

Chapter 11

Free Radical Substitution and Addition Reactions

from

Organic Chemistry

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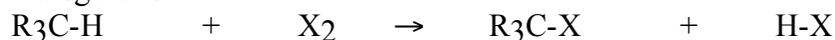
11: Free Radical Substitution and Addition Reactions

- *Free Radicals and Radical Reactions*
- *Halogenation of Alkanes with Br₂*
- *Alternate Bromination Sites*
- *Relative Reactivity of C-H Hydrogens*
- *Halogenation with Cl₂, F₂, or I₂*
- *Radical Additions to Alkenes*
- *Halogenation with Other Reagents (Appendix A)*
- *Halogen Atom Reactivity and Selectivity (Appendix B)*

11.1 Free Radicals and Free Radical Reactions

Many reactions in earlier chapters have ionic reagents and ionic intermediates. The reactions in this chapter involve electrically neutral **free radicals**. These reactions include **free radical halogenations of alkanes** and **free radical additions to alkenes**.

Alkane Halogenation



Alkene Addition



Some aspects of these reactions cause them to be more complex than ionic reactions. In order to address these details adequately without overwhelming this general presentation, we include some topics in "Asides" (in small font) in the chapter text, while some are in *Appendices* at the end of the chapter.

Free Radicals (11.1A)

Important *free radicals* that we see in this chapter include *halogen atoms* (X·), *alkoxy radicals* (RO·), and *carbon free radicals* (R₃C·).

Halogen Atoms. The atoms in column 7A (or 17) of a periodic table are the *halogen atoms*. Of these, *chlorine* (Cl) and *bromine* (Br) atoms are particularly important in the free radical reactions that we describe here. To clearly contrast them with *halide ions* (X⁻), organic chemists often write halogen atoms as X· where the (·) is an unshared electron.

As with all atoms, each halogen *atom* has the same number of electrons as it has protons and that is why it is electrically neutral. In contrast, halide *ions* (X^-) are negatively charged because each has one more *electron* than it has *protons* (Table 11.1).

Table 11.1. Comparison of Halogen Atoms ($X\cdot$) and Halide Ions (X^-).

$X\cdot$	<u>protons</u>	<u>electrons</u>	X^-	<u>protons</u>	<u>electrons</u>
F \cdot	9	9	F $^-$	9	<u>10</u>
Cl \cdot	17	17	Cl $^-$	17	<u>18</u>
Br \cdot	35	35	Br $^-$	35	<u>36</u>
I \cdot	53	53	I $^-$	53	<u>54</u>

We represent halide ions as X^- that shows the reactive unshared electron pair (e.g. see Chapter 7). We obtain the symbol $X\cdot$ for the neutral halogen atom by simply removing one electron with a -1 charge (an e^-) from X^- .

We can also visualize the meaning of $X\cdot$ by picturing its formation from its parent molecular halogen X_2 .



The covalent bond between the two halogen atoms ($X-X$) is an electron pair ($X:X$). When that bond breaks **homolytically** (undergoes **homolysis**), each halogen atom retains one of the two electrons in that bond.

Alternatively we can visualize the formation of the molecular halogens X_2 from individual halogen atoms.



Halogen atoms are highly reactive. They do not exist alone, but in molecules such as X_2 , $H-X$, or CH_3-X where they are bonded to other atoms. We will see at the end of this section why organic chemists also refer to halogen atoms as **free radicals**.

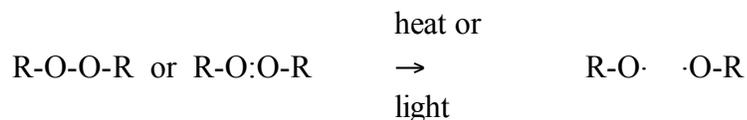
Alkoxy Radicals. Another free radical in this chapter is the *alkoxy* (or *alkoxyl*) radical ($RO\cdot$). We saw *alkoxide ions* (RO^-) in earlier chapters where they were nucleophiles and also strong bases. *Alkoxy radicals* ($RO\cdot$) are also highly reactive, but they are electrically neutral.

You can see that they are electrically neutral by imagining their formation from alkoxide ions by removal of one e^- [next page].



This is not a real reaction, but by showing that you can formally make $\text{RO}\cdot$ by removing an e^{-} from $\text{RO}^{-\cdot}$, the requirement that we keep charges equal on both sides of the equation shows that $\text{RO}\cdot$ must be electrically neutral.

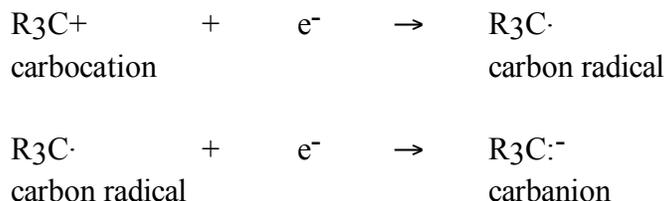
One way that chemists make *alkoxy radicals* is by decomposing organic peroxides (R-O-O-R).



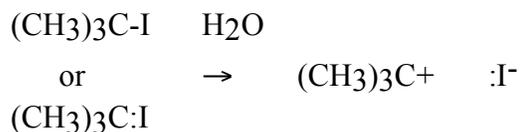
Organic peroxides are structurally analogous to hydrogen peroxide ($\text{H}_2\text{O}_2 = \text{H-O-O-H}$) where the Hs are replaced by alkyl groups (R).

Carbon Radicals. All organic reactions in this chapter include carbon radicals ($\text{R}_3\text{C}\cdot$). We represent them by showing the unshared electron (\cdot) to distinguish them from carbocations (R_3C^+) and carbanions (R_3C^{-}).

We can account for their neutral charge (absence of an electrical charge) by imagining their formation, or reaction, in the hypothetical reactions shown here.

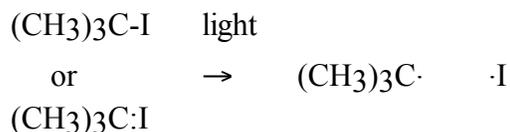


Let's look at some real reactions that illustrate why a carbon radical is neutral and symbolized as $\text{R}_3\text{C}\cdot$. In Chapter 7, we learned that 3° haloalkanes such as $(\text{CH}_3)_3\text{C-I}$ ionize in water.



The two electrons in the C-I bond go with the iodide ion causing it to become negative (see above) and leaving behind a positively charged carbocation ($(\text{CH}_3)_3\text{C}^+$).

In contrast, if we *irradiate* $(\text{CH}_3)_3\text{C-I}$ with light (when it is in a non-polar solvent) we make iodine atoms ($\text{I}\cdot$) and $(\text{CH}_3)_3\text{C}\cdot$ radicals.



The $\text{I}\cdot$ and $(\text{CH}_3)_3\text{C}\cdot$ each retain one electron of the two originally in the C-I bond. Each of those species is electrically neutral because each has an equal number of protons and electrons.

Counting Protons and Electrons. You can count up protons and electrons in $(\text{CH}_3)_3\text{C}\cdot$ and in $\text{I}\cdot$ in order to verify that each species is electrically neutral. But it is easier to simply recognize that since $\text{I}\cdot$ is electrically neutral (see Table 11.1), $(\text{CH}_3)_3\text{C}\cdot$ must also be electrically neutral since they both come from the electrically neutral molecule $(\text{CH}_3)_3\text{C-I}$.

Why Call Them "Radicals"? We can explain why $\text{R}_3\text{C}\cdot$ species are called *radicals* (or *free radicals*) by understanding that the symbol "R" that we have used so often is derived from the word "Radical". Early chemists referred to the organic parts of molecules as "Radicals" and wrote general examples of these molecules such as $\text{CH}_3\text{-OH}$, or $(\text{CH}_3)_3\text{C-I}$, as R-OH and R-I , respectively.

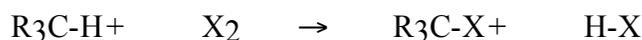
They called the CH_3 group in $\text{CH}_3\text{-OH}$ the "methyl radical", and the $(\text{CH}_3)_3\text{C}$ group in $(\text{CH}_3)_3\text{C-I}$ the "t-butyl radical". Using the general formula R-I for $(\text{CH}_3)_3\text{C-I}$, we can symbolize how light causes it to react to form $\text{I}\cdot$ as we show here.



When the R-I bond breaks, $\text{R}\cdot$ becomes a "free" radical ($\text{R}\cdot$). Now days, organic chemists reserve the terms "radical" or "free radical" to refer to neutral species such as $(\text{CH}_3)_3\text{C}\cdot$ and have extended those terms to include neutral species such as $\text{RO}\cdot$ and $\text{X}\cdot$.

11.2 Halogenation of Alkanes with Br_2

Free radical halogenation reactions of alkanes and cycloalkanes are *substitution* reactions in which a C-H is converted to a C-X.



While any of the molecular halogens F_2 , Cl_2 , Br_2 , and I_2 will halogenate alkanes and cycloalkanes, Br_2 or Cl_2 are used most often. We will use bromination ($\text{X} = \text{Br}$) to illustrate alkane

halogenation. We discuss chlorination with Cl_2 , and possible halogenation using the other molecular halogens in later sections.

Bromination of Ethane (11.2A)

We describe the general mechanism of alkane halogenation using bromination of ethane (CH_3CH_3) to give bromoethane ($\text{CH}_3\text{CH}_2\text{Br}$).

Figure 11.01

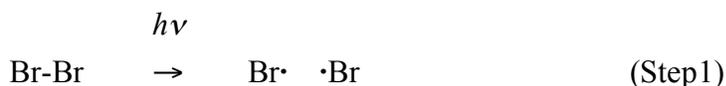


The Symbol $h\nu$. This reaction occurs when we **irradiate** a mixture of ethane and Br_2 , either as gases or in a solvent, with ultraviolet (UV) or visible light. The symbol $h\nu$ represents UV or visible light energy since the energy (E) of light is proportional to its frequency (ν) ($E = h\nu$) (Chapter 5). We call this reaction a **photochemical reaction** because it is initiated by light, but we will also see many radical reactions that are not photochemical reactions.

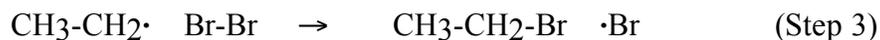
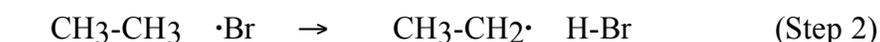
Mechanism. The overall reaction for photochemical bromination of ethane includes several separate steps. We will group the first three of these steps (Figure 11.02 [next page]) into two categories called **initiation** and **propagation**. In order to emphasize that these species are electrically neutral, we have omitted the traditional "+" signs used in chemical reactions.

Figure 11.02. Initiation and Propagation Steps for Bromination of Ethane.

Initiation

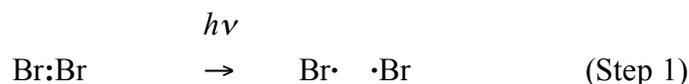


Propagation



It is important for you to note that the two products of ethane bromination, ($\text{CH}_3\text{-CH}_2\text{-Br}$ and H-Br) (Figure 11.01), are formed in different reaction steps. H-Br is formed in *Step 2* of this three step sequence, while $\text{CH}_3\text{-CH}_2\text{-Br}$ is formed in *Step 3* of the same sequence. We will see that this a characteristic of all chain reactions is that reaction products are formed in different steps.

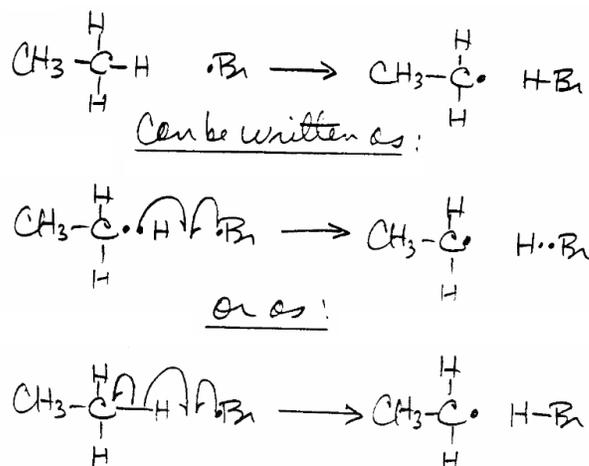
Initiation Step. In Step 1, light energy breaks the Br-Br bond giving two separate bromine atoms (Br·). As we described in the previous section, the "dot" (·) written with each Br represents one of the two electrons that originally constituted the chemical bond between the two bromine atoms in Br-Br.



For the sake of clarity, we do not show the other 3 unshared pairs of electrons on each Br·. We call this type of bond breaking reaction, where a bonding electron pair divides equally between previously attached atoms, **homolytic scission** or **homolytic cleavage**.

Propagation Steps. Each Br· formed in Step 1 (Figure 11.02) has the ability to **abstract** (remove) an H from ethane. We show this in Step 2 of Figure 11.03a, where Br· removes an H along with one of the electrons in the C-H bond. H-Br forms in Step 2 and leaves behind a reactive molecular fragment (CH₃-CH₂·) called an **ethyl radical** (CH₃CH₂·) (Figure 11.03a).

Figure 11.03a



Arrows in Radical Reactions. We show this **abstraction** of an H by Br· in two different ways in Figure 11.03a. In the first reaction, we use curved arrows to portray the way that the electrons in the C-H and C-Br bonds move as the C-H bond breaks and the H-Br bond forms. These curved arrows begin at an electron and point to where the electron ends up in the product of the chemical process.

The second reaction in Figure 11.03a is the same process as the first reaction. While we do not show the individual electrons in the C-H and C-Br bonds, we do use the arrows to represent the movement of the electrons.

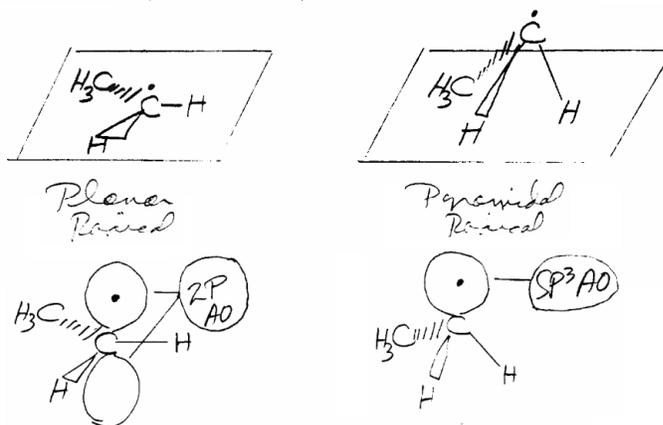
It is important to note that these curved arrows shown in Figure 11.03a have only one-half (1/2) of an arrowhead. Organic chemists use such "half-arrowhead" arrows to show the movement of single electrons.

Curved arrows with full arrowheads show the movement of a pair of electrons (two electrons) in a chemical process as we showed in earlier chapters

The $\text{CH}_3\text{-CH}_2$ Radical. The ethyl radical ($\text{CH}_3\text{-CH}_2\cdot$) shown above is a neutral (uncharged) chemical species that forms when $\text{Br}\cdot$ removes (abstracts) a neutral H atom from a neutral ethane molecule. Its geometry might be either *planar* or *pyramidal (tetrahedral)* (Figure 11.03b).

Figure 11.03b

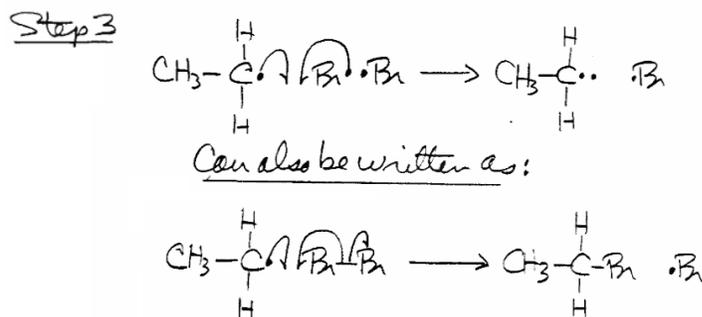
Planar and Pyramidal Shapes of the Ethyl Radical.



If it is *pyramidal*, the C \cdot atom is sp^3 hybridized (Chapter 1) and the single unpaired electron is in an sp^3 orbital. If it is *planar*, the C \cdot atom is sp^2 hybridized (Chapter 1) and the single unpaired electron is in a 2p atomic orbital perpendicular to the plane containing the C-H and C-C bonds. Experimental results and calculations indicate that alkyl radicals generally prefer to be *planar*.

The ethyl radical, like most alkyl radicals, is very reactive because of its unshared electron. Alkyl radicals rapidly react with other molecules or other radicals that provide another electron to form a chemical bond. During ethane bromination, the ethyl radical reacts primarily with molecular bromine (Br_2) by abstracting a Br to form a C-Br bond (Step 3, Figure 11.02). We provide more details for that reaction in Figure 11.04 using the curved "half-arrowhead" arrows that are sometimes used to show the movement of electrons in radical reactions.

Figure 11.04



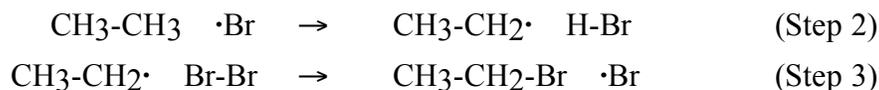
A Comment About Radicals. If you have already studied Chapter 5 (Organic Spectrometry), then you should note that this ethyl radical, formed as an intermediate in bromination of ethane, is identical to ethyl radicals formed in the mass spectral fragmentation reactions of alkanes such as butane, pentane, hexane, *etc.* that we described in that chapter.

Radical Chain Reactions (11.2B)

Free radical alkane halogenation reactions are **chain reactions**.

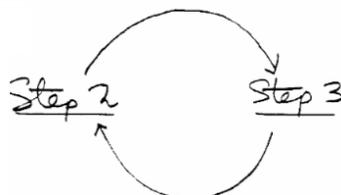
Propagation Steps Repeat. The Br· that forms in Step 3 (see below) reacts with another ethane molecule in Step 2 (see below) and the resulting ethyl radical reacts with a new Br₂ in Step 3 to once again form Br·.

Propagation



This cycle of "Step 2 followed by Step 3" repeats many times giving high yields of the product CH₃CH₂Br from Step 3, and the product HBr from Step 2 (Figure 11.05).

Figure 11.05



Since free radicals are intermediates in each of Steps 2 and 3, and because these two steps seem to form a continuous reaction "chain", we call the bromination of ethane a **radical chain reaction**.

We call Steps 2 and 3 *propagation* reactions because in each of them, one radical species generates another radical keeping the "chain" alive. For example, Br· reacts with ethane to give CH₃-CH₂· in Step 2, while CH₃-CH₂· reacts with Br₂ to regenerate Br· in Step 3.

Many Chains Occur Simultaneously. We call homolytic decomposition of Br₂ into Br· atoms (Step 1, Figure 11.02) an *initiation* reaction because it gives the radicals that start the "chains". When we irradiate the reaction mixture, many Br₂ molecules simultaneously undergo homolytic scission into Br· atoms (although this represents only a small fraction of the Br₂

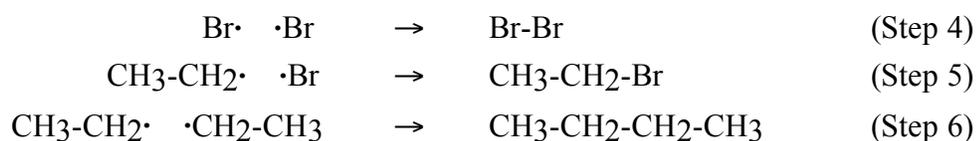
molecules that are present). Br₂ continues to decompose by Step 1 as long as the reaction mixture is irradiated with light. As a result, many Br· are produced at the same time, so many "chains" of Steps 2 and 3 start at the same time in the reaction flask.

Termination Reactions (11.2C)

Since there are many radicals present at the same time, these radicals formed in *initiation* or in *propagation* reactions (Figure 11.02) sometimes react with each other instead of reacting in the *propagation* steps. These reactions between two radicals lead to **combination** or **disproportionation** reactions that we collectively call **termination** reactions.

Combination Reactions. Br· atoms and CH₃CH₂· radicals can **combine** with each other in the 3 ways shown in Figure 11.06.

Figure 11.06. Termination Combination Reactions in Bromination of Ethane.

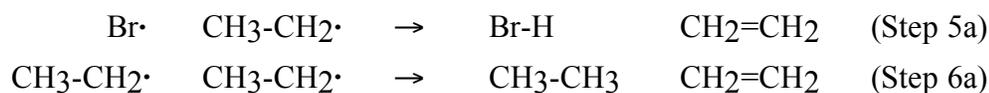


If two Br· radicals encounter each other they can combine to form Br₂ (Step 4). Similarly, if a Br· encounters a CH₃CH₂· they can also combine (Step 5). Finally, two ethyl radicals (CH₃CH₂·) sometimes encounter each other and combine to give **butane**.

Comment About Butane. We do not show *butane* as a reaction product in the overall reaction for ethane bromination (Figure 11.01) because this combination reaction occurs so infrequently compared to the propagation reactions that *butane* is only formed in very low yield. We comment on this further in an "Aside" at the end of this section.

Disproportionation Reactions. Besides undergoing *combination* reactions, two radicals sometimes react by **disproportionation** as we show for CH₃-CH₂· and Br· radicals in Figure 11.07.

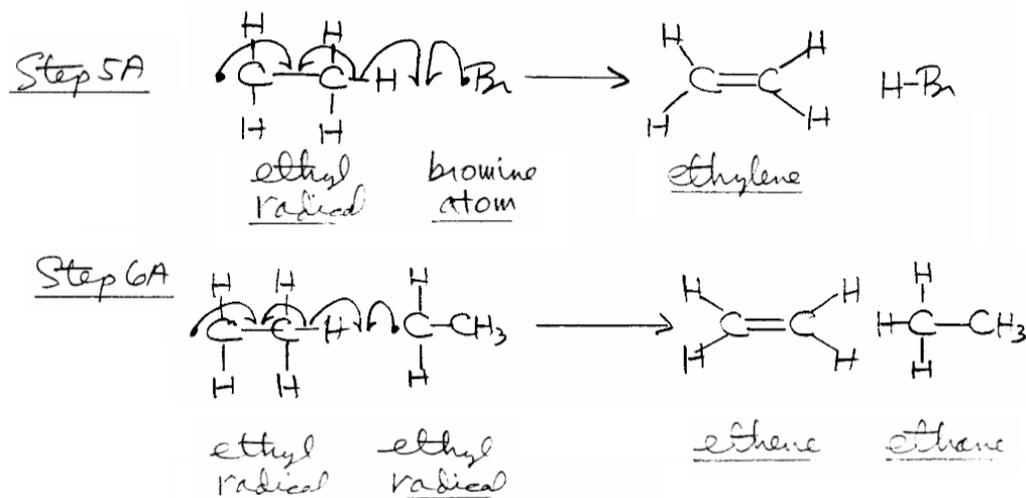
Figure 11.07. Termination Disproportionation Reactions in Bromination of Ethane.



In these *disproportionation* reactions, a radical (Br· or CH₃CH₂·) abstracts a hydrogen atom from

an ethyl radical ($\text{CH}_3\text{CH}_2\cdot$) as we show in Figure 11.08 using curved arrows.

Figure 11.08



In Step 5a, the $\text{Br}\cdot$ that abstracts H becomes H-Br while the $\text{CH}_3\text{-CH}_2\cdot$ that loses the H becomes *ethene* ($\text{CH}_2=\text{CH}_2$). In Step 6a, an ethyl radical ($\text{CH}_3\text{-CH}_2\cdot$) abstracts an H from another $\text{CH}_3\text{-CH}_2\cdot$ giving *ethane* and *ethene*.

Termination Reaction Products. The combination reactions involving $\text{Br}\cdot$ (Step 4 and Step 5) are chemically "invisible" because Step 4 forms Br_2 that is one of the starting materials, while Step 5 leads to bromoethane ($\text{CH}_3\text{CH}_2\text{Br}$) that is one of the reaction products. But this is not the case for some of the other termination products.

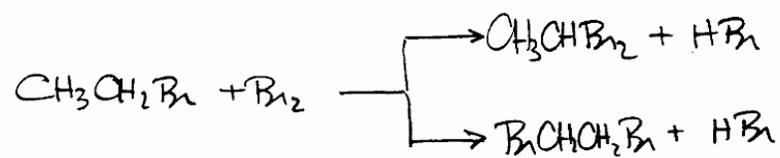
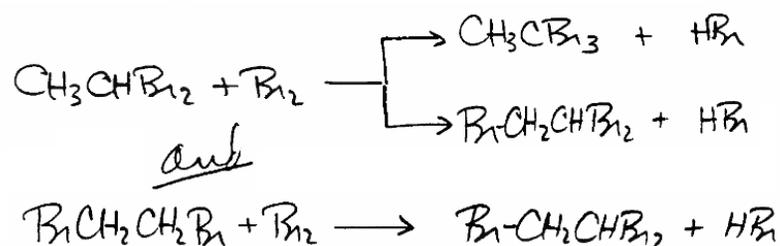
For example, we did not show the termination reaction products from Steps 5a and 6a (*ethene*, *ethane*, and *butane*) in the overall reaction for bromination of ethane (Figure 11.01). Ethane is the starting material, so its formation in a termination reaction is invisible. However, *butane* and *ethene* are undesired side products. We ignore them because their yields are very low compared to that of the desired organic product bromoethane ($\text{CH}_3\text{CH}_2\text{Br}$). The propagation steps (Steps 2 and 3 in Figure 11.02) leading to bromoethane occur many times before Step 5a and/or 6a occurs.

Because two radicals that react with each other can no longer propagate chains (Steps 2 and 3), all three of these **combination** reactions are called **termination reactions**. Each *termination reaction* stops two chains.

Polybromination (11.2D)

A disadvantage of radical halogenation reactions, such as bromination of ethane, is that the desired product (in this case $\text{CH}_3\text{CH}_2\text{Br}$) may be further brominated. The 5 H's that remain on bromoethane ($\text{CH}_3\text{CH}_2\text{Br}$) are reactive toward $\text{Br}\cdot$ like those on ethane. As a result, it is difficult to prevent the bromination of bromoethane to give *dibromoethanes* (Figure 11.09)[next page].

Figure 11.09

Formation of DibromoethanesFormation of Tribromoethanes

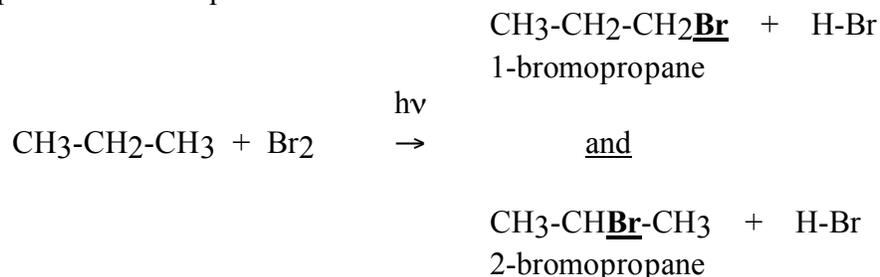
These *dibromoethanes* in turn may undergo further bromination to *tribromoethanes*. Ultimately the products can also include *tetrabromoethanes*, *pentabromoethane*, or *hexabromoethane*.

Minimizing Polybromination. While we cannot prevent the formation of these **polybromoalkanes**, we can minimize them by using a large excess of the alkane reactant compared to Br_2 . We can also minimize *polybromination* by permitting the monobromination reaction to proceed only partly to completion.

Each of these strategies causes the unreacted alkane to have a higher concentration than that of the bromoalkane product. As a result, bromine atoms in the reaction mixture encounter and react with unreacted ethane molecules much more frequently than with bromoethane molecules that are present in much lower concentration.

11.3 Alternate Bromination Sites

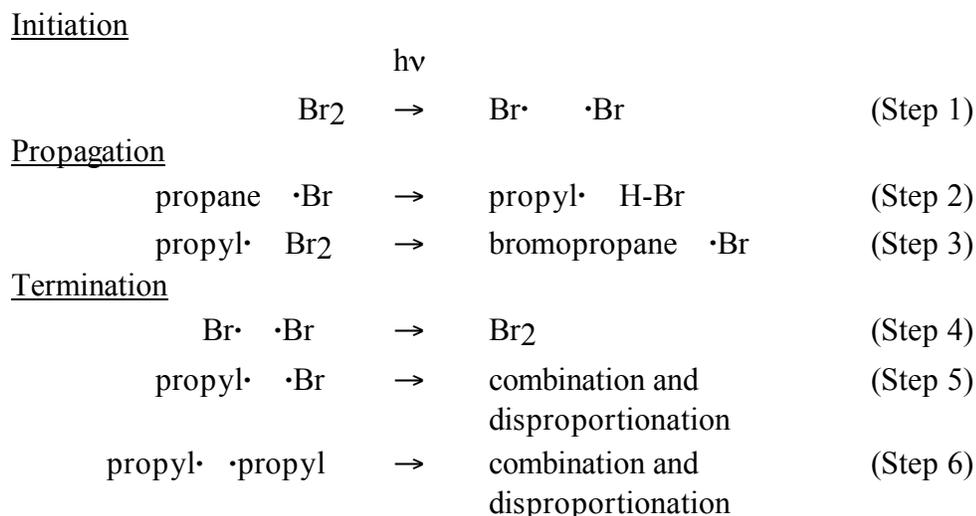
All 6 H's on ethane (CH_3CH_3) are chemically equivalent so abstraction of any of them gives only bromoethane. However, this is not true for most other alkanes. For example, propane has two different types of H's and its bromination simultaneously gives both 1-bromo-propane and 2-bromopropane as reaction products.



General Mechanism for Propane Bromination (11.3A)

The reaction mechanisms for formation of 1-bromopropane and 2-bromopropane from bromination of propane are analogous to that for bromination of ethane (Figure 11.10).

Figure 11.10. General Mechanism for Formation of Monobromopropane Products from Bromination of Propane.



We will not distinguish between the two types of H's in propane, nor the different pathways to formation of 1- or 2-bromopropane, in this figure so that you can see its similarity to ethane bromination (Figures 11.1 and 11.6). This mechanism has *initiation*, *propagation* and *termination* steps like those for ethane bromination.

The *initiation* step (Step 1) is identical to that for ethane bromination Figure 11.02. In the first *propagation* step (Step 2), a $\text{Br}\cdot$ from Step 1 reacts with a *propane* molecule to give a *propyl* radical and H-Br. The *propyl* radical reacts with Br_2 in the second *propagation* step (Step 3) to give a molecule of *bromopropane* and $\text{Br}\cdot$. That $\text{Br}\cdot$ reacts with another molecule of *propane* by repeating Step 2. *Termination* steps include *combination* of two $\text{Br}\cdot$ to give Br_2 , reaction of a $\text{Br}\cdot$ and a *propyl* radical by *combination* or *disproportionation*, and *combination* or *disproportionation* of two *propyl* radicals.

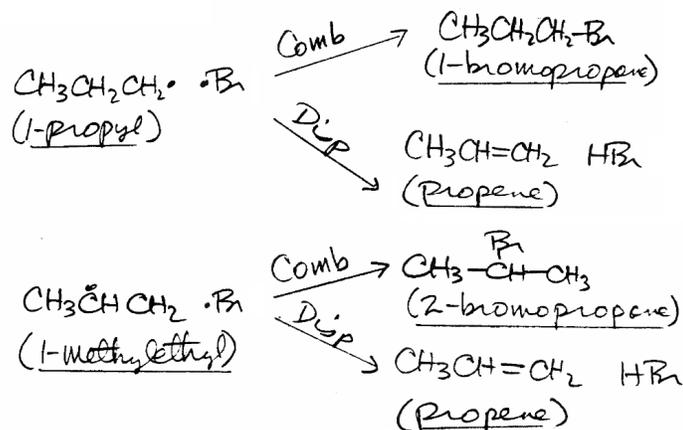
Origins of 1-Bromopropane and 2-Bromopropane (11.3B)

1-bromopropane and 2-bromopropane form at the same time in this reaction because each $\text{Br}\cdot$ has the choice to abstract two different types of H atoms from propane.

The Various Termination Reactions. The termination/combination reactions (Step 5 in Figure 11.10) give both *1-bromopropane* as and *2-bromopropane*.

Figure 11.13

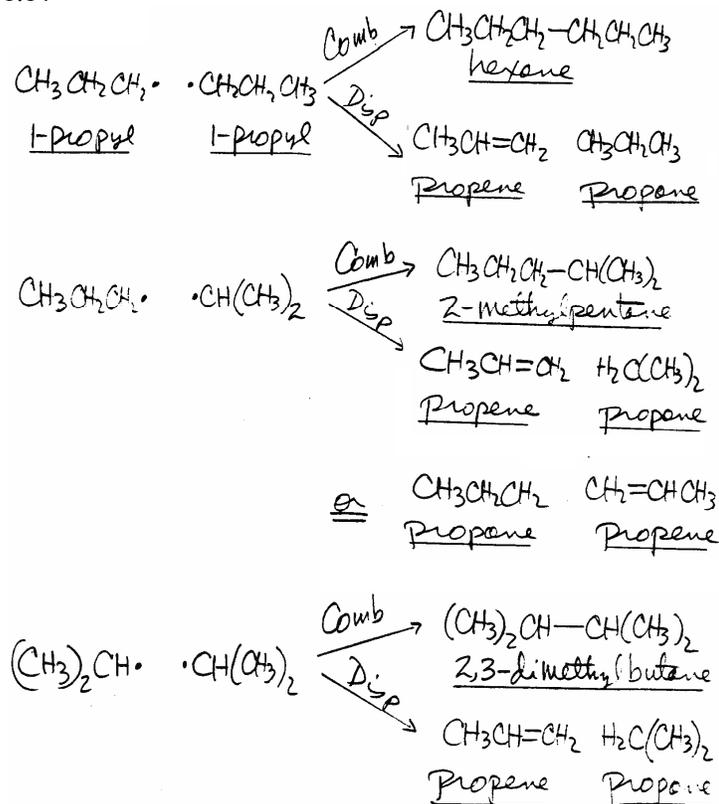
Termination Reactions Between Propyl Radicals and Br·



In the *disproportionation* reactions (Step 5 in Figure 11.10) Br· abstracts an H from either of the two different alkyl radicals to give propene and H-Br. These reactions are analogous to the *disproportionation* reaction between Br· and ethyl radical that gives ethene (Step 5A, Figure 11.07).

Termination reactions between propyl radicals (Step 6 in Figure 11.10) include several *combination* and *disproportionation* reactions analogous to those for ethyl radicals in Figures 11.06 and 11.07.

Figure 11.14



The *combination* products of Step 6 are hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$), 2-methylpentane ($(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3$) or 2,3-dimethylbutane ($(\text{CH}_3)_2\text{CH}-\text{CH}(\text{CH}_3)_2$). The *disproportionation* reactions give only propene ($\text{CH}_3\text{CH}=\text{CH}_2$) and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). As was the case with ethane bromination, the yields of these side products are much lower than those of the desired products 1-bromopropane and 2-bromopropane.

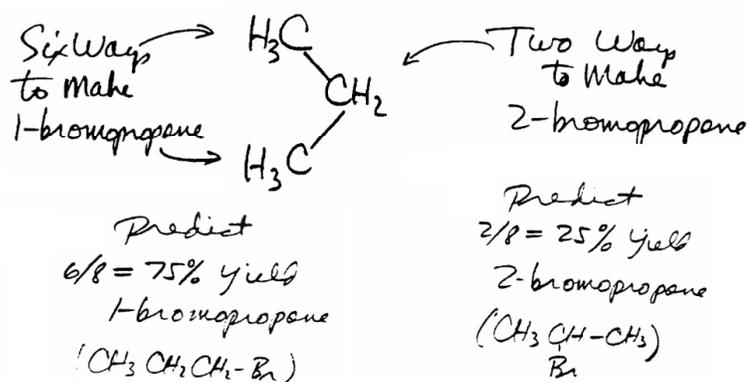
Polybromination. The products 1-bromopropane and 2-bromopropane can be further brominated to give a variety of polybromopropanes as we described in Section 11.2 for polybromination of ethane. We can minimize formation of polybrominated compounds using the same strategies that we described for ethane bromination.

Relative Yields of 1-Bromopropane and 2-Bromopropane (11.3C)

The yields of 1-bromopropane and 2-bromopropane are not the same. At 150° , the relative yield of 1-bromopropane is 8% of the monobrominated products, while 2-bromopropane has a 92% relative yield. This result is surprising since if all H's on propane were equally reactive to Br, the relative yield of 1-bromopropane should be 75%, and that of 2-bromopropane should be 25%.

Figure 11.15

Different Ways to Make 1-Bromopropane and 2-Bromopropane by Bromination of Propane.



This is because 6 of the 8 H's (75% of the H's) on propane are on CH_3 groups whose abstraction leads to 1-bromopropane. In contrast, only 2 of the 8 H's (25% of the H's) are on the CH_2 group whose abstraction leads to 2-bromopropane.

The much greater yield of 2-bromopropane (92%) compared to 1-bromopropane (8%) occurs because an H on the CH_2 group of propane is more reactive than an H on either of the CH_3 groups. We describe this reactivity difference, and its origin, in the following section.

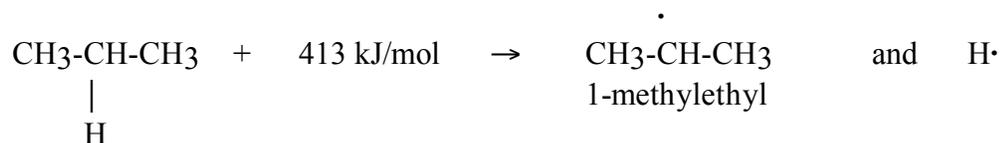
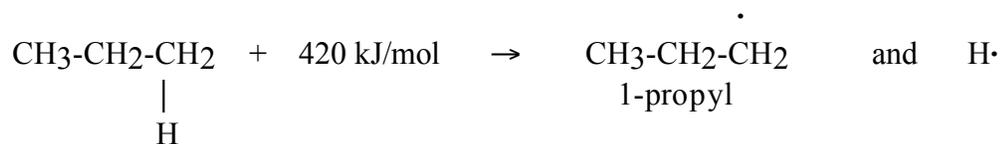
11.4 Relative Reactivity of C-H Hydrogens

The relative product yields in free radical alkane halogenation reactions depend not only on the numbers of H's available for abstraction, but also on the relative strengths of their C-H bonds.

C-H Bond Strengths (11.4A)

The H's on the CH₂ group of propane are more reactive than those on the CH₃ groups because of differences in the relative **bond strengths** of these C-H bonds.

Bond Strengths. C-H *bond strengths* are the amount of energy required to break the indicated C-H bond to give the corresponding carbon radical and H•.



While these specific reactions do not occur during bromination of propane, the lower bond strength of the CH₂ bonds compared to the CH₃ bonds, tells us that it is easier for Br• to abstract an H from CH₂ than from CH₃. We see this direct correlation between C-H *bond strength* and C-H *reactivity* in bromination of alkanes when we examine product distributions in alkane bromination.

C-H Bond Strength and Alkane Structure. Alkane C-H bond strengths (Table 11.2) generally decrease in the order CH₃-H > RCH₂-H > R₂CH-H > R₃C-H (Table 11.2 [next page]). While there is only one example for R₃C-H, the two examples for R₂CH-H, and three examples for RCH₂-H, show that the same trends apply to different alkyl groups (R).

Table 11.2. Approximate Bond Strengths for Various C-H Bonds in Alkanes

C-H Bond Type	Compound	Bond Strength (kJ/mol)
CH ₃ -H (methyl)	CH ₃ -H	438
RCH ₂ -H (1°)	CH ₃ CH ₂ -H	423
	CH ₃ CH ₂ CH ₂ -H	420
	(CH ₃) ₃ CCH ₂ -H	420
R ₂ CH-H (2°)	(CH ₃) ₂ CH-H	413
	(CH ₃ CH ₂)(CH ₃)CH-H	411
R ₃ C-H (3°)	(CH ₃) ₃ C-H	404

When one alkyl group (R) replaces an H on CH₄, we call the 3 remaining H's on RCH₃ **primary (1°)** H's. Similarly, the 2 H's on R₂CH₂ are **secondary (2°)** C-H's, while the single H on R₃C-H is a **tertiary (3°)** C-H. You can see that 1°, 2°, and 3° are "numbers" that directly reflect the number of R groups substituted for H's on CH₄ and that the trend in *C-H bond strength* is *methyl* > 1° > 2° > 3°.

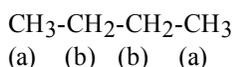
Table 11.2 includes the two different types of C-H bonds in propane that we mentioned earlier (Figure 11.15). The more reactive C-H's on propane's CH₂ group (shown as (CH₃)₂CH-H in Table 11.2) are *secondary (2°)* C-H's, while the less reactive C-H's on propane's CH₃ groups (shown as CH₃CH₂CH₂-H) are *primary (1°)* C-H's.

The C-H reactivity trend is 2° > 1° opposite to the trend in C-H bond strengths that is 1° > 2°. We can extend this correlation for propane bromination to other alkanes as we describe in the next section.

Example

Q: According to the data in Table 11.2, the bond strength for the indicated C-H bond in (CH₃CH₂)(CH₃)CH-H is 411 kJ/mol. Predict the approximate bond strengths for all of the other types of C-H bonds in this compound.

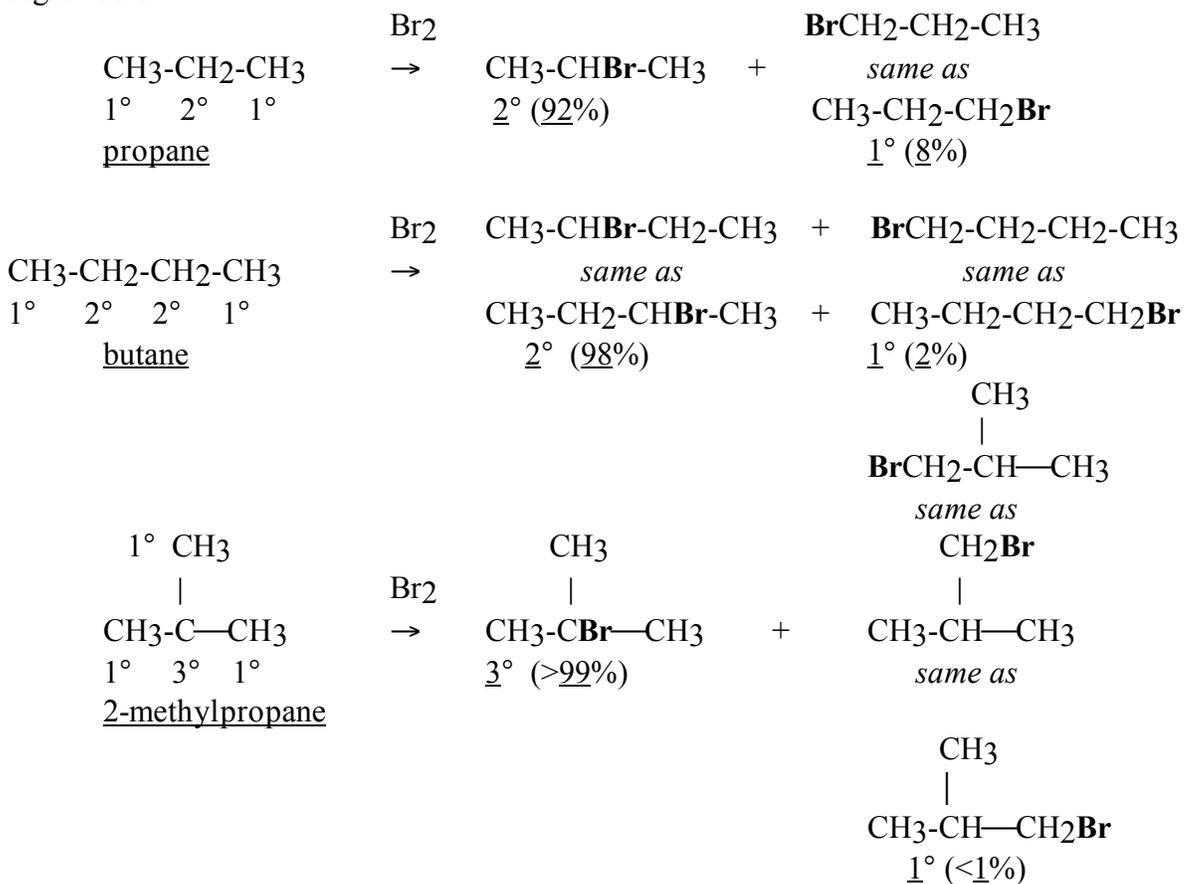
A: The structure of the compound showing all of the different types of H's is



The compound has only two different types of H's, those labelled (a) and (b). Each of the H's labelled (b) corresponds to the indicated C-H and has the bond strength of 411 kJ/mol. The bond strengths of the H's labelled (a) can be approximated by those on the CH₃ group on propane (CH₃CH₂CH₂-H) which are given as 420 kJ/mol in Table 11.2.

Relative Reactivities of C-H's. The *relative reactivity order* of alkane C-H bonds in all radical bromination reactions is R₃C-H > R₂CH-H > RCH₂-H > CH₄, and this is exactly opposite the C-H bond strength order shown in Table 11.2. We show relative product yields for bromination of three different alkanes in Figure 11.16 [next page] that confirm this reactivity order. These include bromination of *propane*, of *butane*, and of *2-methylpropane* under comparable reaction conditions.

Figure 11.16



These and other experimental results for alkane bromination reactions lead to **average relative reactivity values** (Table 11.3) for alkane C-H bonds.

Table 11.3. Relative Reactivities for C-H Abstraction by Br· (150°)

Type of C-H Bond	Relative Reactivity (reaction with Br·)
CH ₃ -H (methyl)	1
RCH ₂ -H (1°)	500
R ₂ CH-H (2°)	40,000
R ₃ C-H (3°)	850,000

Relative Reactivity Values. Each relative reactivity value is the average rate of bromination of a one H of the type shown, divided by the rate of bromination of one H of methane (CH₃-H) under the same conditions (150°). This means that the average rate of bromination of one H of the type RCH₂-H is approximately 500 times greater than the rate of bromination of one H on methane (CH₄ or CH₃-H).

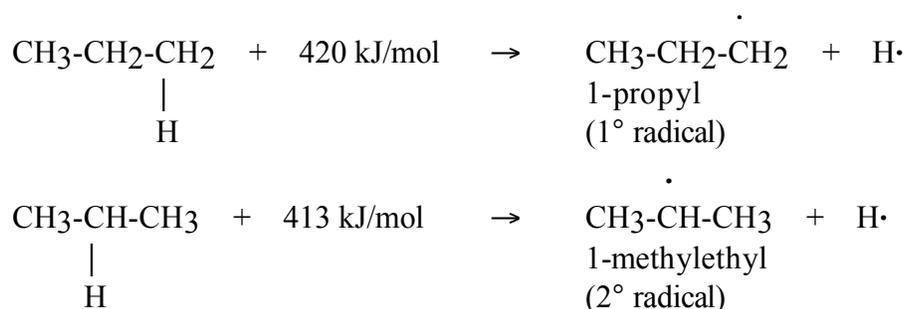
Similarly, compared to one H of methane, the average bromination rate of one H of the type R₂CH-H is approximately 40,000 times faster, while the average bromination rate of one H of the type R₃C-H is

about 850,000 times faster. These relative rates (reactivities) clearly show the reactivity order $R_3C-H > R_2CH-H > RCH_2-H > CH_3-H$ that we also describe as $3^\circ C-H > 2^\circ C-H > 1^\circ C-H > \text{methyl } C-H$.

Radical Stability (11.4B)

The C-H bond strengths in Table 11.2 also reflect the relative stabilities of the alkyl radicals ($R\cdot$) that form when a $Br\cdot$ abstracts an H from a particular C-H bond in an alkane. We explain this using the two different C-H bonds of propane as our example.

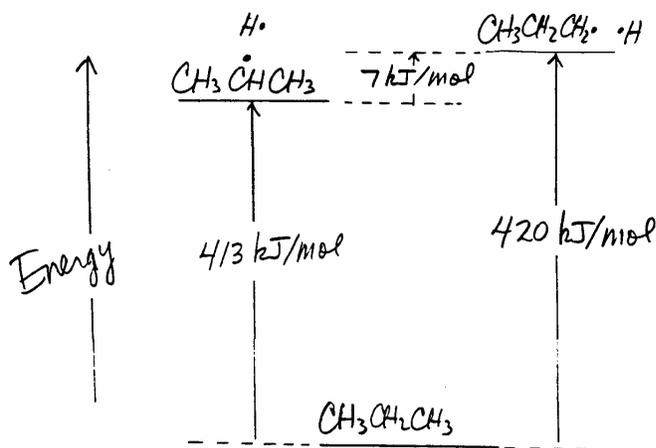
Relative Stabilities of Alkyl Radicals. The C-H bond strengths (**bond dissociation energies**) (Table 11.2) for the two types of C-H bonds in propane are the energies required to cleave those bonds into alkyl radicals and H atoms.



Both equations have propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) as the reactant, and both produce $\text{H}\cdot$, so the difference in their *bond dissociation energies* of 7 kJ/mole ($420 \text{ kJ/mole} - 413 \text{ kJ/mole}$) is the difference in the stabilities of the two different alkyl radicals. Since it takes more energy to make the 1-propyl radical than the 1-methylethyl radical, the 1-propyl radical must be less stable (have a higher energy) than the 1-methylethyl radical (Figure 11.17).

Figure 11.17

Energy Diagrams Showing the Relative Energies of 1-Propyl and 1-Methylethyl Radicals Formed from Propane.

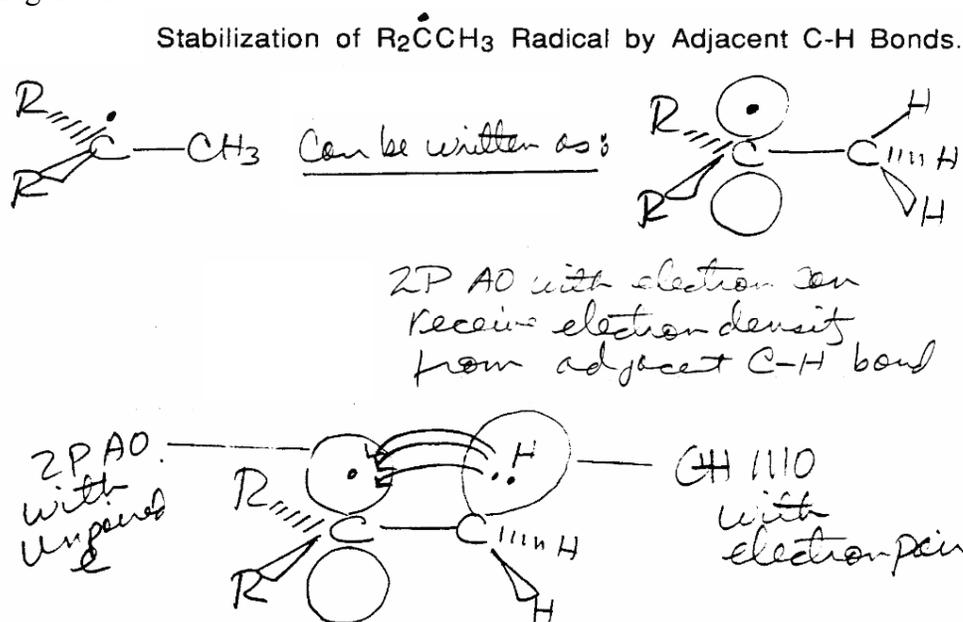


The 1-propyl radical forms from cleavage of a 1° C-H bond, so we call it a **1° radical**. The 1-methylethyl radical is a **2° radical** because it forms by cleavage of a 2° C-H bond. Based on the results in Figures 11.16 and 11.17, we can conclude that 2° radicals are more stable than 1° radicals and this is true for a wide variety of alkanes.

The 1° C-H bond strengths (bond dissociation energies) are all about the same and greater than those for 2° C-H bonds (Table 11.2). These in turn are greater than that shown for the 3° C-H bond. As a result, we can generalize that the order for relative stabilities of simple alkyl radicals is $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\cdot$.

Origin of Radical Stability Order. The radical stability order suggests that the radical center (C \cdot) is stabilized by substitution of one or more R groups for H's on the C \cdot center. An explanation is that the atomic orbital on C containing the unpaired electron overlaps with molecular orbitals of adjacent C-H bonds (Figure 11.18) stabilizing the substituted radical.

Figure 11.18



We show the radical as a planar species with its unpaired electron in a 2p orbital. When we increase the number of alkyl groups bonded to the C \cdot center, we increase the possibilities for this favorable C-H MO overlap with the 2p AO containing the unshared electron. This stability order for radicals parallels that we described for carbocations (R_3C^+) in Chapter 7.

C-H Bond Dissociation Energies in Cycloalkanes. We show the C-H bond dissociation energies for unsubstituted cycloalkanes in Table 11.4 [next page].

Table 11.4. Approximate Bond Dissociation Energies for Various C-H Bonds in Cycloalkanes

Type	Compound	Bond Dissociation Energy (kJ/mol)
-CH ₂ - (2°)	cyclopropane	445
	cyclobutane	404
	cyclopentane	404
	cyclohexane	400

While all of these cycloalkane C-H bonds are 2°, the C-H bond dissociation energy for cyclopropane is much higher than any of the values for acyclic C-H bonds (Table 11.2). In contrast, the others are about the same as those for 3° acyclic C-H bonds.

The high value for cyclopropane probably reflects:

- (1) the significant increase in the C-C-C angle, due to the change in hybridization of the C-H carbon atom, that occurs when the H is removed,
- (2) the larger amount of s character in cyclopropane C-H bonds compared to the other cycloalkane C-H bonds.

The C-C-C bond angles in cyclopropane are constrained to be 60°, so the amount of 2s and 2p character in the ring C's is not the same as for normal tetrahedral C. Rather than being described as sp³ hybridized, the ring C's of cyclopropane are better described as s^{1.2}p^{2.8}. This means that there is about 30% s and 70% p character in the cyclopropane ring C atoms rather than the 25% s and 75% p character that is present in a normal sp³ hybridized C.

The relatively low bond dissociation energies for the larger ring systems probably reflect a combination of effects. These include relief in both torsional and steric interactions (eg. 1,3-nonbonded interactions) associated with the change in hybridization from sp³ to sp². In addition, these larger rings can more easily accommodate the increase in C-C-C angle associated with this change in hybridization than is the case for cyclopropane. Finally, the adjacent CH₂ MO's in these larger rings are able to stabilize the C· center by C-H electron donation while this is unlikely for geometric reasons in cyclopropane.

11.5 Alkane Halogenation with Cl₂, F₂, or I₂

We have used free radical *bromination* of alkanes to illustrate characteristics of free radical reactions and intermediate carbon free radicals. We can apply this knowledge to alkane halogenation reactions with molecular halogens (X₂) other than Br₂.

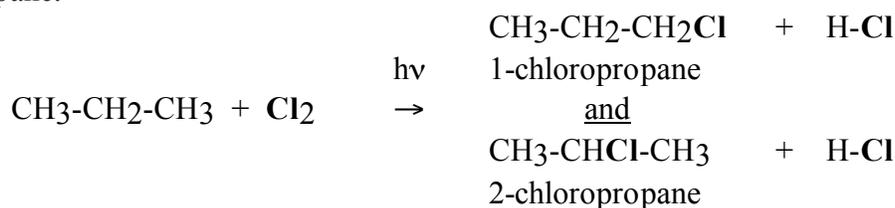
Chlorination (11.5A)

The reactions and mechanisms for **chlorination** (X₂ = Cl₂) of alkanes and cycloalkanes are entirely analogous to those for bromination.

General. If we replace Br by Cl in every *bromination* reaction and mechanism that we have presented, we obtain the corresponding reaction and mechanism for alkane *chlorination*. The

relative stabilities of the alkyl radicals formed in these reactions, and the C-H bond strengths in the alkanes and cycloalkanes, are completely independent of whether the halogenation reaction is *bromination* or *chlorination*. However the *relative yields* of the various *chloroalkanes* formed in a *chlorination* reaction are much different than the *relative yields* of the *bromoalkanes* formed in a *bromination* reaction on the same alkane.

Relative Product Yields in Chlorination and Bromination. When we chlorinate propane using Cl_2 , we obtain the expected monochlorinated products 1-chloropropane and 2-chloropropane.



However, the relative yields of 1-chloropropane (43%) and 2-chloro-propane (57%) are quite different than those of 1-bromopropane (8%) and 2-bromopropane (92%) from bromination of propane. This is because chlorine atoms ($\text{Cl}\cdot$) are more reactive than bromine atoms ($\text{Br}\cdot$).

Cl· is More Reactive and Less Selective than Br·. When a $\text{Cl}\cdot$ and a propane molecule encounter each other, the greater *reactivity* of $\text{Cl}\cdot$ (compared to $\text{Br}\cdot$) causes $\text{Cl}\cdot$ to be less **selective** (than $\text{Br}\cdot$) in "choosing" which H atom to abstract. As a result, the relative yields of 1-chloro-propane and 2-chloropropane are closer to the predicted **statistical yields** of 75% and 25% than are those for 1-bromopropane and 2-bromopropane (Table 11.5).

Table 11.5. Comparative Product Yields for Halogenation of Propane

Reaction	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{X}$	$\text{CH}_3\text{-CHX-CH}_3$
bromination (X = Br)	8%	92%
chlorination (X = Cl)	43	57
"statistical"(any X)	75	25

The *statistical yields* in this table are those we predicted earlier (Figure 11.15) based solely on the relative numbers of H atoms that a halogen atom might abstract from CH_3 or CH_2 groups of propane.

These relative product yields from chlorination of propane (Table 11.5), together with data for chlorination of other alkanes, lead to **average relative reactivities** for C-H abstraction by $\text{Cl}\cdot$ that we show in Table 11.6 [next page] along with the earlier data for bromination in Table 11.3.

Table 11.6. Relative Reactivities for C-H Abstraction by Cl· and Br·

Type of C-H Bond	Relative Reactivity	
	Cl· (100°)	Br· (150°)
CH ₃ -H (methyl)	1	1
RCH ₂ -H (1°)	250	500
R ₂ CH-H (2°)	1,100	40,000
R ₃ C-H (3°)	1,800	850,000

The results for chlorination and bromination show the same reactivity pattern $R_3C-H > R_2CH-H > RCH_2-H > CH_4$, but reactivity differences between different types of C-H's are significantly smaller for chlorination than bromination. This shows that Cl· is less selective than Br·.

Temperature Effects. There is a difference in reaction temperature for the chlorination (100°) and bromination (150°) data in Table 11.6. However, for theoretical reasons we would expect relative reactivity differences between chlorination and bromination to be even greater for chlorination data at 150°. The numbers in Table 11.6 are *relative* reactivities rather than *absolute* reaction rates. While *absolute* reaction rates usually increase with increasing temperature, the opposite is true for *relative* rates because increasing temperature also decreases selectivity.

Correlation Between Reactivity and Selectivity. The greater *selectivity* of Br· compared to Cl· occurs because Br· is *less reactive* than Cl·. This *inverse* relationship between *reactivity* and *selectivity* is a general phenomenon in chemistry that we summarize here:

High Reactivity generally means **Low Selectivity**
and
Low Reactivity generally means **High Selectivity**

We rationalize this *inverse* relationship between *selectivity* and *reactivity* in Appendix B at the end of the chapter, where we consider detailed energy and structural changes that occur as these molecules are transformed from reactants into products.

Practical Examples of Reactivity and Selectivity. We can imagine examples outside of chemistry that illustrate the inverse correlation between reactivity and selectivity. One example is that *you won't be as selective if you are in a hurry (eg. Cl·), as you would be if you took your time (eg. Br·)*. Another example is that *you shouldn't go grocery shopping when you are hungry* because you won't be as selective as you would be if you were not hungry. Can you think of any others? :-)

Fluorination and Iodination of Alkanes (11.5B)

Fluorine atoms (F·) are the most reactive of all of the halogen atoms and iodine atoms (I·) are the

least reactive. $I\cdot$ is so unreactive that it does not abstract H from most alkanes. The overall *reactivity* trend for halogen atoms is $F\cdot > Cl\cdot > Br\cdot > I\cdot$ and this is the same order as they appear in the next to the last column of a periodic table.

Because of the low reactivity of $I\cdot$, there are insufficient data to determine its quantitative relative reactivities for different C-H bonds. However, a few experimental results for reaction of alkanes with $F\cdot$ permit calculations of its approximate relative reactivities (Table 11.7)[next page].

Table 11.7. Comparative Relative Reactivities of $F\cdot$, $Cl\cdot$, and $Br\cdot$

Type of C-H Bond	$F\cdot$	$Cl\cdot$	$Br\cdot$
CH_3 -H (methyl)	1	1	1
RCH_2 -H (1°)	2	250	500
R_2CH -H (2°)	2.5	1,100	40,000
R_3C -H (3°)	3	1,800	850,000

The relative reactivities for $F\cdot$ show that it is not very selective in its choice of an H atom to abstract. As a result, relative yields of monofluoroalkanes formed from fluorination of alkanes are close to *statistical yields*.

The low selectivity and high reactivity of $F\cdot$ means that fluorination is not a particularly useful reaction for making monofluoroalkanes. The high reactivity of $F\cdot$ also leads to the formation of products with more than one F atom substituted for H. In addition, molecular F_2 is so highly reactive that it cleaves alkanes into smaller fragments by breaking their C-C bonds.

Example : Q. What would be the relative reactivity values for each type of alkane in Table 11.7 for an $X\cdot$ which shows absolutely no selectivity?

A. Each relative reactivity value for CH_3 -H, RCH_2 -H, R_2CH -H, and R_3C -H would be exactly 1.0 in this case. This is because the values in Table 11.7 and earlier tables correspond to the rate of abstraction of one H of each type shown. That means that the relative reactivity of 2 for fluorination of RCH_2 -H compared to that of CH_3 -H means that the one C-H indicated on RCH_2 -H is twice as likely to react with $F\cdot$ than is the one indicated C-H on CH_3 -H. The relative reactivity of 2 shows that although the selectivity is low, $F\cdot$ is still slightly more willing to react with a 1° C-H than with a methyl C-H.

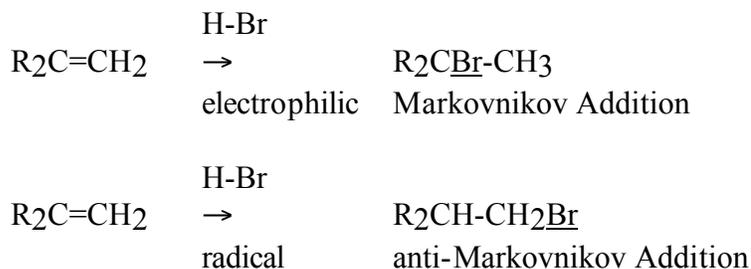
11.6 Radical Additions to Alkenes

We learned in Chapter 10 that hydrogen halides (H-X) and molecular halogens (X_2) add to alkenes by electrophilic addition mechanisms. We will see here that H-Br, as well as Br_2 and Cl_2 ,

add to alkenes by radical mechanisms.

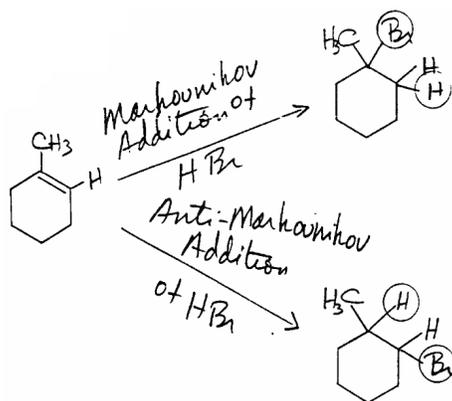
H-Br Addition (11.6A)

We can distinguish *electrophilic* and *radical* addition of H-Br to alkenes by examining the regiochemistry of the addition product. While *electrophilic* addition has *Markovnikov* regiochemistry, *free radical* addition has the opposite regiochemistry that we will refer to as "anti-Markovnikov" addition.



We show this contrasting regiochemistry in the electrophilic and radical additions of H-Br to 1-methylcyclohexene in Figure 11.19.

Figure 11.19



Before we explain the origin of this difference let's examine the details of the reaction mechanism.

H-Br Addition Mechanism (11.6B)

We outline the general mechanism for radical addition of H-Br to alkenes in Figure 11.20 [next page]. This chain reaction mechanism is similar to those that we saw earlier for alkane halogenation.

Propagation. We also show in Figure 11.21 [next page], the two specific propagation steps (Steps 2 and 3 in Figure 11.20) of this radical chain mechanism for H-Br addition to 1-methylcyclohexene. A bromine atom ($Br\cdot$) adds to the C=C bond to give a carbon radical that abstracts an H from H-Br to give the product 1-bromo-2-methylcyclohexane and another

bromine atom ($\text{Br}\cdot$). This $\text{Br}\cdot$ subsequently reacts with another molecule of 1-methylcyclohexene by Step 2 repeating the chain made up of Steps 2 and 3.

Figure 11.20

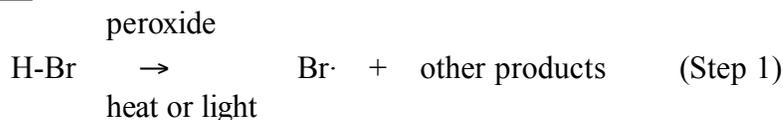
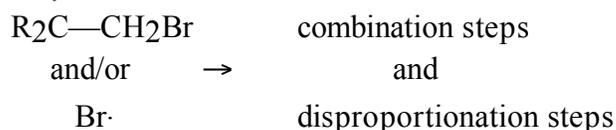
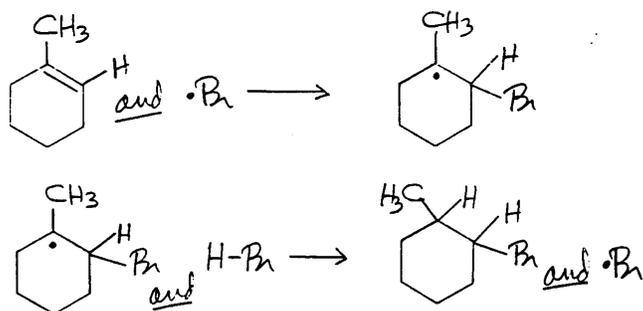
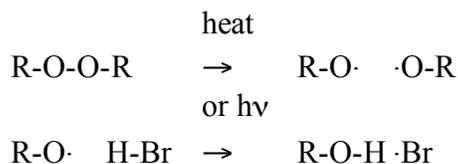
InitiationPropagationTermination

Figure 11.21



Initiation. The general mechanism does not show the specific origin of $\text{Br}\cdot$ in Step 1. A **peroxide** (R-O-O-R) gives radical(s) that ultimately lead to $\text{Br}\cdot$ formation by the following sequence of reactions.



Light or heat energy breaks the weak O-O bond of the peroxide to give two $\text{R-O}\cdot$ radicals (alkoxy radicals). They abstract H from H-Br to give the "first" $\text{Br}\cdot$ for Step 2 of the propagation chain.

Peroxide Initiators. Peroxides that we use for Step 1 are called **free radical initiators** or simply **initiators**. They are present in low concentration compared to the other reactants since one $\text{R-O}\cdot$ radical

leads to many product molecules. Once started, propagation steps repeat many times.

Peroxides commonly used as initiators include **di-*t*-butyl peroxide (A)** and **benzoyl peroxide (B)**.

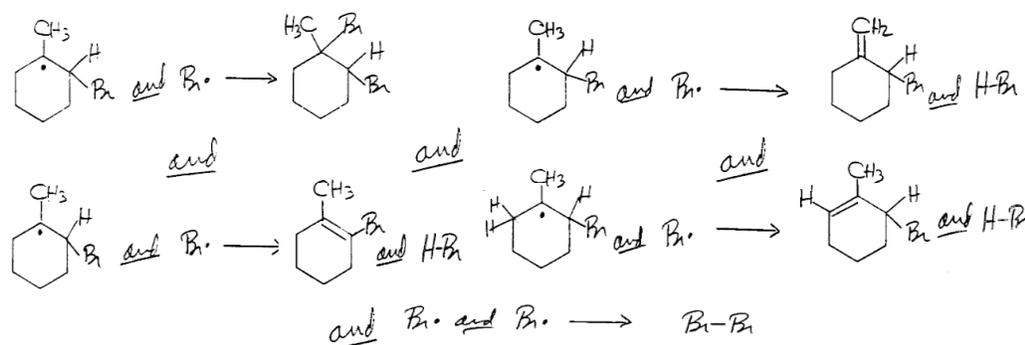


The $(\text{CH}_3)_3\text{CO}\cdot$ radicals from (A) are properly referred to as alkoxy radicals, but the

$\text{Ph}-\text{C}(=\text{O})\text{O}\cdot$ radicals from (B) should be called acyloxy radicals.

Termination. The chain propagation steps (Figures 11.20 and 11.21) do not repeat endlessly because termination reactions between two radicals periodically stop chains. We show examples in Figure 11.22 of termination reactions in free radical addition of H-Br to 1-methylcyclohexene.

Figure 11.22



H-Br Addition Regiochemistry (11.6C)

The difference in regiochemistry for H-Br addition to alkenes in *radical* and *electrophilic* additions reflects a difference in the first species that reacts with the alkene in these addition reactions.

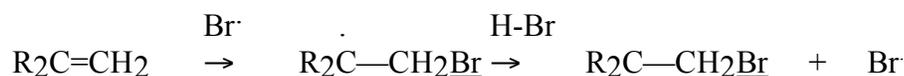
Radical versus Electrophilic Addition. In *electrophilic* addition, H-Br protonates $\text{C}=\text{C}$ on its least substituted C to give the most highly substituted C^+ . That carbocation then reacts in a second step with Br^- (Figure 11.x) causing Br^- to end up on the most highly substituted C.

Figure 11.23

Electrophilic Addition



Radical Addition



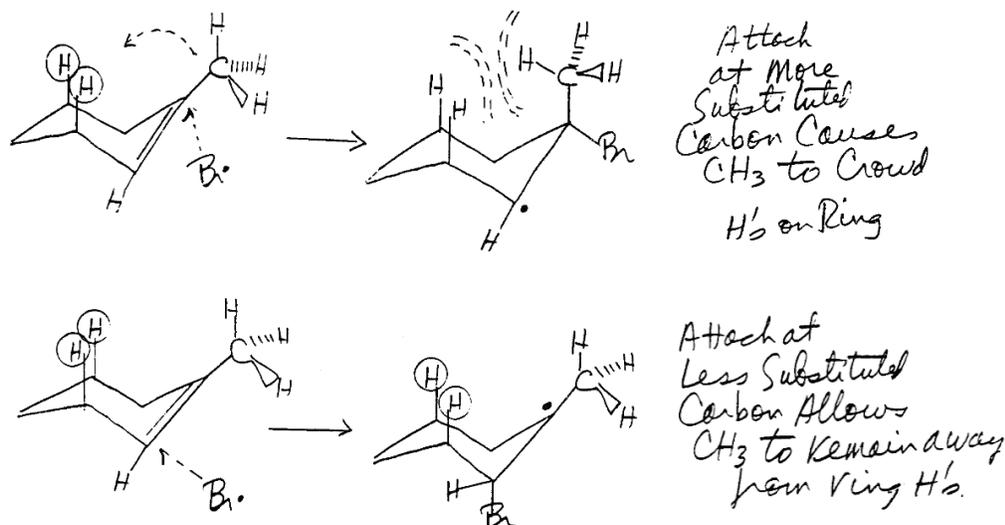
In *radical* addition (Figure 11.23), the first species also adds to C=C at the least substituted C to give the most highly substituted C \cdot , but that first species to add is Br \cdot . As a result, after the intermediate C \cdot radical abstracts an H from H-Br, the Br is on the least substituted C.

We explained the regiochemistry for electrophilic addition in terms of C $^+$ stability. The explanation for radical addition regiochemistry appears to be due to both radical stability and steric effects.

Radical Stability. When Br \cdot adds to the C=C of an alkene, the most substituted C \cdot forms. Since carbon radical stability has the order 3 $^\circ$ >2 $^\circ$ >1 $^\circ$ >methyl (Section 11.4B, the most substituted carbon radical is also the most stable C \cdot . However, some chemists argue that formation of the most substituted R $_3$ C \cdot may be a consequence of Br \cdot addition to the least substituted C for steric reasons. In that event, radical stability may not be the driving force that determines the site of Br \cdot addition.

Steric Effects. While Br \cdot addition to an alkene at the least substituted C gives the most highly substituted radical, it also is a reaction pathway with the least steric strain. We illustrate this once again using the radical addition of H-Br to 1-methylcyclohexene (Figure 11.24).

Figure 11.24

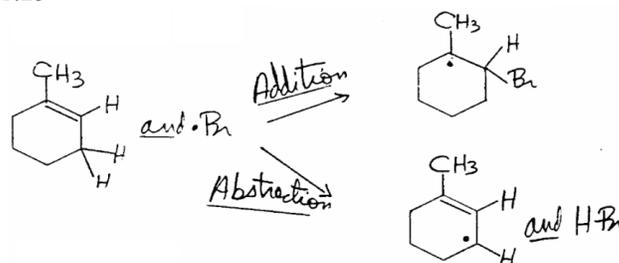


As Br \cdot bonds to a C of the C=C, the groups already on that C move closer together because the hybridization at C changes from sp 2 (planar) to sp 3 (pyramidal). The steric crowding that results from this hybridization change increases as the substitution on C increases. As a result, the overall *anti-Markovnikov* addition of H-Br by the free radical mechanism may occur because Br \cdot adds by the most sterically favorable pathway.

Competing Reactions . You may wonder about some reactions that could compete with radical addition of H-Br to alkenes.

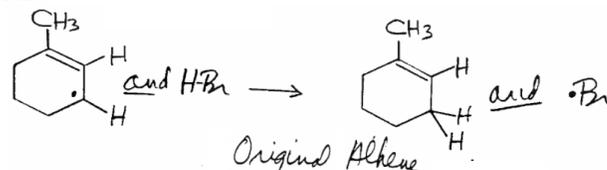
(1) Abstraction of H by Br \cdot . In the first propagation step of H-Br addition (Figure 11.x), Br \cdot adds to the C=C of an alkene. However, earlier in the chapter (Figure 11.21) we saw that Br \cdot also abstracts H's from C-H bonds. As a result, we can imagine that a reaction like that in Figure 11.25 could compete with Br \cdot addition.

Figure 11.25



In fact, both of these reactions can compete with each other. However, we expect that the carbon radical resulting from C-H abstraction (Figure 11.25) will react with H-Br to regenerate the alkene (Figure 11.26).

Figure 11.26



This means that C-H abstraction by Br \cdot in competition with its addition to a C=C is often an invisible reaction during H-Br addition to alkenes.

(2) Competing Radical and Electrophilic Addition. When H-Br and an alkene are present in the same reaction mixture, they can always react by the electrophilic mechanism described in Chapter 10. However, when a radical initiator such as a peroxide is present, the radical chain reaction occurs much more rapidly than electrophilic addition.

Organic compounds often contain trace amounts of peroxides formed by air oxidation of the organic compound. These peroxide impurities can serve as initiators in the same manner as an added initiator such as di-*t*-butyl peroxide. As a result, the radical reaction sometimes occurs even when a peroxide initiator has not been specifically added to the reaction mixture.

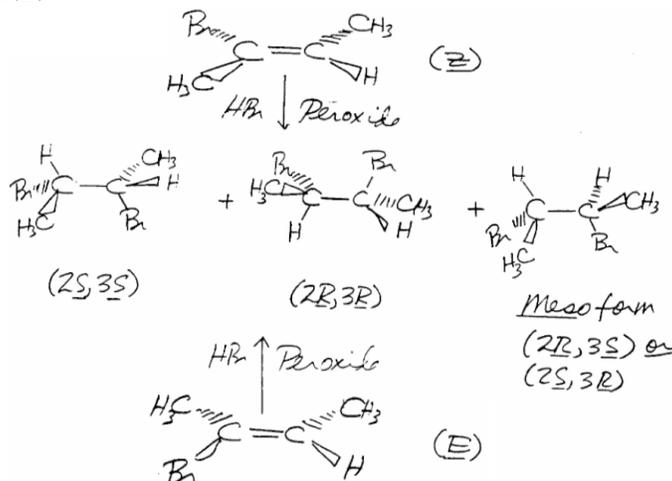
Because alkene free radical addition of H-Br is so much more rapid than electrophilic addition of HBr, chemists take special precautions to prevent the free radical reaction when electrophilic addition is the desired reaction. These include careful purification of the alkene to exclude any peroxide impurity and the addition of **free radical inhibitors** to the reaction mixture. *Free radical inhibitors* are types of organic compounds that stop radical chains. They react with any carbon centered radicals formed in the reaction mixture preventing them from participating in the chain propagation reactions.

H-Br Addition Stereochemistry (11.6D)

The stereochemistry of radical addition of H-Br to an alkene depends on the reaction temperature. At very low temperatures, H-Br adds by overall *anti* addition. However at higher temperatures, the addition reaction is not stereospecific.

H-Br Addition to 2-Bromo-2-Butene. Figure 15a shows the stereochemical possibilities for the products from H-Br addition to (*E*) or (*Z*)-2-bromo-2-butene .

Figure 11.27



The (*2S,3S*) and (*2R,3R*) isomers of 2,3-dibromobutane are a pair of enantiomers. They are also diastereomers of the single *meso* form that we can name as either the (*2S,3R*) or (*2R,3S*) isomer. We show the yields of these products at different reaction temperatures in Table 11.8.

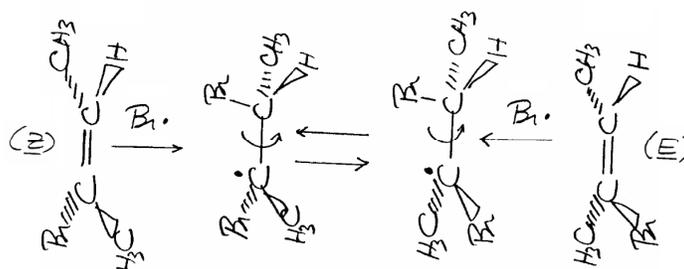
Table 11.8. Product Yields from Radical Addition of H-Br to (*E*) or (*Z*)-2-Bromo-2-butene.

2-bromo-2-butene	Product (%-Yield)	
	(<i>2R,3R</i>)+(<i>2S,3S</i>)	<i>meso</i> form
(<i>Z</i>) isomer		
-78°	100	0
0°	83	17
(<i>E</i>) isomer		
-78°	4	96
0°	71	29

At -78°, the (*Z*) alkene gives 100% of the mixture of the (*2R,3R*) and (*2S,3S*) enantiomers and no *meso* form, while the (*E*) alkene gives mostly the *meso* form (96%). However when the reaction temperature is 0°, the product distributions from the two alkenes are very similar . The major product in each case is the enantiomeric pair, while the minor product is the *meso* form.

The lack of stereospecificity at 0° suggests that the initial radicals formed from either alkene equilibrate due to rotation about the C-C bond (Figure 11.28)[next page].

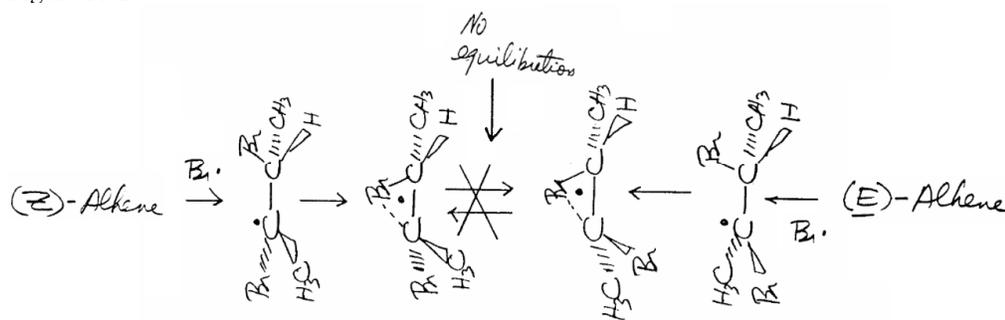
Figure 11.28



The final product distributions reflect a combination of the relative equilibrium stabilities of these two radicals as well as their relative reactivities with H-Br.

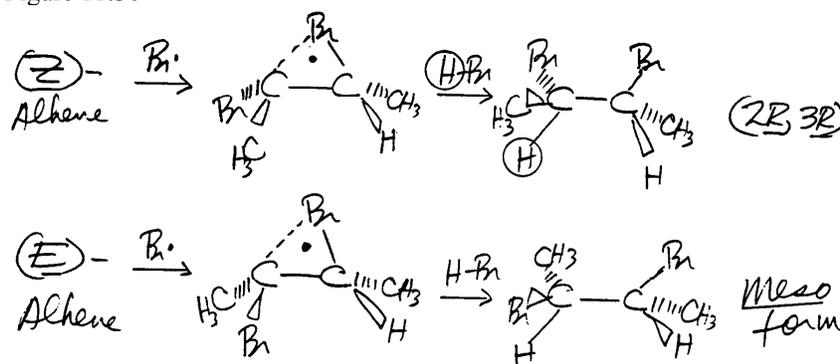
In contrast, at -78° the initial radicals do not equilibrate. They may be stabilized by bridging as we show in Figure 11.29.

Figure 11.29



Subsequent reaction with H-Br (Figure 11.30) leads to stereospecific product formation reflected by the data in Table 11.8.

Figure 11.30

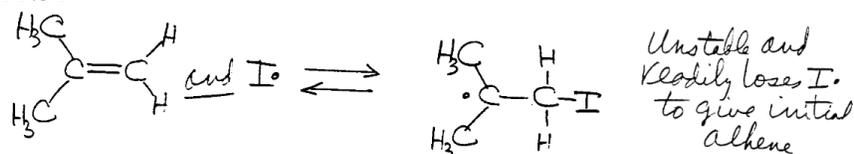


H-I, H-Cl, and H-F Additions are Electrophilic (11.6E)

H-I and H-F do not undergo free radical addition to alkenes, and H-Cl only rarely reacts by the free radical mechanism described for H-Br. The strengths of the H-X bonds for H-Cl (432 kJ/mol) and H-F (570 kJ/mol) are much greater than that of H-Br (366 kJ/mol). As a result, hydrogen abstraction by a carbon radical from either H-F or H-Cl is too endothermic (requires too much energy) to sustain an efficient chain reaction.

The H-I bond strength (298 kJ/mol) is relatively low, however the radical that forms when I· adds to a C=C is too unstable to sustain the chain reaction. Rather than abstracting an H from H-I, the intermediate radical formed by addition of I· to the alkene most often reversibly loses I· to regenerate the alkene (Figure 11.31).

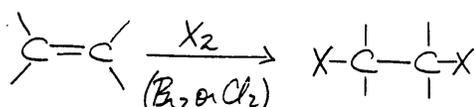
Figure 11.31



Radical Addition of Br₂ or Cl₂ (11.6F)

We saw in Chapter 10 that alkenes add Br₂ or Cl₂ to give dihaloalkanes (Figure 11.32).

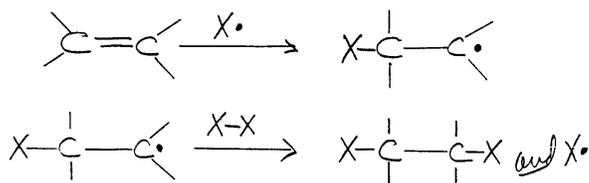
Figure 11.32



Those reactions took place by electrophilic addition mechanisms, but Br₂ and Cl₂ additions can also occur by radical reactions.

Mechanism. We show the propagation steps for the radical addition of either Br₂ or Cl₂ to an alkene in Figure 11.33.

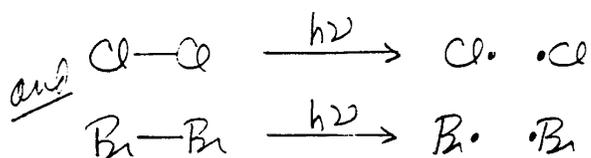
Figure 11.33



A halogen atom (X·) adds to the C=C to give an intermediate carbon radical. This radical then abstracts an X atom from X₂ to give the dihalogenated product and another halogen atom (X·) that continues the chain. Since the Cl-Cl bond (243 kJ/mol) is much weaker than the H-Cl bond (432 kJ/mol), radical chlorination occurs with Cl₂ even though it doesn't with H-Cl.

Initiation does not require a peroxide because both Cl₂ and Br₂ decompose into their constituent halogen atoms when treated with light (Figure 11.34).

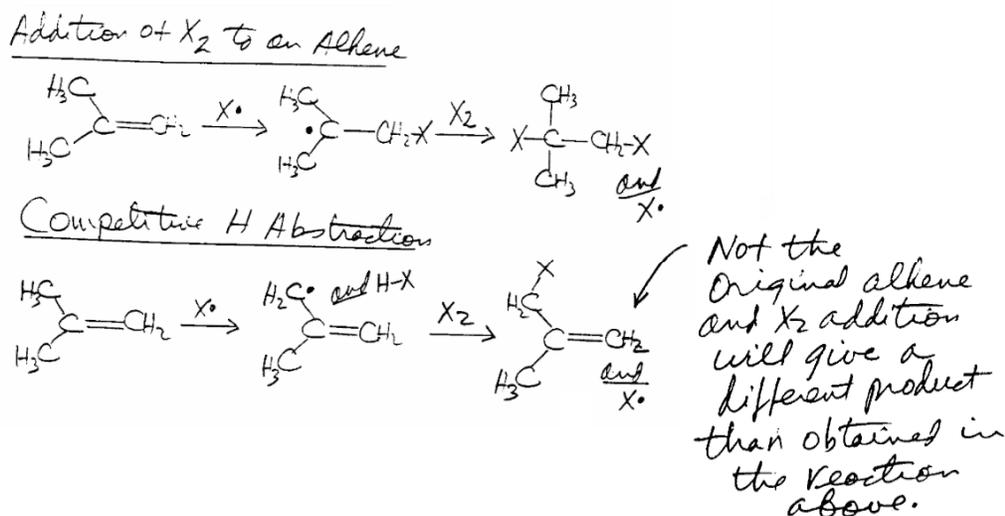
Figure 11.34



The termination reactions in Br₂ or Cl₂ radical additions are analogous to those we have previously seen for halogenation of alkanes and addition of H-Br to alkenes.

Competitive Substitution. Br· abstracts H's from the alkenes in competition with its addition to the C=C and this is also true for Cl·. When this occurs, the intermediate carbon radical reacts with Br₂ or Cl₂ to give halogenated substitution products that are quite different than what we expect for the addition reactions (Figure 11.35).

Figure 11.35

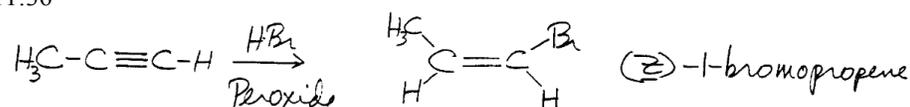


For this reason, it is best to avoid free radical additions of Br₂ or Cl₂ to alkenes. We can accomplish this by keeping light out of the reaction mixture so that it does not catalyze the decomposition of these molecular halogens, and by making certain that other free radical initiators are not present.

F₂ and I₂. Neither F₂ nor I₂ add efficiently to alkenes. In the case of I₂, the 1,2-diiodoalkane product is unstable and reversibly loses I₂. In contrast, 1,2-difluoroalkanes are very stable, but F₂ is so reactive that a wide range of side reactions occur in competition with its addition to the C=C.

Radical Additions to Alkynes. H-Br adds by a free radical mechanism to alkynes (e.g. propyne) to give an anti-Markovnikov haloalkene (e.g. (Z)-1-bromopropene) (Figure 11.36).

Figure 11.36



Like electrophilic addition of H-Br to alkynes, the stereochemistry of this reaction is *anti*.

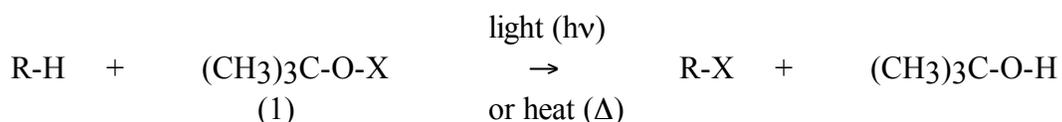
Appendix A

11.7 Alkane Halogenation with Other Reagents

Our examples of alkane halogenation reactions have all used molecular halogens (X_2). They have also been reactions where we provided energy in the form of light (photochemical reactions). This section shows some examples using other sources of halogens, other initiators, and heat as the source of energy.

t-Butyl Hypohalites (11.7A)

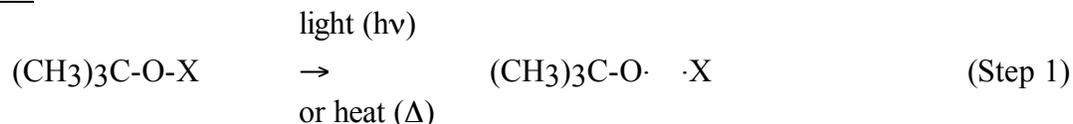
The highly reactive compounds *t*-butyl hypochlorite (1, $X=Cl$) and *t*-butyl hypobromite (1, $X=Br$) chlorinate or brominate alkanes.



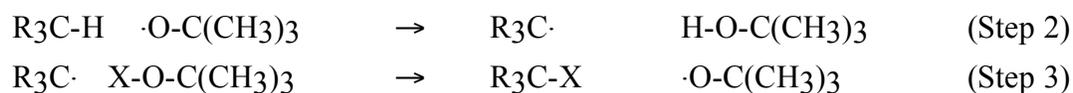
Mechanism. Both *t*-butyl hypohalites halogenate alkanes by the same general mechanism.

Figure 11.37

Initiation



Propagation



The *t*-butoxy radical ($(CH_3)_3C-O\cdot$) that forms in the initiation step (Step 1), abstracts an H from the alkane (R_3C-H) to give $R_3C\cdot$ (Step 2). The alkyl radical then abstracts a halogen atom (X) from the *t*-butyl hypohalite (Step 3) to give the haloalkane product and another *t*-butoxy radical.

The *t*-butoxy radical is the "chain carrying radical" since it reacts by abstracting an H from R_3C-H in Step 2 and is reformed in Step 3. In halogenations of R_3C-H with the molecular halogens X_2 , the *chain carrying radical* is $X\cdot$.

What about $X\cdot$ from *t*-Butyl Hypohalite? The $X\cdot$ that forms in Step 1, also reacts with R_3C-H as we show here.

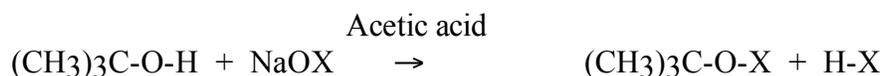


But the resulting alkyl radical then reacts with *t*-butyl hypohalite *via* Step 3 shown above to give R_3C-X and *t*-butoxy radical. As a result, the chain carrying radical almost immediately becomes *t*-butoxy ($(CH_3)_3C-O\cdot$) even though $X\cdot$ was the first radical to react with the alkane.

Termination reactions in *t*-butyl hypohalite halogenation of alkanes include combination and disproportionation reactions involving alkyl radicals ($R_3C\cdot$) and *t*-butoxy radicals.



***t*-Butyl Hypohalite Preparation.** Organic chemists prepare *t*-butyl hypohalites by reacting *t*-butyl alcohol with the corresponding sodium hypohalite in the presence of acetic acid.

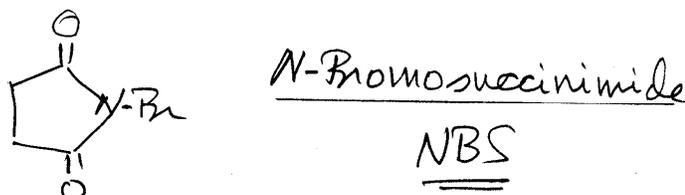


For *t*-butyl hypochlorite, the recommended source of NaOCl is household Chlorox™ bleach.

***N*-Bromosuccinimide (11.7B)**

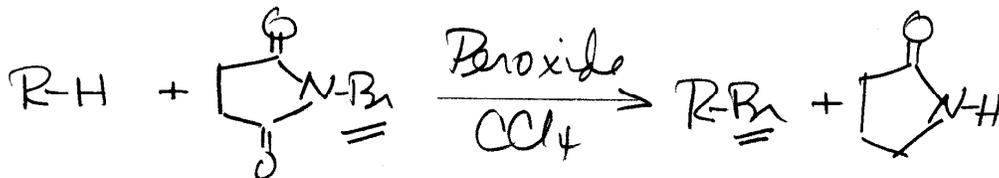
Another reagent used for alkane halogenation is *N*-bromosuccinimide (NBS) (Figure 11.38).

Figure 11.38



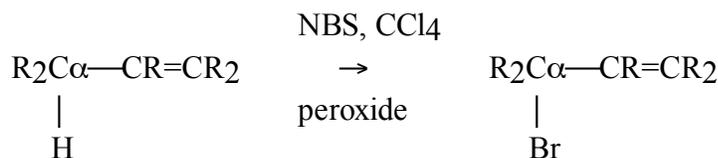
Overall Reaction. We show the overall halogenation reaction for NBS bromination in Figure 11.39.

Figure 11.39



You can see that the Br on NBS is replaced by an H in the product **succinimide**. We discuss compounds like succinimide in a later chapter. For now you only need to know that succinimide is a relatively unreactive solid that is easily removed from the reaction mixture. NBS is commercially available.

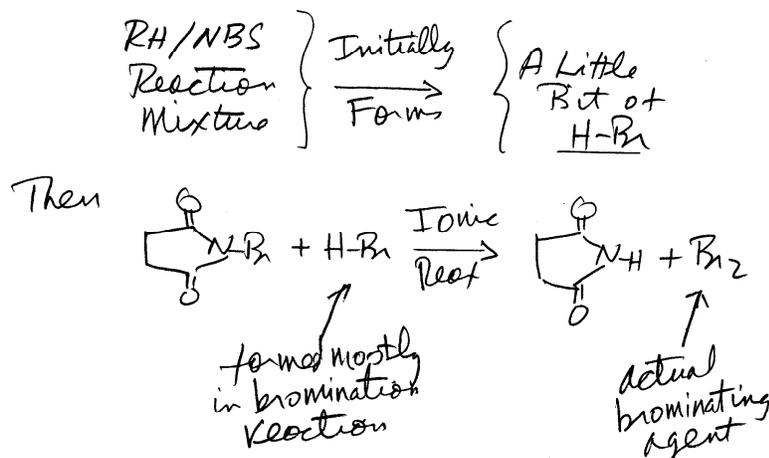
NBS is a particularly useful reagent for carrying out the type of bromination reaction shown here.



C α is directly bonded to a C=C and organic chemists refer to such C's as **allylic**. As a result, the C α -H is called an *allylic* H, while the bromination reaction is called *allylic* bromination. We will discuss the special reactivity of groups on *allylic* C's in Chapter 12.

Mechanism. In this bromination reaction, NBS serves as a source of molecular bromine (Br₂). Early in the reaction, a Br· forms and abstracts an H from R₂CH—CR=CR₂ to give H-Br (Figure 11.40).

Figure 11.40



The resultant H-Br quickly reacts with NBS to produce molecular bromine (Br₂) (Figure 11.40). As soon as Br₂ forms, the halogenation reaction becomes a free radical bromination like that we described in Section 11.2.



Br· is the chain carrying radical in propagation steps identical to those that we described at the beginning of this chapter for alkane bromination with Br₂ (Figure 11.02).

Appendix B

11.8 Halogen Atom Reactivity and Selectivity

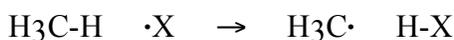
We have stated that the *relative reactivity* of halogen atoms in C-H abstractions is F· > Cl· > Br· > I·, while their *relative selectivity* in abstracting H from a C-H has the reverse order I· > Br· > Cl·.

> F. While this inverse relationship may seem reasonable, some questions arise when we examine the details of these reactions more closely: *For example, "how does a halogen atom 'know' the strength of a C-H bond so it can be selective in its choice of the C-H to abstract"?*

In order to explain how strengths of C-H bonds and reactivities of halogen atoms translate into the observed selectivity patterns, we will consider some fundamental details of chemical reactions. These include energy changes accompanying the molecular changes that occur as reactants are transformed into products.

Reaction of Methane with X· (11.8A)

We will use reactions between methane (CH₄) and the four different halogen atoms as examples.

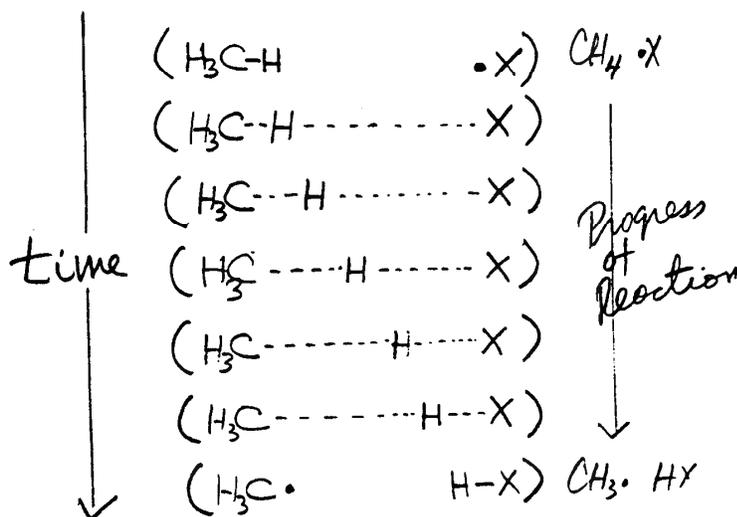


The halogen atom (X·) encounters a methane molecule and abstracts an H atom to form the methyl radical (written H₃C· or CH₃·) and H-X.

Structural Changes During Reaction. This abstraction of an H from methane by X· does not occur as an instantaneous event. Before the abstraction of the H begins, CH₄ and the halogen atom (X·) first must come together by mutual diffusion in the reaction mixture to form an **encounter complex** (CH₄ ·X). After formation of this complex, C-H bond breakage progresses with simultaneous formation of the H-X bond over a very short period of time to ultimately give (CH₃· HX) (Figure 11.41).

Figure 11.41

Stages of C-H Breaking and H-X Formation
in H Abstraction by ·X in the (CH₄ ·X) Complex.



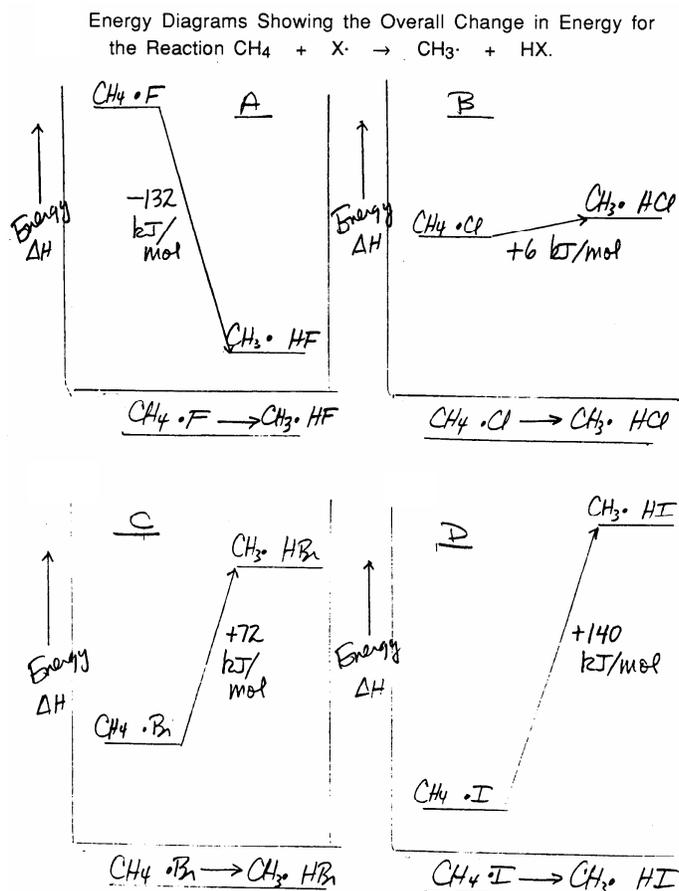
This figure shows the encounter complex ($\text{CH}_4 \cdot \text{X}$) in various stages of the reaction. You can think of these pictures, that show an increasingly longer C-H bond and an increasingly shorter H-X bond, as a series of snapshots taken as the reaction is progressing.

Energy Changes During Reaction. As these structural changes occur, the energy of the system changes. Over the whole reaction, the energy of the system changes from that corresponding to the *reactants* CH_4 and $\text{X}\cdot$ to that corresponding to the *products* $\text{CH}_3\cdot$ and H-X . We show the overall energy changes (ΔH) for these reactions for the different $\text{X}\cdot$ in Table 11.9 and Figure 11.42. You can see that the values have a dramatic dependence on $\text{X}\cdot$.

Table 11.9. Overall Energy Changes for the Reaction of CH_4 and $\text{X}\cdot$ to Give $\text{CH}_3\cdot$ and HX .

$\text{X}\cdot$	ΔH (kJ/mol)
$\text{F}\cdot$	-132
$\text{Cl}\cdot$	+6
$\text{Br}\cdot$	+72
$\text{I}\cdot$	+140

Figure 11.42



Exothermic and Endothermic Reactions. The negative ΔH value for the reaction of CH_4 with $\text{F}\cdot$ (Table 11.9) tells us that this reaction is highly **exothermic**. That means that energy is released in this reaction as we show in energy diagram A (Figure 11.42)[previous page]. In dramatic contrast, the reaction of CH_4 with $\text{I}\cdot$ has a large positive value of ΔH . It is a highly **endothermic** reaction with products that are higher in energy than the reactants (energy diagram D in Figure 11.42).

You can see from the other two diagrams in this figure, that the overall energy changes for the reactions of $\text{Cl}\cdot$ and $\text{Br}\cdot$ with methane are intermediate between the two extremes for $\text{I}\cdot$ and $\text{F}\cdot$. The reaction involving $\text{Br}\cdot$ is *exothermic*, but less exothermic than that for $\text{I}\cdot$. In contrast, the reaction involving $\text{Cl}\cdot$ reaction is very close to **thermoneutral** (no energy difference between reactants and products).

These differences in overall energy change that depend on $\text{X}\cdot$ result from the vastly different *bond strengths (bond dissociation energies)* of the H-X product molecules (Table 11.10).

Table 11.10. Bond Dissociation Energies of H-X Bonds

H-X	Bond Dissociation Energy (kJ/mol)
H-F	570
H-Cl	432
H-Br	366
H-I	298

The H-F bond formed in fluorination of methane is much stronger (570 kJ/mol) than the C-H bond of CH_4 that is broken (438 kJ/mol)(Table 11.2). This leads to an overall decrease in energy of the system as the reaction proceeds from reactants to products and the extra energy is released as heat.

In contrast, the bond dissociation energy (bond strength) of H-Cl (432 kJ/mole) and that of a C-H bond in CH_4 (438 kJ/mole) are almost the same, while those of both H-Br (366 kJ/mole) and H-I (298 kJ/mole) are significantly less than that of a C-H of CH_4 (438 kJ/mole). You can calculate the ΔH values in Table 11.9 from the data in Tables 11.2 and 11.10 using the relationship $\Delta H = (\text{Bond Dissociation Energy})_{\text{Methane}} - (\text{Bond Dissociation Energy})_{\text{H-X}}$.

Transition States or Activated Complexes (11.8B)

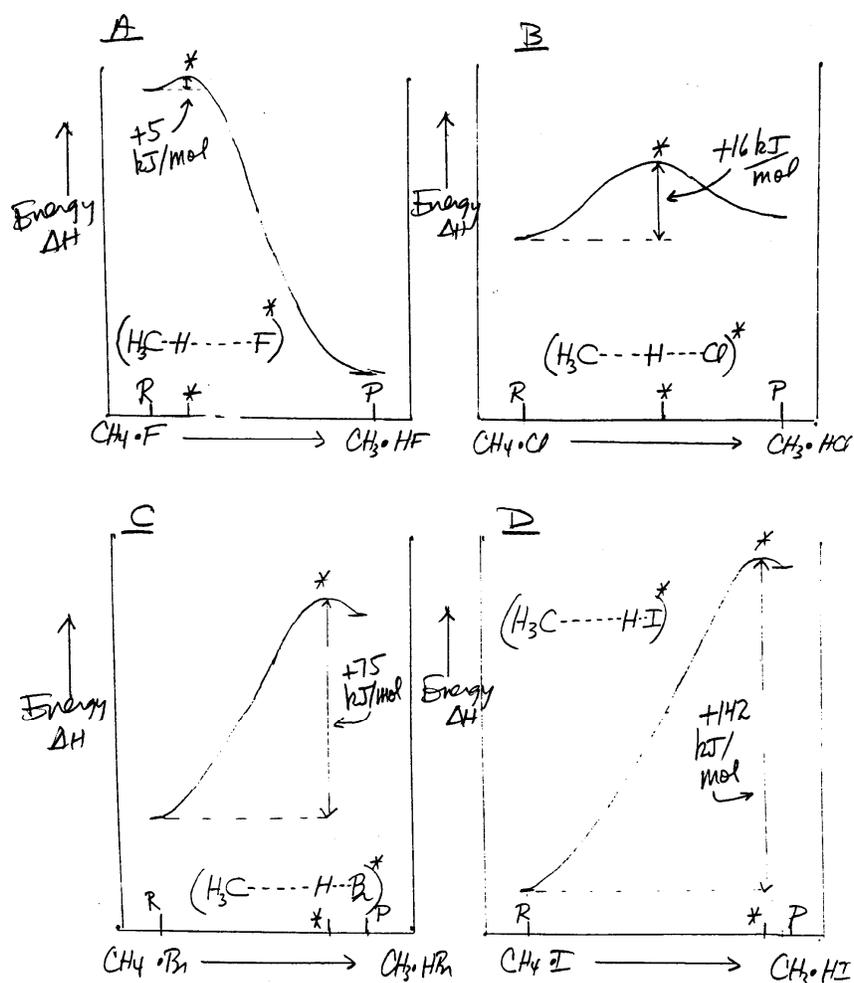
The energy diagrams in Figure 11.42 suggest that the intermediate complexes of CH_4 and $\text{X}\cdot$ with different amounts of C-H bond breaking and H-X bond formation (Figure 11.41) have energies

that are intermediate between those of the reactants and products. This is only partly true as we explain below.

Energy Maximum and Transition State. The energy of the complex between CH_4 and $\text{X}\cdot$ smoothly changes as the C-H and H-X bonds respectively increase and decrease in length. However, the energy actually passes through a maximum value as it changes from the value for the reactants to the value for the products as shown for each of these reactions in Figure 11.43.

Figure 11.43

Energy Diagrams Showing the Overall Energy Changes as well as Transition State Energies and Positions for the Reaction $\text{CH}_4 + \text{X}\cdot \rightarrow \text{CH}_3\cdot + \text{HX}$.



The smooth curve in each diagram traces the actual energy change for the reacting system as it passes from reactants to products. You can see there is a maximum in the energy curve for each reaction. We call the configuration of a system with this maximum energy value, the **transition state** or the **activated complex**, and we designate it on each diagram with an (*).

Reaction Rates and Activation Energy. The energy maximum actually determines how fast a particular reaction proceeds! You can see that in each case, no matter whether the reaction is *endothermic* or *exothermic*, there is an initial increase in energy as the reactants move toward the *transition state*. Once the *transition state* is reached, the energy of each system decreases as the system progress from the *transition state* to the products.

We call the energy difference between the reactants and the transition state the **activation energy** (E_a). We must supply this *activation energy* to each reacting system in order for the reaction to occur. We show the approximate values of these *activation energies* in the diagrams in Figure 11.43 and summarize them in Table 11.11 along with the overall energy changes (ΔH) from Table 11.9.

Table 11.11. Activation Energies for the Reaction of CH₄ and X·

X·	E_a (kJ/mol)	ΔH (kJ/mol)
F·	+5	-132
Cl·	+16	+6
Br·	+75	+72
I·	+142	+140

You can see that the *activation energy* (E_a) for the reaction of F· with methane is very small, but that values of E_a increase in the order F· < Cl· < Br· < I·. While the numbers in Table 11.11 are specifically for reaction of these halogen atoms with CH₄, the comparative results are the same for all other alkanes. For each type of C-H bond, the order of activation energies for H abstraction is $E_a(\text{F}\cdot) < E_a(\text{Cl}\cdot) < E_a(\text{Br}\cdot) < E_a(\text{I}\cdot)$.

Reactivity and Activation Energies. This order of activation energies is actually responsible for the reactivity pattern F· > Cl· > Br· > I· observed in the halogenation of alkanes that we described earlier. F· is more reactive than the other halogen atoms because its E_a for reaction with a particular C-H is always less than those of the other halogens. In contrast, I· is always less reactive than the other halogens because its C-H abstraction reactions have much higher E_a values than those of the other halogens.

The halogen atom reactivities are directly related to the E_a values because the rates of all chemical reactions are determined by their E_a values rather than their overall energy changes. In order to react, the reacting system must pass through the configuration of the reactants with the maximum energy and this requires an input of energy corresponding to the difference in energy between the

reactants and the transition state (*). Figuratively speaking, it's all "downhill" after that.

An Explanation for Selectivity-Reactivity Correlation (11.8C)

The concept that reaction rates are determined by activation energies of reactions provides an explanation for the relationship between *reactivity* and *selectivity* that we described earlier.

Resemblance of Transition States to Reactants and Products. You can see from the diagrams in Figure 11.43 that the "location" of the transition state (*) between the reactants (R) and products (P) is different for each reaction. The transition state configuration labelled (*) is very close to that of the reactants (R) in the reaction of CH₄ with F· (diagram A), while the transition state (*) is very close to that of the products (P) in the reaction of CH₄ with Br· or I· (diagrams C and D).

This means that the *transition state* for fluorination has little C-H bond breaking and little H-F bond formation [(H₃C·H······F)] so it closely resembles the reactants. In contrast, the *transition states* for bromination and iodination have a great deal of C-H bond breaking and significant H-Br or H-I bond formation [for example (H₃C······H··Br)], so they closely resemble the products. Finally, the extent of C-H bond breaking and H-Cl bond making are intermediate between these extremes in the transition state for chlorination [(H₃C······H····Cl)] (Figure 11.43).

Radical Character in the Transition State. Another way of describing the differences between the *transition states* for these halogenation reactions of methane is in terms of their "amount of CH₃· radical character". For example, the transition state for iodination has the most CH₃· radical character of any of the halogenation reactions because the C-H bond has been almost completely broken in the transition state. The "amount of CH₃· character" in the transition state decreases in the order *iodination* > *bromination* > *chlorination* > *fluorination* because C-H bond breaking decreases in that order.

This trend applies not only to halogenation of methane, but to halogenation of any alkane. The amount of alkyl radical character in the transition state for C-H abstraction is always greatest for iodination followed by bromination, least for fluorination, and intermediate for chlorination.

As a result, the relative rates of *iodination* and *bromination* reactions depend most on the relative stabilities of the different possible alkyl radicals formed in the reaction, while these relative rates

are increasingly less dependent on radical stability for chlorination and fluorination, in that order. We see this in the relative reactivities for F·, Cl· and Br· in Table 11.7.

Even though 3° radicals are much more stable than 2° radicals, and 2° radicals are much more stable than 1° radicals, relative rates of abstraction of 3°, 2°, and 1°

C-H's are very similar for F· indicating that radical stability plays only a small part in the fluorination reaction. In contrast, bromination shows big differences in reactivity between 3°, 2°, and 1° systems that clearly reflect radical stability.

The Hammond Postulate. The energy diagrams in Figure 11.43 show that the transition state for the very *exothermic* fluorination reaction is close to the reactants and therefore resembles the *reactants*. In contrast, the transition states for the very *endothermic* bromination and iodination reactions are close to the products and therefore resemble the *products*. Finally, the transition state for the relatively *thermoneutral* chlorination reaction is *intermediate* between the reactants and products.

This relationship between the *position* of a transition state relative to the reactants and products, and the *exothermicity* or *endothermicity* of a reaction, is general and was described in 1955 by Professor George Hammond when he was a faculty member at Iowa State University. This observation is now referred to as the **Hammond Postulate** and it is used throughout this text to help explain the behavior of chemical reactions.

I was privileged to have Professor Hammond as my Ph.D. dissertation director during my graduate studies at Caltech from 1959 through 1962.