i.e., when vibrations and rotations are included for temperature T.
 - (b) In this case some experimental data is utilized as noted below (this is not required since one can determine the adiabatic potentials and TS directly, but this simplifies things considerably)

From the usual Arrhenius and transition state theory expression for the rate constant:

$$\begin{aligned}k &= A e^{-E_a/RT} \\ &= \frac{kt}{h} e^{(1+\Delta S_0^\ddagger/R)} e^{-E_a/RT}\end{aligned}$$

Where ΔS_0^\ddagger is the entropy of activation.

For the dissociation: $A_{-1} = \frac{kt}{h} e^{(1+\Delta S_0^{-1}/R)}$

For the association: $A_{+1} = \frac{kt}{h} e^{(1+\Delta S_0^{+1}/R)}$

Then,
$$\ln\left(\frac{A_{-1}}{A_{+1}}\right) = 1 + \frac{\Delta S_o^{-1}}{R} - \left(1 + \frac{\Delta S_o^{+1}}{R}\right) = \frac{\Delta S_{rxn}^o}{R}$$

- 1) obtain the reaction entropy, ΔS_{rxn}^o , from the *ab initio* calculations on the products and reactants (frequencies and moments of inertia of H_2SiCO , SiH_2 , and CO)
- 2) fix A_{+1} based on experimentally known $\text{SiH}_2 + \text{C}_2\text{H}_4$ reaction
- 3) locate the transition state for temperature T by finding the point on the minimum energy path where the computed entropy (from the frequencies and structures along the path) yields the correct A_{-1} (see Tables 4 and 5).