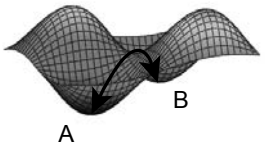
Transition States

1

PES

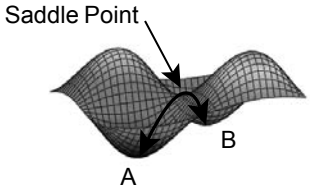
A → B

- Minima represent A and B
  - Reactant and product
  - Conformers
- Reaction Path
  - Path between two minima



2

- Saddle Point
  - Energy passes through maximum for movement along reaction pathway connecting minima
  - Minima in all other directions "perpendicular" to reaction pathway
  - One imaginary vibrational frequency



3

Terminology

- Transition State
  - Geometry at the peak of the *free energy* (*G*) profile
- Transition Structure
  - Geometry at the peak of the *potential energy* (*E*) profile

Rate Constants

Transition State Theory

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger}/RT}$$

- Rate Constant
  - $\Delta G^{\ddagger}$ is *G*(TranState) - *G*(reactant)
- "Transmission" Coefficient
  - 0.5 - 2
  - "Recrossings" (reflect back)
  - Tunneling

Rate Constants

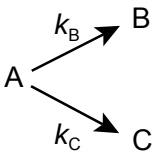
Arrhenius Theory

$$k = Ae^{-E_a/RT}$$

- Rate Constant
  - E_a = *E*(TranStructure) - *E*(reactant)
  - *A* from hard sphere collision theory

Rate Constants

Relative Values



$$\frac{k_B}{k_C} = \frac{A_B e^{-E_{a,B}/RT}}{A_C e^{-E_{a,C}/RT}} \approx e^{-(E_{a,B}-E_{a,C})/RT}$$

e.g., ortho/para subsititution

If ($E_{a,B}$-$E_{a,C}$) = 2 kcal mol^{-1}, then at 25 °C, k_B/k_C = 1/29.

7

Methods to Find Transition Structures

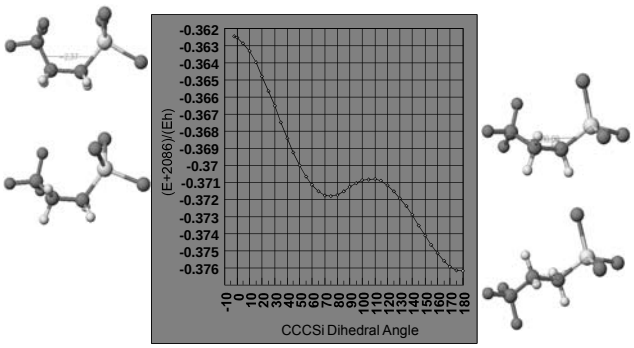
General Approaches

- Guess at geometry
  - Refine
- Modify structure from similar reactions
  - Refine
- Run saddle point calculations
  - Several techniques
- Run optimized grid
  - Vary parameters to get PES
  - Not practical for large molecules

8

Conformer Transition Structure

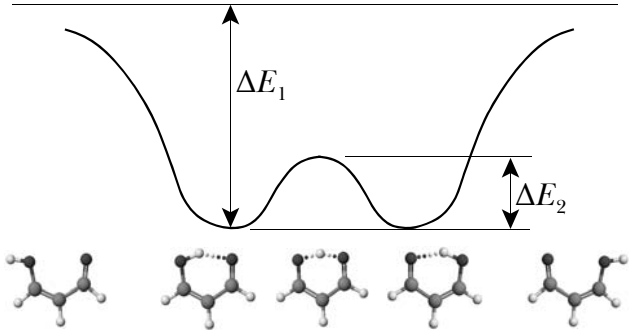
Conformers of $CF_3CH_2CH_2SiCl_3$ (B88-LYP/DZVP)



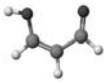
9

A Common Example

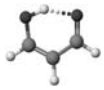
Proton Transfer in Malonaldehyde Enol (B88-LYP/DZVP)



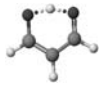
10



E = -267.12258 Eh



E = -267.14500 Eh
r_{OH} = 1.021 Å, 1.705 Å (1.68 Å)
r_{OO} = 2.622 Å (2.58 Å)



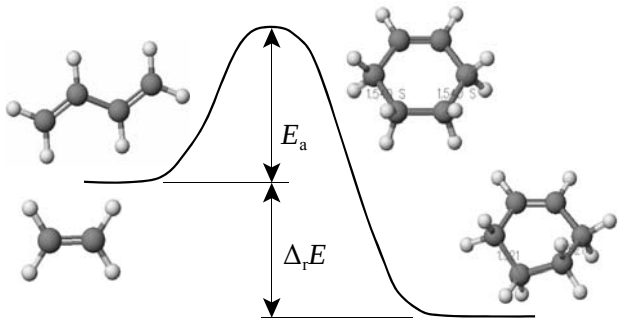
E = -267.14112 Eh
r_{OH} = 1.233 Å, 1.232 Å (1.20 Å)
r_{OO} = 2.413 Å (2.36 Å)

ΔE_1 = 14.1 kcal mol^{-1} (12.4 kcal mol^{-1})
ΔE_2 = 2.4 kcal mol^{-1} (4.0 kcal mol^{-1})

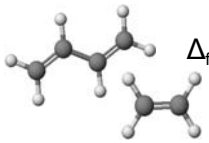
11

A Common Example

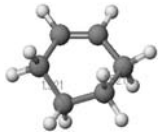
Diels-Alder Addition of *trans*-Butadiene and Ethylene (PM3)



12



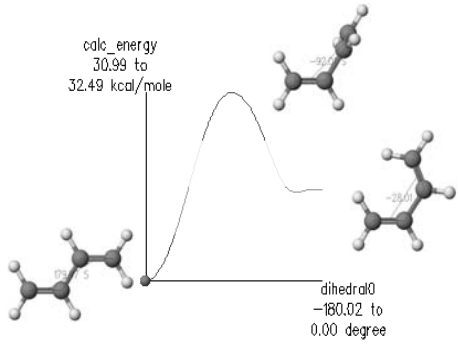
$\Delta_f H$ = (30.9881 + 16.6088)
= 47.5969 kcal mol^{-1}



$\Delta_f H$ = -4.9536 kcal mol^{-1}

$\Delta_r H$ = -52.5505 kcal mol^{-1}
($\Delta_r E$ = -38 kcal mol^{-1} literature)

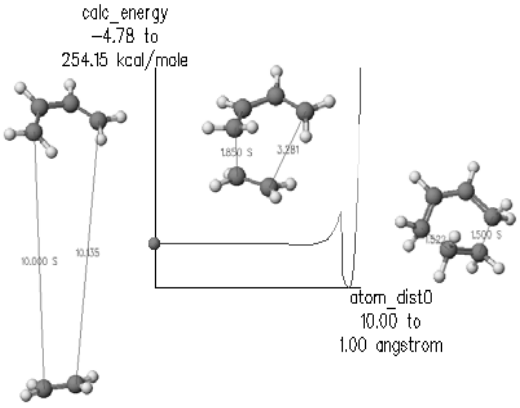
13



$\Delta_r H$ = 0.7912 kcal mol^{-1} (2.3 kcal mol^{-1} literature)
E_a = 1.5 kcal mol^{-1}

14

Map Reaction / PM3 / 10.00 to 1.00 at 180 steps



15

E_a = 84.691 - 48.331 = 36.36 kcal mol^{-1}
(Literature 27 ± 2 kcal mol^{-1})

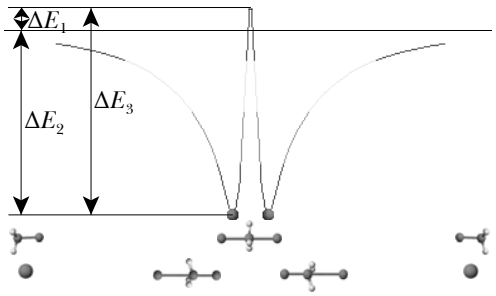
$\Delta_r H$ = (-4.776) - (48.331) = -53.107 kcal mol^{-1}
correction:
$\Delta_r H$ = (-53.107) + (0.7912) = -52.3158 kcal mol^{-1}

16

A Common Example

S_N2 Reaction (Walden Inversion) between Cl^- and CH_3Cl (PM3)

$$Cl^- + CH_3Cl \rightarrow [ClCH_3Cl]^- \rightarrow ClCH_3 + Cl^-$$



17