# 1.33: Radical Reactions

Homolytic Bond Cleavage -- Fishhook Symbols

Last time we looked at how the benzene ring changes the reactivity of an atom or group to which it is directly attached. Today we'll finish presenting new material in the course by taking a brief look at reactions in which bond making and bond breaking events involve electrons moving singly rather than as pairs. To put this in perspective, lets recall how we envisioned the breaking of a covalent bond in the reactions we've encountered so far. The dissociation of HCl into H^+ and Cl^- is an example.

$$H\!-\!Cl \longrightarrow H^{\oplus} \ + \ \ddot{\ddot{Cl}}^{\ominus}$$

Heterolytic Bond Cleavage
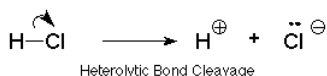
We interpreted this to mean that the shared electron pair which formed the covalent bond between the hydrogen and the chlorine atoms moved together to become an unshared electron pair on chlorine. This is often called a "heterolytic" bond cleavage since in the products the electron pair is distributed quite unevenly. We have used the curved arrow symbol to show the origin and the destination of electron pairs in these steps. The reaction mechanisms we have worked with so far have all involved making and breaking bonds by processes like this in which pairs of electrons move together.

Now let's look at a bond cleavage in which each partner in the bond takes one electron of the bonding electron pair. The dissociation of molecular chlorine (Cl_2) is a good example. This occurs when Cl_2 is heated strongly or when it is illuminated by bright light.

$$Cl\!-\!Cl \longrightarrow Cl\cdot \ + \ \cdot Cl$$
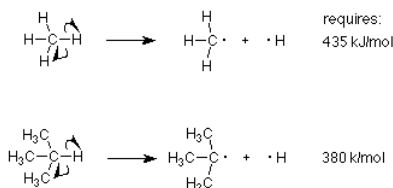
Homolytic Bond Cleavage
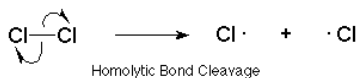
This is called "homolytic" bond cleavage since in the products the distribution of the electron pair is quite even. We use the "fishhook" (curved arrow with only one "barb" on the arrowhead) to show the motion of one electron. Such homolytic bond cleavages occur when the bond involved is not polar and there is no electrophile or nucleophile at hand to promote heterolytic patterns.

Bond Strength and Radical Energy

When a bond is made, the product has a lower energy than the reactants. It follows that breaking bonds requires energy. When the bond breaking process is homolytic there is no residual ionic attraction because there are no charges on the products, so the energy required to dissociate the bond is a good measure of how strong that bond is. Table 9.1 on page 237 of Atkins & Carey lists such "Bond Dissociation Energies."

A brief glance at this table shows us some interesting trends. First, all the halogen-halogen bonds (the Cl-Cl bond for example) are relatively weak. Carbon-carbon and carbon hydrogen bonds are stronger as are carbon-oxygen and hydrogen-oxygen bonds. Second, if we examine the trend in C-H bond dissociation energies as the structure of the alkyl group is changed, we notice that the strongest (435 kJ/mol) C-H bond is between the carbon of a methyl group and a hydrogen atom. The weakest (343 kJ/mol) is between the central carbon of a tertiary butyl group and a hydrogen atom.

$$\text{H}_3\text{C}\!-\!\text{C}\!-\!\text{H} \longrightarrow H\!-\!\overset{H}{\underset{H}{C}}\cdot \ + \ \cdot H \qquad \begin{array}{l}\text{requires:}\\ \text{435 kJ/mol}\end{array}$$

$$\text{H}_3\text{C}\!-\!\overset{H_3C}{\underset{H_3C}{C}}\!-\!H \longrightarrow \text{H}_3\text{C}\!-\!\overset{H_3C}{\underset{H_3C}{C}}\cdot \ + \ \cdot H \qquad \text{380 kJmol}$$

We can interpret this to mean that the tertiary butyl free radical is more stable than the methyl free radical. (The term "free radical" or "radical" is used to mean an atom or group in which one of the bonding orbitals is occupied by a single electron. Radicals are normally uncharged.) That would explain why it is easier to break the tertiary C-H bond than the methyl C-H bond; the products from breaking the tertiary C-H bond are more stable.

Looking at the structures which would be formed by breaking the C-H bonds which lie between the methyl-H bond and the tert-butyl-H bond we can see that we have a familiar pattern. Just like carbocations, the order of stability of carbon free radicals is:

tertiary > secondary > primary > methyl

We have seen that intermediates which are more stable are also those which are formed most rapidly and that this fact often dominates the composition of product mixtures. Recall that this idea was the basis for our explanation of Markovnikov's rule and of directive and activation/deactivation effects in electrophilic aromatic substitution. The more stable intermediate (carbocation in those cases) was formed faster. More reaction occured through the faster pathway so the product mixture was dominated by the product formed through the more stable intermediate. In the next section we will see how this idea can be used to understand some free radical reactions.

Radical Addition to Alkenes

We have made much of Markovnikov's rule. When we apply this rule to the addition of HBr to propene, we confidently predict that the product will be 2-bromopropane. It happens that occasionally considerable amounts of 1-bromopropane are formed. In fact it can happen that 1-bromopropane is the only product under some circumstances. This is puzzling and it tells us that something unusual is going on.

It took many experiments to pin down the details which control whether the reaction follows the Markovnikov pattern or the unusual course. It was eventually determined that the Markovnikov pattern is followed if the reagents are carefully purified just before they are used. The unusual pattern is followed if the reagents are "aged" before use. It was later learned that "aging" produces peroxides, compounds in which two alkyl groups or similar groups are joined through two oxygen atoms which share an O-O bond.
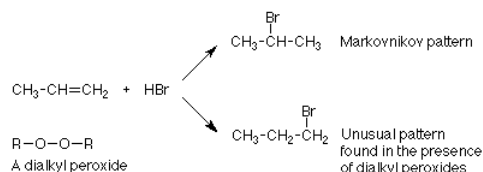

The O-O bond is weak (bond dissociation energy = 154 kJ/mol, much like the I-I bond) and it is non-polar so that we are not surprised that it breaks homolytically to give two oxygen free radicals.
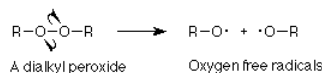

Next one of these oxygen free radicals reacts with HBr to give an alcohol (strong O-H bond) and a bromine atom radical.

These steps (called chain initiation steps for reasons we'll come to later) set the stage for the reaction with propene. The bromine atom radical can either attack propene's primary carbon to give a secondary free radical or propene's secondary carbon to give a primary free radical. We know that the secondary free radical is the lower energy intermediate and we know that reactions proceeding through lower energy intermediates are faster than those going through higher energy intermediates. We predict that attack of the bromine on the primary carbon to give the secondary free radical will be faster and the major product will be formed through this pathway.
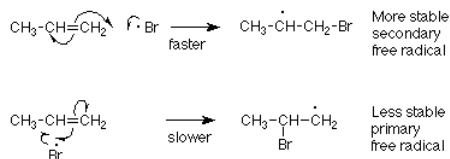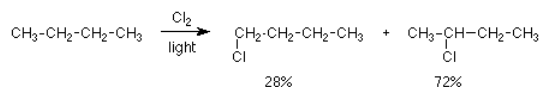

The reaction is completed when the secondary free radical reacts with another HBr molecule to produce the product -- 1-bromopropane -- and a new bromine atom.
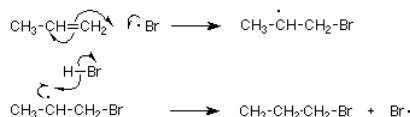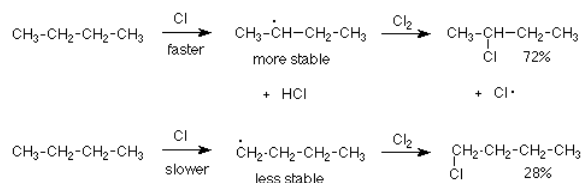
Notice that the second step regenerates a bromine atom which can begin a new cycle by attacking a fresh molecule of propene. The two steps together are called a chain reaction mechanism because a product of each one is a reactant of the other, creating a chain of events which stops when the reagents are used up. The sum of these two steps is an anti-Markovnikov addition of HBr to propene. While the outcome is different from the Markovnikov pattern we studied earlier, the underlying principle is the same: *We see the products of faster reactions, reactions which proceed by way of more stable intermediates.* In this instance the intermediates are free radicals and the secondary free radical is formed faster than the primary free radical. In the reactions which proceeded by way of carbocations (Markovnikov's rule) the more stable carbocation was formed.

Radical Substitution on Alkanes

There are also free radical mechanisms for substitution reactions of alkanes. These are of use for synthesis only in rather restricted cases, but the products we see are also controlled by competition in which the more stable intermediates are formed faster. An example is the chlorination of butane.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow[\text{light}]{Cl_2} \underset{28\%}{CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3} + \underset{72\%}{CH_3\text{-}CH\text{-}CH_2\text{-}CH_3}$$
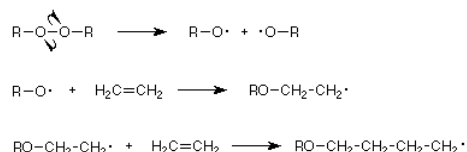
We see that a secondary hydrogen has been replaced by a chlorine more often than a primary hydrogen, even though there are six primary hydrogens and only four secondary hydrogens. This would make sense if the reaction mechanism went through a free radical, since we would expect a more stable secondary free radical to be formed faster (more often) than a less stable primary free radical. Such a mechanism would be:

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow[\text{faster}]{Cl} \underset{\text{more stable}}{CH_3\text{-}\overset{\cdot}{C}H\text{-}CH_2\text{-}CH_3} \xrightarrow{Cl_2} \underset{72\%}{CH_3\text{-}CH\text{-}CH_2\text{-}CH_3}$$
$$+ \ HCl \qquad\qquad + \ Cl\cdot$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \xrightarrow[\text{slower}]{Cl} \underset{\text{less stable}}{\overset{\cdot}{C}H_2\text{-}CH_2\text{-}CH_2\text{-}CH_3} \xrightarrow{Cl_2} \underset{28\%}{CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3}$$

Again the more abundant product is produced through the more stable (secondary) free radical rather than through the less stable (primary) free radical. Notice that this reaction is also a chain reaction, since the second step produces a chlorine atom which can react with another butane molecule to continue the chain. The reaction is initiated in this case by homolytic cleavage of the weak Cl-Cl bond by light to produce chlorine atoms.
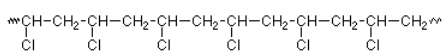
Radical Polymerization

Finally, let's return to another application of free radical additions to alkenes. We saw earlier that the HBr adds to alkenes through a peroxide initiated free radical chain mechanism to produce an anti-Markovnikov product. The key step in this reaction was the addition of a bromine atom radical to the alkene to give the more stable of the two possible free radicals. Suppose that there was no HBr present. Then a carbon free radical, once formed, would have to react with an alkene to make a new carbon-carbon bond. Here's an example where ethylene is the alkene.

$$R\text{-}O\text{-}O\text{-}R \longrightarrow R\text{-}O\cdot + \cdot O\text{-}R$$

$$R\text{-}O\cdot + H_2C=CH_2 \longrightarrow RO\text{-}CH_2\text{-}CH_2\cdot$$

$$RO\text{-}CH_2\text{-}CH_2\cdot + H_2C=CH_2 \longrightarrow RO\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\cdot$$
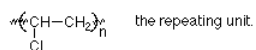
The new molecule would also be a free radical and could add to another molecule of ethylene. The product of that reaction would also be a free radical and could add to another molecule of ethylene, etc. The outcome is that the each reaction extends the growing chain by two carbons and produces a free radical intermediate at the end of the chain which can continue the reaction. In this way very long molecules are produced. These polymers such as polyethylene and polystyrene are produced in billion pound per year amounts and are very important commercial products.

Other polymerization reactions also are important, and Table 9.2 on p 251 of Atkins & Carey lists many of them. We can figure out the structure of the alkene from which the polymer was made by looking for the "repeating unit" in the polymer and thinking backwards to the alkene which was "added to" in making the polymer. Here's how it works for poly(vinyl chloride):
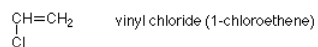
Poly(vinyl chloride)

~CH–CH₂-CH–CH₂-CH–CH₂-CH–CH₂-CH–CH₂-CH–CH₂~
    | | | | | |
    Cl   Cl   Cl   Cl   Cl   Cl

can be expressed as:

~(CH–CH₂)ₙ~   the repeating unit.
   |
   Cl

The monomer is:

CH=CH₂   vinyl chloride (1-chloroethene)
|
Cl

Since the repeating unit is formed by adding to each end of the double bond of the monomer, the structure of the monomer can be discovered by mentally cutting loose a repeating unit from the polymer and placing a double bond between its carbon atoms.

Contributors

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