Radical Reactions

Last time: the steps of initiation, and propagation were discussed. Termination was also discussed briefly but it did not appear in your notes.

Termination

Radical reactions can terminate by radicals reacting with radicals.

\[ \text{Br}^\cdot + \text{Br}^\cdot \rightarrow \text{Br}\text{-Br} \]

Also

Another way radical chain reactions can terminate is via the production of a very stable radical that does not react with any ground state singlet molecule. These products can slowly combine.

BHT (butylatehydroxytoluene) and BHA (butylatehydroxyanisole)

Radical reactions spoil food. \( \text{O}_2 \) tends to initiate radical reactions. BHT is a common food preservative. Believe me you have eaten a lot of this stuff!

REMEMBER
Since there was not much radical concentration in the reaction, since there was not a lot of initiator at the start of the reaction there is not a lot of termination products at the end of the reaction. By far most or the reaction can be characterized by the equation below.

\[ \text{ROOR} + \text{HBr} \rightarrow \text{ROBr} \]

- Addition is antiMarkovnikov due to the change in mechanism
- The reaction is exothermic. \( \pi \)-bonds are destroyed and \( \sigma \)-bonds are formed.

REARRANGEMENT

Why don’t carbon radicals rearrange like carbocations?

THE REARRANGEMENT ABOVE DOES NOT HAPPEN WITH RADICALS

- remember we considered radicals beta to bromine in organic structures
  - unlike the cation the radical does not exist in a closed shell intermediate
  - to draw such a structure we would have to populate antibonding orbitals with electrons
- this consideration applies to the hypothetical t-state of a methyl or a hydride shift in a radical
- these transition states are relative high energy compared to cation rearrangements because to pass through these transition states, the structure has to put electrons into net antibonding orbitals.
Before the radical addition mechanism was elucidated people wondered why only HBr addition sometimes resulted in the anti-Markovikov product.

- the radical mechanism should explain the observation that HBr addition is different from HCl and HI addition to alkenes. If these acids add across the double bond the products will be Markovnikov addition.
- A thermochemical analysis explains the observation.
1) \[
\text{hv or heat} \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \quad \rightarrow \quad \begin{array}{c}
2 \text{O} \\
\text{.} \\
\text{.}
\end{array}
\]

2) \[
\text{O} \\
\text{.} \quad \begin{array}{c}
\text{.} \\
\text{.} \\
\text{+ HX}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{O} \\
\text{.} \\
\text{H} \\
\text{+ X}
\end{array}
\]

3) \[
\text{X} \\
\text{.} \quad \begin{array}{c}
\text{.} \\
\text{.}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{X}
\end{array}
\]

4) \[
\text{X} \\
\text{.} \quad \begin{array}{c}
\text{.} \\
\text{.} \\
\text{+ HX}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \\
\text{X}
\end{array} \quad \begin{array}{c}
\text{+ X} \\
\text{.}
\end{array}
\]

<table>
<thead>
<tr>
<th>X</th>
<th>Pi bond (kcal/mol)</th>
<th>C-X bond (kcal/mol)</th>
<th>ΔH (step 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>66</td>
<td>82</td>
<td>-16</td>
</tr>
<tr>
<td>Br</td>
<td>66</td>
<td>69</td>
<td>-3</td>
</tr>
<tr>
<td>I</td>
<td>66</td>
<td>54</td>
<td>12</td>
</tr>
</tbody>
</table>

The first propagation step for HI is significantly uphill (endothermic).
- this means that this step will be slow.
The second propagation step for HCl is significantly uphill (endothermic).
- this means that this step will be slow.
- Slow compare to the Markovnikov addition mechanism involving carbocation intermediates instead of radical intermediates.

Radical addition to alkynes.

- Instructor discusses mechanism
- Another way to initiate the radical process is with light. How can light initiate the radical process???
RADICAL POLYMERIZATION

A: ethylene → polyethylene
B: tetrafluoroethylene → polytetrafluoroethylene (Teflon)
C: vinylchloride → polyvinylchloride (PVC)
D: methylacrylate → polymethylacrylate
E: methylmethacrylate → polymethylmethacrylate
F: styrene → polystyrene

- The n in the polymers above is a large average number.
- The regiochemistry is uniform in the polymers from free radical chain polymerization.
  - Why?
Each sequential radical addition will favor regiochemistry that gives the most stable radical for thousands of sequential reactions.

- High concentration of the alkene favors the formation of polymer.
- Control of chain length is often a function of the polymer becoming insoluble and precipitating into an insoluble material.
- Processing involving heat and pressure make these materials into items with which you are familiar.