These are homework exercises to accompany Chapter 3 of Vollhardt and Schore's "Organic Chemistry" Textmap.

3.1: Strength of Alkane Bonds: Radicals

3.2: Structure of Alkyl Radicals: Hyperconjugation

3.3: Conversion of Petroleum: Pyrolysis

3.4: Chlorination of Methane: The Radical Chain Mechanism

3.5: Other Radical Halogenations of Methane

3.6: Keys to Success: Using the "Known" Mechanism as a model for the "Unknown"

3.7: Chlorination of Higher Alkanes: Relative Reactivity and Selectivity

3.8: Selectivity in Radical Halogenation with Fluorine and Bromine

3.9: Synthetic Radical Halogenation

3.10: Synthetic Chlorine Compounds and the Stratospheric Ozone Layer

3.11: Combustion and the Relative Stabilities of Alkanes

Problems
Q15
Indicate whether each Hydrogen present is primary, secondary, or tertiary. Why is quaternary not an option?
(a) ethane (b) 2,2-dimethylpropane (c) 1-methylcyclobutane

Q16
In each pair of radicals, determine whether the radical is primary, secondary, or tertiary and also decide which radical is more favorable. Give the general reason why for all of the cases.
(a)

(b)

(c)

Q17
Draw the electron pushing arrow mechanism for all possible pyrolysis radicals that can form from butane, assuming only C-C bonds are broken. What type of bond cleavage is this, heterolytic or homolytic?

Q18
Draw all the possible pyrolysis radical products for 2-methylbutane, and determine which bond is most likely to be broken.

Q19
Calculate the $\Delta H^0$ (kJ/mol) of the following reactions using the given bond dissociation energies.
Bond Dissociation Energies (Homolytic)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dissociation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃-H (methane)</td>
<td></td>
</tr>
<tr>
<td>C₂H₅-H (ethane)</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₃C-H</td>
<td></td>
</tr>
<tr>
<td>H-H</td>
<td></td>
</tr>
<tr>
<td>H-Cl</td>
<td></td>
</tr>
<tr>
<td>H-Br</td>
<td></td>
</tr>
<tr>
<td>CH₃-Cl</td>
<td></td>
</tr>
<tr>
<td>CH₃-Br</td>
<td></td>
</tr>
<tr>
<td>C₂H₅-Cl</td>
<td></td>
</tr>
<tr>
<td>C₂H₅-Br</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂C-Cl</td>
<td></td>
</tr>
<tr>
<td>(CH₃)₂C-Br</td>
<td></td>
</tr>
<tr>
<td>Cl-Cl</td>
<td></td>
</tr>
<tr>
<td>Br-Br</td>
<td></td>
</tr>
</tbody>
</table>

(a) CH₄ + Cl₂ → CH₃Cl + HCl  
(b) CH₄ + Br₂ → CH₃Br + HBr  
(c) C₂H₆ + Cl₂ → C₂H₅Cl + HCl  
(d) C₂H₆ + Br₂ → C₂H₅Br + HBr  
(e) (CH₃)₃CH + Cl₂ → (CH₃)₂CCl + HCl  
(f) (CH₃)₃CH + Br₂ → (CH₃)₂CBr + HBr  
(g) H₂ + Cl₂ → 2HCl  

Q20

Predict all possible constitutional isomers possible if monohalogenation were performed on the molecules in problem 15 with Br₂. Give the name of the haloalkane.

Q21

Given the following alkanes, draw the most likely product to form upon monohalogenation with Br₂ (keep in mind that
this may not be the only product to form though). If the reaction was performed with Cl\textsubscript{2} would there be more or less selectivity in the desired product formation? Why?

(a) 

(b) 

(c) 

Q22

Draw out the full mechanism of the monochlorination of ethane with electron-pushing arrows. Label the three overall steps of the mechanism.

Q23

Calculate the statistical probability of monobromination of propane on each unique carbon, and discuss why this is not likely. Given that the experimental monobromination produces two products, 97% one and 3% the other, assign these percentages to the corresponding product.

Q24

Draw the mechanism of the bromination of propene using Br\textsubscript{2}, on the carbon adjacent to the double bond. Can you draw any resonance structures for the intermediates in the propagation steps? Would you expect this to make the radical more or less stable?

Q25

Based on the previous question, how do you think the \(\Delta H^0\) to form the propene radical would compare to that of a propane radical?
Q26

Similar to problem 21, describe the resemblance to products and reactants of an early and a late transition state. In a monohalogenation, what step is early what step is late (propagation and termination)?

Q27

Draw the line-bond structure of the major product for the following reaction, if a reaction occurs, assume monohalogenation.

(a)

\[
\text{ } + \text{Cl}_2 \xrightarrow{\text{Heat}}
\]

(b)

\[
\text{CH}_4 + \text{I}_2 \xrightarrow{\text{Heat}}
\]

(c)

\[
\text{ } + \text{Cl}_2 \xrightarrow{\text{Heat}}
\]

(d)

\[
\text{ } + \text{Br}_2 \xrightarrow{\text{Heat}}
\]

(e)

\[
\text{ } + \text{Br}_2 \xrightarrow{\text{Heat}}
\]

Q28

For problem 27.c, calculate the product ratios using the following information (hint use the number of hydrogens in each category present to calculate the ratios).

Chlorination: \(^1\text{O} \text{ Reactivity}=1 \ 2^0 \text{ Reactivity}=4 \ 3^0 \text{ Reactivity}=5\)
Q29
Halo alkanes are synthetically useful compounds as you'll learn later. However, the radical halogenation is not always selective as seen in problem 27. If any of the products of the reactions were to be used as subsequent reagents, which would be more useful, 27.c or 27.d?

Q30
What are potential problems of trying to brominate the second carbon in hexane? If however, this does form draw the Newman Projection of the most favorable staggered conformation looking down the C2-C3 axis.

Q31
Calculate the $\Delta H^0$ value for the bromination and iodination of propene, on the secondary carbon, assume monohalogenation. The bond dissociation values are as follows. What is the major difference between the two values? (Note this problem uses kcal mol$^{-1}$)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Dissociation Energy (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-Br</td>
<td>46</td>
</tr>
<tr>
<td>I-I</td>
<td>36</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CH-H</td>
<td>98.5</td>
</tr>
<tr>
<td>H-Br</td>
<td>87</td>
</tr>
<tr>
<td>H-I</td>
<td>71</td>
</tr>
<tr>
<td>Secondary C-I</td>
<td>56</td>
</tr>
<tr>
<td>Secondary C-Br</td>
<td>71</td>
</tr>
</tbody>
</table>

Q32
Draw the bond polarity present of chloroethane, explain how this affects the electronics of the carbon attached to the chloro group.

Q33
Write a balanced combustion reaction for the following hydrocarbons, sugars, and alcohols. Assume complete combustion, what is one typical product of incomplete combustion?

(a) butane (b) octane (c) glucose (C$_6$H$_{12}$O$_6$) (d) methanol
Q34

At 25°C the heat of combustion of 2-butanone, CH₂CHOCH₂CH₃, is 2444.1 kJ mol⁻¹ and the heat of combustion of butanal, CHOCH₂CH₂CH₃, is 2470.3 kJ mol⁻¹. Which combustion is more endothermic? What does this tell us about the relative stability of the two compounds?

Q35

Often times NBS, N-bromosuccinimide, is substituted for Br₂ in radical halogenation reactions to keep the concentration of Br₂ low. This low concentration favors the radical halogenation and not other alkene reactions, that you will learn later on. Using NBS, drawn below, draw the radical bromination of propene.

\[ \text{N-bromosuccinimide} \]

Q36

Peroxides are also good initiators for radical reactions. Given the peroxide, RO-OR, draw the initiation step of the general peroxide and the propagation of that radical to create bromine radicals with HBr.

Q37

One radical inhibitor BHT, butylated hydroxytoluene, is often added to diethylether, CH₃CH₂OCH₂CH₃, to prevent explosive peroxides from forming. Given BHT's structure below, draw the radical formation on the oxygen of BHT with a general radical, R'. The phenoxy radical is stabilized/made unreactive by steric hindrance of the tertbutyl groups and also resonance.

\[ \text{BHT} \]
Q38

Draw the two radical halogenation products of 2-methylpropane, also known as isobutane, with Cl₂. Given the percentages of the two products are 37% and 63%, calculate the reactivity of each hydrogen and the ratio between the two.

Q39

Given the following reactions and the relative ΔH°, what is most likely the rate limiting step of the radical halogenation mechanism?

1) X-X → 2X: ΔH₁°>0
2) R-CH₃ + X' → R-CH₂' + HX: ΔH₂°>ΔH₁°
3) R-CH₂' + X' → R-CH₂X: ΔH₃°<0

Q40

Explain or use a mechanism to show how BHT, or other radical inhibitors, could cause a radical halogenation to come to a stop?

Q41

Given the following heats of combustion; propane ΔH=-2202 kJ/mol, gasoline ΔH=-44,000 kJ/kg, diesel ΔH=-45,000 kJ/kg; what fuel could potentially provide the most miles per weight of fuel?

Q42

Write out the reactions for the complete combustion of propane and gasoline, assuming gasoline is completely C₈H₁₈ (gasoline is actually a mixture of smaller and larger hydrocarbons).

Q43

Draw the transition states of the reaction of Cl' and Br' with a secondary carbon, compare the radical character of that carbon between the two transition states.

Q44

CFC’s, chlorofluorocarbons (CF₂Cl₂), saw widespread use as refrigerants and as aerosols. However, due to their low boiling point, when sprayed into the air they rise up to the atmosphere and are exposed to large amounts of uv radiation. This light, often seen as hv in chemical equations, provides the energy needed to break the CFC's into radicals. Chlorine radicals are formed and this degrades the protective layer of ozone into oxygen, O₂. Draw the formation of the chlorine
radical from a CFC.

Q45

N-bromosuccinimide, NBS, is a reagent with what purpose?

(a) a strong base (b) a strong acid (c) radical initiator (d) radical inhibitor

Q46

Name the following compound.

\[ \text{Cl} \]

Q47

A polymer scientist is trying to perform a halogenation on the following polymer to perform a subsequent reaction (the structure repeats itself to form a length of n units). She/he has been using \( \text{Cl}_2 \) to perform the radical halogenation, but cannot obtain a uniformly halogenated product. What suggestion would you give her/him to try and achieve a more uniformly halogenated product?

Q48

Given that a radical halogenation with chlorine yields an early transition state, as defined in Hammond's Postulate, is the halogenation likely to be endothermic or exothermic?

Solutions

S15

(a)
There can be no quaternary Hydrogen because a Carbon can only have four covalent bonds. In (b) the central carbon has no attached Hydrogen, but it is a quaternary carbon.

\[
\begin{array}{c}
1^\circ & 1^\circ \\
H_3C-CH_3
\end{array}
\]  
(b)

\[
\begin{array}{c}
1^\circ & 1^\circ \\
H_3C-C & CH_3 \\
& 1^\circ \\
& CH_3
\end{array}
\]  
(c)

\[
\begin{array}{c}
2^\circ & 3^\circ & 1^\circ \\
H_2C-C & H.CH_3 \\
H_2C-CH_2 \\
2^\circ & 2^\circ
\end{array}
\]

For all of these cases the more favorable radical is as follows $3^\circ > 2^\circ > 1^\circ$. Since the radical is electron deficient, the more carbon substituents the more hyperconjugation that can occur. This stabilizes the radical, this "rule" is also true for carbocations as you will see later.
S17

\[ \text{H}_3\text{C}^-\text{CH}_3 \quad \rightarrow \quad \cdot\text{CH}_3 \quad \text{H}_2\text{C}^-\cdot\text{CH}_3 \]

\[ \text{H}_3\text{C}^-\text{CH}_3 \quad \rightarrow \quad \text{H}_3\cdot\text{CH}_2 \quad \text{H}_2\cdot\text{CH}_3 \]

Make sure to draw single electron arrows. Also, this is homolytic bond cleavage because one electron goes to each atom involved in bonding.

S18

\[ \text{CH}_3 \quad \rightarrow \quad \cdot\text{CH}_3 \quad \text{H}_2\cdot\text{C}^-\cdot\text{CH}_3 \]

\[ \text{CH}_3 \quad \rightarrow \quad \text{H}_3\cdot\text{CH}_2 \quad \text{H}_2\cdot\text{C}^-\cdot\text{CH}_3 \]

The stability of radicals is as follows: \(3^0 > 2^0 > 1^0 > \text{CH}_3\), and so the second pair of radicals is most likely to form. A secondary and a primary radical are formed, compared to the other products that contain a methyl radical.

S19

\[ \Delta H^0 = (\Delta H^0 \text{ Bonds Broken}) - (\Delta H^0 \text{ Bonds Formed}) \]

(a) \( \text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl} \quad \Delta H^0 = (\text{CH}_3\cdot\text{H} + \text{Cl}^-\text{Cl}) - (\text{CH}_3\cdot\text{Cl} + \text{H}^-\text{Cl}) = (439+242) - (356+431) = -106 \text{ kJ mol}^{-1} \)

(b) \( \text{CH}_4 + \text{Br}_2 \rightarrow \text{CH}_3\text{Br} + \text{HBr} \quad \Delta H^0 = (\text{CH}_3\cdot\text{H} + \text{Br}^-\text{Br}) - (\text{CH}_3\cdot\text{Br} + \text{H}^-\text{Br}) = (439+192) - (293+364) = -26 \text{ kJ mol}^{-1} \)

(c) \( \text{C}_2\text{H}_6 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{HCl} \quad \Delta H^0 = (\text{C}_2\text{H}_5\cdot\text{H} + \text{Cl}^-\text{Cl}) - (\text{C}_2\text{H}_5\cdot\text{Cl} + \text{H}^-\text{Cl}) = (423+242) - (352+431) = -118 \text{ kJ mol}^{-1} \)

(d) \( \text{C}_2\text{H}_6 + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{HBr} \quad \Delta H^0 = (\text{C}_2\text{H}_5\cdot\text{H} + \text{Br}^-\text{Br}) - (\text{C}_2\text{H}_5\cdot\text{Br} + \text{H}^-\text{Br}) = (423+192) - (293+364) = -42 \text{ kJ mol}^{-1} \)

(e) \( \text{(CH}_3\text{)}_3\text{CH} + \text{Cl}_2 \rightarrow \text{(CH}_3\text{)}_3\text{CCl} + \text{HCl} \quad \Delta H^0 = ((\text{(CH}_3\text{)}_3\text{C}^-\cdot\text{H}) + \text{Cl}^-\text{Cl}) - ((\text{(CH}_3\text{)}_3\text{C}^-\cdot\text{Cl} + \text{H}^-\text{Cl}) = (404+242) - (356+431) = -141 \text{ kJ mol}^{-1} \)
(f) \((\text{CH}_3)_3 \text{CH} + \text{Br}_2 \rightarrow (\text{CH}_3)_3 \text{CBr} + \text{HBr}\) \(\Delta H^0 = ((\text{CH}_3)_3 \text{C-H} + \text{Br-Br}) - ((\text{CH}_3)_3 \text{C-Br} + \text{H-Br}) = (404 + 192) - (297 + 364) = -65 \text{ kJ mol}^{-1}\)

(g) \(\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}\) \(\Delta H^0 = (\text{H-H} + \text{Cl-Cl}) - 2(\text{H-Cl}) = (435 + 242) - 2(431) = -185 \text{ kJ mol}^{-1}\)

(a) ethane; bromethane (b) 2,2-dimethylpropane; 1-bromo-2,2-dimethylpropane (c) 1-methylcyclobutane; (bromomethyl)cyclobutane, 1-bromo-1-methylcyclobutane, 1-bromo-2-methylcyclobutane, 1-bromo-3-methylcyclobutane

If the reaction were performed with \(\text{Cl}_2\) the product formation would not likely be as selective. This is due to the fact that the radical formation with chlorine is exothermic and the radical formation with bromine is endothermic. Hammond's postulate explains that the transition state of exothermic reaction will be more similar to the reactants, less like a radical, leading to a less selective radical formation. Whereas the transition state of an endothermic reaction will be more similar to the products, more radical like, leading to a selective radical formation.
The statistical distribution is calculated from the following: Total Carbons=3, Two external carbons are not unique, so probability=2/3 x 100% The center carbon probability is 1/3 x 100%. However, this is not likely, because the secondary carbon forms a much more stable radical than a primary radical.
As you'll learn, this is not the only reaction that can occur. Alkene chemistry will be discussed later on.

S25

Since the propene radical is more favorable than the propane radical, the $\Delta H^0$ would be lower than that of propane.

S26

An early transition state resembles the reactants, and a late transition state resembles the products (Hammond's postulate). The formation of the alkyl radical, propagation, is an early transition state (if you draw the reaction coordinate diagram for this step it should be endothermic), and the formation of the alkyl halide, termination, is a late transition state (if you draw the reaction coordinate diagram for this step it should be exothermic).

S27

(a)

\[ \text{ + Cl}_2 \xrightarrow{\text{Heat}} \text{Cl} \]

(b)

\[ \text{CH}_4 + \text{I}_2 \xrightarrow{\text{Heat}} \text{No Reaction, Endothermic} \]

(c)

\[ \text{ + Cl}_2 \xrightarrow{\text{Heat}} \text{Cl} \]

(d)

\[ \text{ + Br}_2 \xrightarrow{\text{Heat}} \text{Br} \]

Notice how the chlorination is not as selective as the bromination.

(e)
Assuming there is no primary chlorination, which in reality is likely not the case, only 2° and 3° hydrogen atoms are taken into account.

# 2°=2 Multiply by reactivity=Relative Yield => 8 Ratio= 8/(5+8) x 100%=62% 2°

# 3°=1 Multiply by reactivity=Relative Yield => 5 Ratio=5/(5+8) x 100%=38% 3°

27.d produces a much more pure mixture of products, and thus is more likely to be useful. Whereas, the chlorination, 27.c, of the same alkane potentially yields a mixture of products. This mixture would require a difficult separation, and is much less likely to be synthetically useful.

However, if a different haloalkane were desired, then this could be useful after purification. As you see later on, though, there are other methods of creating haloalkanes that are more selective.

The problem with this is that there are several secondary carbons, all about as equally likely to form a radical. There are three groups of unique hydrogens on the molecule, the two primary, the adjacent secondary, and the most interior secondary. Statistically speaking the inner two and second most outer two are equally likely to be brominated, there are equal number of hydrogens. If however, the second carbon is brominated, the following is the most favorable conformation.

Since the methyl group is much larger than the bromine, the rest of the carbon chain is adjacent to the bromine to reduce the steric interaction. It is also anti to the methyl group to further reduce steric interaction.

This problem could be broken up into the individual steps of the mechanism, and the ΔH° values for each step could be summed together to get the same value.
Bromination:

\[ \Delta H^0 = \text{Bonds Broken} - \text{Bonds Made} = (\text{Br-Br} + \text{Secondary C-H}) - (\text{Secondary C-Br} + \text{H-Br}) = (46 + 98.5) - (71 + 87) = -13.5 \text{ kcal mol}^{-1} \]

Iodination:

\[ \Delta H^0 = \text{Bonds Broken} - \text{Bonds Made} = (\text{I-I} + \text{Secondary C-H}) - (\text{Secondary C-I} + \text{H-I}) = (36 + 98.5) - (56 + 71) = +7.5 \text{ kcal mol}^{-1} \]

The main difference between the two is that the bromination is exothermic, whereas the iodination is endothermic. This explains why no reaction occurs in 27.b

\[ \text{S32} \]

The connectivity to a chlorine atom produces a highly polarized bond. This chlorination has further reactivity as you will see later on, taking advantage of the electron deficient carbon.

\[ \text{S33} \]

With any complete combustion reaction the only products are CO\(_2\) and H\(_2\)O.

(a) butane \(2\text{C}_4\text{H}_{10} + 13\text{O}_2 \rightarrow 8\text{CO}_2 + 10\text{H}_2\text{O}\)

(b) octane \(2\text{C}_8\text{H}_{18} + 17\text{O}_2 \rightarrow 16\text{CO}_2 + 18\text{H}_2\text{O}\)

(c) glucose \(\text{C}_6\text{H}_12\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}\)

(d) methanol \(4\text{CH}_3 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}\)

If any incomplete combustion occurred, carbon monoxide, CO, would be produced.

\[ \text{S34} \]

Butanal's combustion is more exothermic than that of 2-butanone. The heats of combustion tell us that 2-butanone is more stable, as it has a lower heat of combustion and thus less potential combustion energy in the compound.
Total number of abstractable Hydrogens = (3x3) + 1 = 10

Relative Reactivity = \frac{\text{Percentage}}{\text{Number of Hydrogens}}

Tertiary Reactivity = \frac{63}{1} = 63
Primary Reactivity = 37/9 = 4.1

The ratio between the two is 63/4.1 = 15

S39

The most endothermic step, most positive value of $\Delta H^0$, is most likely to be the rate limiting step. So, (2) is the rate limiting step.

S40

The inhibitor stops interrupts the propagation step, effectively terminating the reaction. If a carbon or halogen radical does form, it will react with the BHT to form the radical in problem 37. The phenoxy radical in BHT is unreactive, and the reaction stops there.

S41

First, convert the 2202 kJ/mol to kJ/kg.

\[
(-2202 \text{ kJ/mol}) \times (1 \text{ mol/44.1 g}) \times (1000 \text{ g/1 kg}) = -49,931 \text{ kJ/mol} \approx 50,000 \text{ kJ/kg}
\]

Since propane has the largest, most negative, heat of combustion it is likely to yield the best mileage. It, and natural gas, is commonly used as a fuel in buses.

S42

Propane: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

"Gasoline": $2C_8H_{18} + 27O_2 \rightarrow 16CO_2 + 18H_2O$

S43

The transition state with the chlorine radical is considered an early transition state and more similar to the reactants. The
transition state with the bromine radical is considered a late transition state and more similar to the products.

(c) NBS is a radical initiator.

As you may have seen in previous problems, radical halogenation with chlorine is less selective than with bromine. A good suggestion would be to use \( \text{Br}_2 \), as it will almost exclusively be added to the tertiary carbon if used in a 1:1 stoichiometric ratio. Whereas, the chlorine will also be added to the secondary carbons, thus producing a non-uniform product.

From Hammond's Postulate, an early transition state indicates an endothermic reaction.