Hydrocarbons

We consider the fragments that make the molecules.

\[ \text{CH}_3 \text{ is planar} \]

We can make a σ bond between two of these methyls.

The bonds will become close to tetrahedral and that will cost us some of the energy that we gain from the bond.

Consider rotation around the bond.

\[ \text{Eclipsed} \quad \text{or} \quad \text{Staggered} \]

Eclipsed is about 2.7 kcal/mol higher than staggered.

Consider a longer compound.

\[ \text{Now the barrier is only about 0.03 kcal/mol and it prefers to be eclipsed.} \]

We find out that this interaction is not primarily electrostatic because it drops off too quickly. At those distances, electrostatic interactions are still important. We conclude then that the barrier is due to overlap repulsion. It can actually be
shown through simple calculations that the eclipsed configuration minimizes the total repulsion interactions: each hydrogen is close to another hydrogen, and not as close to two others.

In the other case (staggered) each hydrogen is somewhat close to two other hydrogens and not as close to one hydrogen.

\[
\begin{align*}
&d_2 \\
&d_1 \\
&d_2 \\
&H \\
&H \\
&H \\
&H
\end{align*}
\]

**ECLIPSED (BETTER)**

\[
\begin{align*}
&d_3 \\
&d_4 \\
&d_2 \\
&H \\
&H \\
&H \\
&H
\end{align*}
\]

**STAGGERED**

d_1 < d_3 < d_2 < d_4

These interactions fall off exponentially with increasing distance.

Rotational barrier of CH₃-CH₃ as a function of torsion angle:

\[
\begin{align*}
&2.7 \text{ kcal/mol} \\
&\quad \text{C-C bond is } \sim 1.54 \text{ Å} \\
&\quad \text{C-H bond is } \sim 1.09 \text{ Å} \\
&\quad \text{H-C-H bond angle is } \sim 108^\circ
\end{align*}
\]
Let's now consider the dissociation of the \( \text{CH}_3 - \text{CH}_3 \) bond.

\[ D_{300} = 90 \]
\[ D_0 = 87.5 \text{ kcal/mol} \]
\[ 4RT \times 2 = 8RT \]
\[ \text{Z.P.E.} \quad 2\text{CH}_3 \]
\[ \text{Z.P.E.} \quad \text{C}_2\text{H}_6 \]
\[ D_e = 95 \text{ kcal/mol} \]
\[ D_{300} = \text{energy difference between reactants and products at 300 K} \]
\[ D_e = \text{energy difference between the bottom of the energy wells} \]
\[ D_0 = \text{energy difference between the zero point energies (Z.P.E.)} \]

Consider the zero point energy (Z.P.E.). Ethane has eight atoms and \( \text{CH}_3 \) has 4 atoms. The number of vibrational degrees of freedom (non-linear molecules) is:

\[ \text{C}_2\text{H}_6 : 3N - 6 = 3 \times 8 - 6 = 18 \]
\[ \text{CH}_3 : 3N - 6 = 3 \times 4 - 6 = 6 \times 2 \text{ fragments} = 12 \]

Ethane has six more vibrational degrees of freedom than two \( \text{CH}_3 \) fragments, so it is reasonable to expect that \( D_0 < D_e \).

Now let's consider the thermal energy. At room temperature, ethane will contribute \( 4RT \) above its zero point energy.
and two methyls will contribute $2 \times \frac{1}{2} kT = kT$ above their zero point energy. So $D_{300} > D_0$

$D_{300} \sim 89.9 \text{ kcal/mol}$

**Snap bond energy:**

The relaxation energy of the methyls when the bond is broken is $\sim 7.3 \text{ kcal/mol}$, so for two fragments we have $14.6 \text{ kcal/mol}$.

If we add this to the bond energy we obtain the snap energy

$$D_{\text{snap}} = 89.9 + 14.6 \frac{\text{ kcal}}{\text{ mol}} \sim 105 \text{ kcal/mol}$$

\[\begin{array}{c}
\text{C} \quad \text{C} \\
\text{H} \quad \text{H} \\
\text{H} \quad \text{H} \\
\end{array}\quad \rightarrow \quad \begin{array}{c}
\text{C} \quad \text{H} \\
\text{H} \\
\end{array}\]

Consider now CF₃

Because fluorine bonds preferentially to the p-orbitals, the unpaired (non-bonded) electron that is left, is in a lobe orbital. This structure is pyramidal, so there is very little relaxation energy when the $\text{F}_3\text{C} - \text{CF}_3$ bond is broken.

$$D_{\text{snap}} \sim 105 \text{ kcal/mol}$$

$D_{300} \sim 102 \text{ kcal/mol}$

There are only a few degrees of relaxation.
Consider now CH₂ bonding

If the fragments are oriented such that we can form a planar molecule, both the lobe orbitals and the p-orbitals will overlap and bond to form a singlet. Otherwise, we can also consider bringing the fragments together in a staggered configuration to form a triplet state. Rotation about the bond axis breaks the π (second) bond.

We see that the second bond is worth about 67 kcal/mol. At 90° the triplet state has a minimum. We would expect it to be a little better than the singlet state. However, due to same-spin pairing, the orbitals must become orthogonal to each other and this costs some additional stabilization energy. As a result, even at 90°, the singlet state is still a little better by about 1 kcal/mol.

The rotational barrier for ethylene is then about 67 kcal/mol. The bond distance is about 0.2 Å shorter than the single bond at about 1.3 Å. This is necessary to allow good overlap of the π bond.

For the triplet state, the bond distance is about 1.46 Å, a little shorter than in ethane due to reduced steric effects.

Bond energy of ethene

\[
\text{Bond energy of ethene} = 107 \text{ kcal/mol} + 67 \text{ kcal/mol} = 174 \text{ kcal/mol}
\]

Bond energy of staggered triplet configuration
As in the case of ethane, when the bond is broken the fragments relax to about 132° angles H-C-H. There is some relaxation energy of about 2.4 kcal/mol. Very little.

For the dissociation of ethylene,

\[ D_{298} \approx 178 \text{ kcal/mol} \]
\[ D_0 \approx 170 \text{ kcal/mol} \]
\[ D_e \approx 181 \text{ kcal/mol} \]
\[ D_{snap} \approx 177 \text{ kcal/mol} \]

Consider now

\[
\text{F} = \text{C} = \text{C} = \text{F}
\]

\[ D_e = 79 \text{ kcal/mol} \]
\[ D_0 = 74 \text{ kcal/mol} \]
\[ D_{298} = 75 \text{ kcal/mol} \]

Fluorines bond to p-orbitals leaving a very stable CF₂. When we form the bond in C\textsubscript{2}F\textsubscript{4}, we need to pay a promotion energy to unpair the lobe orbitals. This promotion energy is about 52 kcal/mol.

This is because in order to form a bond, the fragment needs to be transformed to one that has a \( \sigma \) orbital for the first bond, and a \( \pi \) orbital for the second bond. So the real bond energy (starting from ethylene) is: \( 177 - 2 \times 52 = 63 \text{ kcal/mol} \)

Consider now bonding of C\textsubscript{2}H\textsubscript{4} fragments:

We need to start from the 4\( \Sigma^- \) state:

To have 2 p-bonds available.
The triple bond is about 1.205 Å, again due to π-orbital overlap, but also because we are using lobe orbitals to form the first bond.

The C-H bond is about 1.056 Å due to more lobe character.

Bond energy?

\[ \Delta_{\text{e}} = 236 \text{ kcal/mol} \]
\[ \Delta_{\text{o}} = 228 \text{ kcal/mol} \]
\[ \Delta_{\text{a}} = 230 \text{ kcal/mol} \]

This is about 107 kcal/mol from the σ bond and about 62 kcal/mol from each π bond. The snap bond energy is about 254 kcal/mol because the ground state of CH is a 2π.

\[ \text{O} \]

This relaxation takes place after the bond has snapped.

F-C≡C-F has an even lower bond energy. There is a significant promotion energy cost in forcing the fluorine to bond to a lobe orbital.