Probing the Hyperconjugative Captodative Effect by Quantum Chemistry

Julia Stanfield
Macalester College
Stereoselectivity in a Lactonization Reaction

- The trans precursor has the more readily oxidized C(1)-H bond
- How do the identity and orientation of the trans precursor’s substituents lower the C(1)-H bond dissociation energy?
Substituents weaken C-H bonds by stabilizing the carbon centered radicals that form when hydrogens are removed.

When the substituent is bonded directly to the carbon-centered radical, the substituent acts as an electron donor.

The less electronegative X is, the more it can stabilize the radical.
Substituents that are one bond away from the carbon-centered radical act as electron acceptors to help stabilization. The C-Y bond is a hyperconjugative acceptor.

This type of stabilization is known as double-bond / no-bond resonance. It is a minor but non-negligible contributor.
If a radical has both a donor and an acceptor, the two heteroatoms can work together to make an additional resonance structure (bottom right). The effect of two substituents is not necessarily additive, it is not necessarily equal to the sum of the effects of the donor and acceptor acting individually. This combination of donor and acceptor substituents produces what is called the (Hyperconjugative) Captodative effect.
To measure the energy required to break the C-H bond, I found its bond dissociation energy (BDE).

\[
\text{BDE} = (E_{\text{II}} + \text{zpc}_{\text{II}}) + (E_{\text{III}}) - (E_{\text{I}} + \text{zpc}_{\text{I}})
\]

I used 0.9806 as the scaling factor for the zero-point corrections.
Method

- I have tested the effects of heteroatoms from Groups 15, 16, 17 and Periods 2, 3, 4 both as donors (X) and parts of the C-Y acceptor bond.
- All structures were optimized at the B3LYP/6-31G(d) level.
- B3LYP/6-31G(d) was also used to compute vibrational frequencies.
  - If an optimized structure is truly a minimum, all frequencies must be real numbers.
  - Knowing the vibrational frequencies lets us determine the zero-point correction (zpc) to the electronic energy.
- The energies of the structures were also determined with the MPWB1K/6-311+G(3df,2p) and CBS-QB3 methods.
  - These methods also use more time and memory (especially CBS-QB3).
- All BDE’s are calculated by using the most stable conformer of both closed-shell reactant and radical product.
# Substituent as Donor BDE (kcal/mol)

\[
\begin{align*}
\text{H}_2\text{C} \rightarrow \text{CH}_3 & \quad \rightarrow \quad \text{H}_3\text{C} \rightarrow \text{CH}_3 + \text{H}^+ \\
\end{align*}
\]

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<thead>
<tr>
<th>X</th>
<th>B3LYP</th>
<th>MPWB1K</th>
<th>CBS-QB3</th>
<th>Exp</th>
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<tbody>
<tr>
<td>H</td>
<td>98.5</td>
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<td>100.0</td>
<td>99.9 ± 0.3</td>
</tr>
<tr>
<td>F</td>
<td>94.6</td>
<td>95.7</td>
<td>98.3</td>
<td>97.6 ± 2</td>
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<tr>
<td>Cl</td>
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<td>AsH_2</td>
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### Substituent as Donor $\Delta$BDE (kcal/mol)

$$\begin{align*}
\text{X} & \quad \text{H}_2C\text{CH}_3 & \quad \text{H}_2C\text{CH}_3 + \text{H}^* \\
\text{H} & \quad 0 & \quad 0 & \quad 0 & \quad 0 \\
\text{F} & \quad -3.9 & \quad -2.6 & \quad -1.7 & \quad -2.3 \pm 2 \\
\text{Cl} & \quad -4.2 & \quad -4.5 & \quad -3.3 \pm 0.5 \\
\text{Br} & \quad -3.1 & \quad -3.3 & \quad -3.3 \pm 1 \\
\text{OH (OMe)} & \quad -7.6 (-7.3) & \quad -7.1 (-6.9) & \quad -6.1 (-6.0) & \quad -5.7 \pm 0.3 \\
\text{SH (SMe)} & \quad -7.3 (-8.5) & \quad -7.9 (-9.2) \\
\text{SeH (SeMe)} & \quad -5.0 (-6.2) & \quad -5.8 (-7.0) \\
\text{NH}_2 & \quad -10.2 & \quad -10.4 & \quad -9.2 & \quad -10.4 \pm 0.3 \\
\text{PH}_2 & \quad -5.7 & \quad -5.6 \\
\text{AsH}_2 & \quad -2.8 & \quad -3.3
\end{align*}$$
Substituent as Acceptor BDE (kcal/mol)

\[
\begin{array}{c}
\text{Y} \\
\text{H}_2C\text{CH}_3 \\
\end{array}
\rightarrow
\begin{array}{c}
\text{Y} \\
\text{H}_2C\text{CH}_2 + \text{H} . \\
\end{array}
\]

<table>
<thead>
<tr>
<th>Y</th>
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<tr>
<td>H</td>
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<td>100.0</td>
<td>99.9 ± 0.3</td>
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<td>AsH₂</td>
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### Substituent as Acceptor $\Delta$BDE (kcal/mol)

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<th>Exp</th>
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Energy of $\sigma^{*}_{CY}$ (a.u.) vs. Electronegativity

### Substituent as Acceptor $\Delta$BDE (kcal/mol)

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Y</th>
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<td>Br</td>
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<td>-1.3 ± 2</td>
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<td>OH (OMe)</td>
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## Bond Lengths of Closed-Shell Ethanes and Ethyl Radicals With Acceptor Substituents

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<th>Reactant (Å)</th>
<th>Radical (Å)</th>
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BDE of Disubstituted Ethane With Fluorine as a Donor (kcal/mol)

\[
\begin{align*}
\text{H}_2\text{C}-\text{CH}_2 & \quad \rightarrow \quad \text{H}^+\text{C}-\text{CH}_2 + \text{H}^\cdot \\
\end{align*}
\]

<table>
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<tr>
<th>X</th>
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<th>B3LYP</th>
<th>MPWB1K</th>
<th>CBS-QB3</th>
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<td>F</td>
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<td>102.0</td>
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<tr>
<td>F</td>
<td>F</td>
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<td>96.4</td>
<td>98.7</td>
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<tr>
<td>H</td>
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<td>99.3</td>
<td>101.1</td>
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## ΔBDE of Disubstituted Ethane With Fluorine as a Donor With Respect To Ethane (kcal/mol)

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<th>X</th>
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<th>CBS-QB3</th>
<th>Extra Stabilization?</th>
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<tr>
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BDE of Disubstituted Ethane With Oxygen as a Donor (kcal/mol)

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{CH}_2 \\
X & \quad Y \\
\text{H}_2\text{C} & \quad \text{CH}_2 \quad \rightarrow \quad \text{H}^+ \\
& \quad \text{CH}_2 + \quad \text{H}^+ \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>B3LYP</th>
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<th>CBS-QB3</th>
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### ΔBDE of Disubstituted Ethane With Oxygen as a Donor With Respect To Ethane (kcal/mol)

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BDE of Disubstituted Ethane With Nitrogen as a Donor (kcal/mol)

\[ \begin{array}{ccc}
X & Y & \text{H}_2C-C\text{H}_2 \\
\text{NH}_2 & \text{H} & 88.3 \quad 89.9 \quad 90.7 \\
\text{H} & \text{F} & 100.2 \quad 100.2 \quad 102.0 \\
\text{NH}_2 & \text{F} & 87.7 \quad 87.7 \\
\text{H} & \text{OH} & 99.0 \quad 99.3 \quad 101.1 \\
\text{NH}_2 & \text{OH} & 88.6 \quad 87.3 \\
\text{H} & \text{NH}_2 & 98.9 \quad 98.9 \quad 100.7 \\
\text{NH}_2 & \text{NH}_2 & 88.6 \quad 87.2 \\
\text{H} & \text{OMe} & 99.9 \quad 99.7 \quad 101.5 \\
\text{NH}_2 & \text{OMe} & \\
\end{array} \]
$\Delta$BDE of Disubstituted Ethane With Nitrogen as a Donor With Respect To Ethane (kcal/mol)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>B3LYP</th>
<th>MPWB1K</th>
<th>CBS-QB3</th>
<th>Extra Stabilization?</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$</td>
<td>H</td>
<td>-10.2</td>
<td>-8.3</td>
<td>-9.3</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>F</td>
<td>1.7</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>NH$_2$</td>
<td>F</td>
<td>-10.8</td>
<td>-10.5</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>H</td>
<td>OH</td>
<td>0.5</td>
<td>1.1</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>NH$_2$</td>
<td>OH</td>
<td>-9.9</td>
<td>-10.9</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>H</td>
<td>NH$_2$</td>
<td>0.4</td>
<td>0.7</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>NH$_2$</td>
<td>NH$_2$</td>
<td>-9.9</td>
<td>-11.0</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>H</td>
<td>OMe</td>
<td>1.4</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>NH$_2$</td>
<td>OMe</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>
### BDEs and ∆BDEs* of Substituted Cyclohexanes

<table>
<thead>
<tr>
<th></th>
<th>B3LYP</th>
<th>∆ BDE</th>
<th>MPWB1K</th>
<th>∆ BDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>95.2</td>
<td>0.0</td>
<td>95.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Pyran</td>
<td>92.0</td>
<td>-3.2</td>
<td>92.4</td>
<td>-3.3</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>89.0</td>
<td>-6.2</td>
<td>89.9</td>
<td>-5.8</td>
</tr>
<tr>
<td>MeO (axial)</td>
<td>95.3</td>
<td>0.1</td>
<td>96.3</td>
<td>0.6</td>
</tr>
<tr>
<td>MeO (eq)</td>
<td>96.0</td>
<td>0.8</td>
<td>96.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Pyran + Axial MeO</td>
<td>91.4</td>
<td>-3.8</td>
<td>92.3</td>
<td>-3.3</td>
</tr>
<tr>
<td>Pyran + eq. MeO</td>
<td>93.1</td>
<td>-2.1</td>
<td>93.7</td>
<td>-2.0</td>
</tr>
<tr>
<td>OH + axial MeO</td>
<td>87.9</td>
<td>-7.3</td>
<td>89.6</td>
<td>-6.0</td>
</tr>
<tr>
<td>OH + eq. MeO</td>
<td>94.4</td>
<td>-0.8</td>
<td>95.1</td>
<td>-0.6</td>
</tr>
<tr>
<td>Pyran, OH, MeO (axial)</td>
<td>87.3</td>
<td>-7.9</td>
<td>88.6</td>
<td>-7.1</td>
</tr>
<tr>
<td>Pyran, OH, MeO (eq.)</td>
<td>88.5</td>
<td>-6.7</td>
<td>89.2</td>
<td>-6.5</td>
</tr>
</tbody>
</table>

*All ∆BDE values calculated with respect to cyclohexane
Effect of MeO Group Conformation on the C(2)-H Bond Dissociation Energy

B3LYP/6-311+G(d,p)//B3LYP/6-31G(d)

- MeO is hyperconjugated to the C(2) radical
- Is there a hyperconjugative **captodative** effect?
Future Work

• Continue calculations on disubstituted ethane.
• Continue calculations of all applicable molecules using the CBS-QB3 method.
• Examine substituted cyclohexane molecule for presence of hyperconjugative captodative effect.
• Examine Nitrogen centered radicals
Acknowledgments

• Professor Keith Kuwata
• Macalester College Chemistry Department
• Violet Olson Beltmann Fund