Discussing \( \text{E}_{\text{act}} \) - can't be predicted can be measured

A few useful generalities.

1. If bonds are broken, \( \text{E}_{\text{act}} > 0 \)

2. Endothermic run - both breaking + formation -
   \( \text{E}_{\text{act}} > \Delta H^\circ \)

3. Gas-phase - bonds are broken but no bonds are formed - \( \text{E}_{\text{act}} = \Delta H^\circ \)

   ex: chain initiation

\[ \text{O} \cdot \text{O} \quad \text{E}_{\text{act}} = \Delta H^\circ \]
4. Gas-phase: small radicals combine to form molecules (bonds formed but not broken)

\[ \text{Eqn} \approx 0 \]

ex. chain termination
Alkanes + Halogens (F, Cl, Br, I)

methane + X₂  - wide variety of reactivities

F₂ >> Cl₂ > Br₂ >> I₂

1. Look @ Initiation Steps  X-X → 2X⁻

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Exact</th>
<th>ΔH⁰</th>
<th>kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>159</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td>243</td>
<td>243</td>
<td></td>
</tr>
<tr>
<td>Br₂</td>
<td>193</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>I₂</td>
<td>151</td>
<td>151</td>
<td></td>
</tr>
</tbody>
</table>

These #s do not match the observed relative reactivities.
2. Look @ Propagation  
\[ \text{X}^\cdot + \text{CH}_4 \rightarrow \cdot \text{CH}_3 + \text{H-X} \]

<table>
<thead>
<tr>
<th>Halogen</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta H^\circ ) (overall)</th>
<th>Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2 )</td>
<td>+5</td>
<td>-130</td>
<td>-432</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>+16</td>
<td>+8</td>
<td>-101</td>
</tr>
<tr>
<td>( \text{Br}_2 )</td>
<td>+78</td>
<td>+74</td>
<td>-26</td>
</tr>
<tr>
<td>( \text{I}_2 )</td>
<td>+140</td>
<td>+142</td>
<td>+53</td>
</tr>
</tbody>
</table>

This does predict the relative reactivities—seems to be the H abstraction that matters.

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Haloegenation of Higher Alkanes

\[ \text{Cl}_2 + \text{C}_9 \text{H}_{18} \xrightarrow{\text{hv}} \text{C}_9 \text{H}_{18} - \text{Cl} \]

- \( 1^\circ \) H\( ^5 \) : 16.5%  
- \( 2^\circ \) H\( ^5 \) : 33.5%  
- \( 3^\circ \) H : 22%  
- \( 2^\circ \) H, 2 CR : 28%
The product distribution is not a statistical
ratio of products - there is a bias towards
forming 2° + 3° halides.

calculate the bias:

\[
\frac{3°}{1°} : \frac{22/1}{50/9} = \frac{4}{1}
\]

\[
\frac{2°}{1°} : \frac{28/2}{50/9} = \frac{2.5}{1}
\]

A 3° H is 4x as reactive as a 1° H.
A 2° H is 2.5x as reactive as a 1° H.

Not selective enough. Unfortunately, to
reliably get just one product.
This looks much more selective - calculate the bias.

\[ \frac{3/20}{[93/1]} = \frac{93}{3} = \frac{31}{1} \]

3°H is 31x as reactive as 2°H.

\[ \frac{3/10}{[93/1]} = \frac{837}{1} \]

3° H is at least 837x as reactive as 1° H.

\[ \frac{2/10}{[6/2]} = \frac{27}{1} \]

2° H is 27x as reactive as 1° H.

This is very selective.
Why the difference? Again, the Hammond-Leffler Postulate is the explanation.

- **Exothermic**: TS resembles reactants
- **Endothermic**: TS resembles products

Chlorination is exothermic. ⇒ Type of radical doesn't matter.

Bromination is endothermic. ⇒ Radical that is being formed is important (think stabilities here)

Other radicals:
- Allylic
- Benzylic

Both are resonance-stabilized.
overall radical stabilities

vinyl
aryl < CH₃ < 1° < 2° < 3° < allyl benzyl
least stable
most stable

RXN conditions:

\[
\text{Br}_2 \xrightarrow{hv} \text{NBS} \xrightarrow{hv}
\]

source of \( \cdot \text{Br} \)

\( \text{N-bromosuccinimide} \)