Reactions of Alkanes: Radical Halogenations

Sections 5.3, 5.8, 5.9, 10.3 in McMurry; Chapter 3 in Vollhardt

Homolytic cleavage or bond homolysis:

\[ \text{A} - \text{B} \rightarrow \text{A}^* + \cdot \text{B} \]

Heterolytic cleavage:

\[ \text{A} - \text{B} \rightarrow \text{A}^+ + \cdot \text{B}^- \]

Fish-hook (or single-headed) arrows indicate single-electron transfer; double-headed arrows are for electron-pair transfer.

Bond-dissociation energy or bond strength:

\[ \Delta H^0 = 435 \text{ kJ mol}^{-1} \]

Relative stability radicals:

Vinylic < methyl < primary < secondary < tertiary < allylic < benzylic

Structures of Alkyl Radicals and Hyperconjugation

No hyperconjugation

Increasing hyperconjugation

Energy Diagram of a Reaction

By tracking the energy changes along each step of a reaction pathway, it is possible to determine:
- how much product is formed.
- how fast a reaction proceeds.

A reaction coordinate diagram describes the energy changes that take place in each step of the mechanism.

This diagram represents one step in a reaction mechanism.

Indicate:
(a) Reactants
(b) Transition state
(c) Products
(d) \( \Delta G^\circ \) free energy change
(e) \( \Delta G^* \) free energy of activation
Chlorination of Methane: the Radical Chain Mechanism

During the reaction, the first product formed is CH₃Cl (and HCl). If sufficient chlorine is present, further substitution may occur, forming CH₂Cl₂, CHCl₃, and finally CCl₄.

A mechanism is a detailed, step-by-step description of all of the changes in bonding that occur in a reaction.

Initiation:

Propagation:

These two reactions happen repeatedly: chain reaction

Chain termination:

Propagation Step 1: Potential Energy Diagram

Propagation Step 2

Exothermic
Energetics of Methane Halogenations

\[ \text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl} \]

slightly unfavorable

very favorable; "drives" the overall equilibrium

<table>
<thead>
<tr>
<th>Reaction</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>X: ( \text{CH}_4 \rightarrow \text{CH}_3 \text{F} )</td>
<td>-31 (-130)</td>
<td>+2 (+8)</td>
<td>+18 (+75)</td>
<td>+34 (+142)</td>
</tr>
<tr>
<td>-( \text{CH}_3 \text{X} \rightarrow \text{CH}_3 \text{Cl} \text{X} )</td>
<td>-72 (-301)</td>
<td>-27 (-115)</td>
<td>-24 (-100)</td>
<td>-21 (-88)</td>
</tr>
<tr>
<td>CH(_2) X ( \rightarrow \text{CH}_3 \text{X} )</td>
<td>-103 (-631)</td>
<td>-25 (-105)</td>
<td>-6 (-25)</td>
<td>+13 (+54)</td>
</tr>
</tbody>
</table>

On the Energy of the TS\( ^\neq \)

In the TS\( ^\neq \), bonds are being made and bonds are being broken. How far along is bond forming and bond breaking at the time the TS\( ^\neq \) is crossed?

The Hammond Postulate - The structure of the TS\( ^\neq \) will more closely resemble the species it is more similar to in energy.

This TS\( ^\neq \) more closely resembles the ________ structure. It is said to be ________

Chlorination of Propane: Relative Reactivity

Statistical ratio: 3 : 1
Experimental ratio (25 °C): 43 : 57

Relative reactivity:

\[
\frac{2^o \text{H}}{1^o \text{H}} = \frac{\text{product % from } 2^o \text{H abstraction}}{\text{number of } 2^o \text{Hs}} \div \frac{\text{product % from } 1^o \text{H abstraction}}{\text{number of } 1^o \text{Hs}}
\]

\[
\approx ?
\]

Chlorination of Propane: Relative Reactivity

\[ \text{Cl}_2 + \text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{hv}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CHCH}_3 + \text{HCl} \]

1-Chloropropane 2-Chloropropane

Statistical ratio: 3 : 1
Experimental ratio (25 °C): 43 : 57

Relative reactivity:

\[
\frac{2^o \text{H}}{1^o \text{H}} = \frac{\text{product % from } 2^o \text{H abstraction}}{\text{number of } 2^o \text{Hs}} \div \frac{\text{product % from } 1^o \text{H abstraction}}{\text{number of } 1^o \text{Hs}}
\]

\[
\approx ?
\]
**Relative Reactivity Calculation**

Relative reactivity: \[
\frac{3^\circ H}{1^\circ H} = \frac{\text{product } \% \text{ from } 3^\circ H \text{ abstraction}}{\text{number of } 3^\circ Hs} \div \frac{\text{product } \% \text{ from } 1^\circ H \text{ abstraction}}{\text{number of } 1^\circ Hs}
\]

\[
= \frac{36\%}{64} : \frac{9\%}{1} = ?
\]

\[
\text{Chlorination of 1-Methylcyclohexane:}
\]

\[
\text{Br}_2 + (\text{CH}_3)_2\text{CH} \xrightarrow{hv} (\text{CH}_3)_2\text{CBr} + \text{BrCH}_2\text{C} = \text{H} + \text{HBr}
\]

Statistical ratio: 9 : 1

Experimental ratio (25 °C): 64 : 36

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**Selectivity in Radical Halogenation**

Very low selectivity in the fluorination reaction

Very high selectivity in the bromination reaction

**Relative Reactivity of Various Carbon Centers in Halogenations**

\[
\begin{align*}
\text{CH}_4 + \text{I}_2 & \xrightarrow{hv} \text{CH}_3\text{I} + \text{HI} \\
\text{Br}_2 + (\text{CH}_3)_2\text{CH} & \xrightarrow{hv} (\text{CH}_3)_2\text{CBr} + \text{BrCH}_2\text{C} = \text{H} + \text{HBr}
\end{align*}
\]

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**Table 3-5: Relative Reactivities of the Four Types of Alkane C–H Bonds in Halogenations**

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>CH₃–H</td>
<td>0.5</td>
<td>0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>RCH₂–H</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>R₂CH–H</td>
<td>1.2</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>R₃C–H</td>
<td>1.4</td>
<td>5</td>
<td>1700</td>
</tr>
</tbody>
</table>

*For each halogen, reactivities with four types of alkane C–H bonds are normalized to the reactivity of the primary C–H bond.

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