

Chem 2100, "Organic Chemistry I" WS07, Dr. Rainer Glaser

Exam #2

"Radicals and Radical Chain Reactions."

Friday, 3-23-2007, 9:00-9:55 am

Name:

Answer Key

Question 1. Radical Stability.	20	
Question 2. Radical Halogenation I: Products.	20	
Question 3. Radical Halogenation II: Mechanisms.	20	
Question 4. Autoxidation.	20	
Question 5. Initiation & Inhibition.	20	
Total	100	

Question 1. Radical Stability. (20 points)

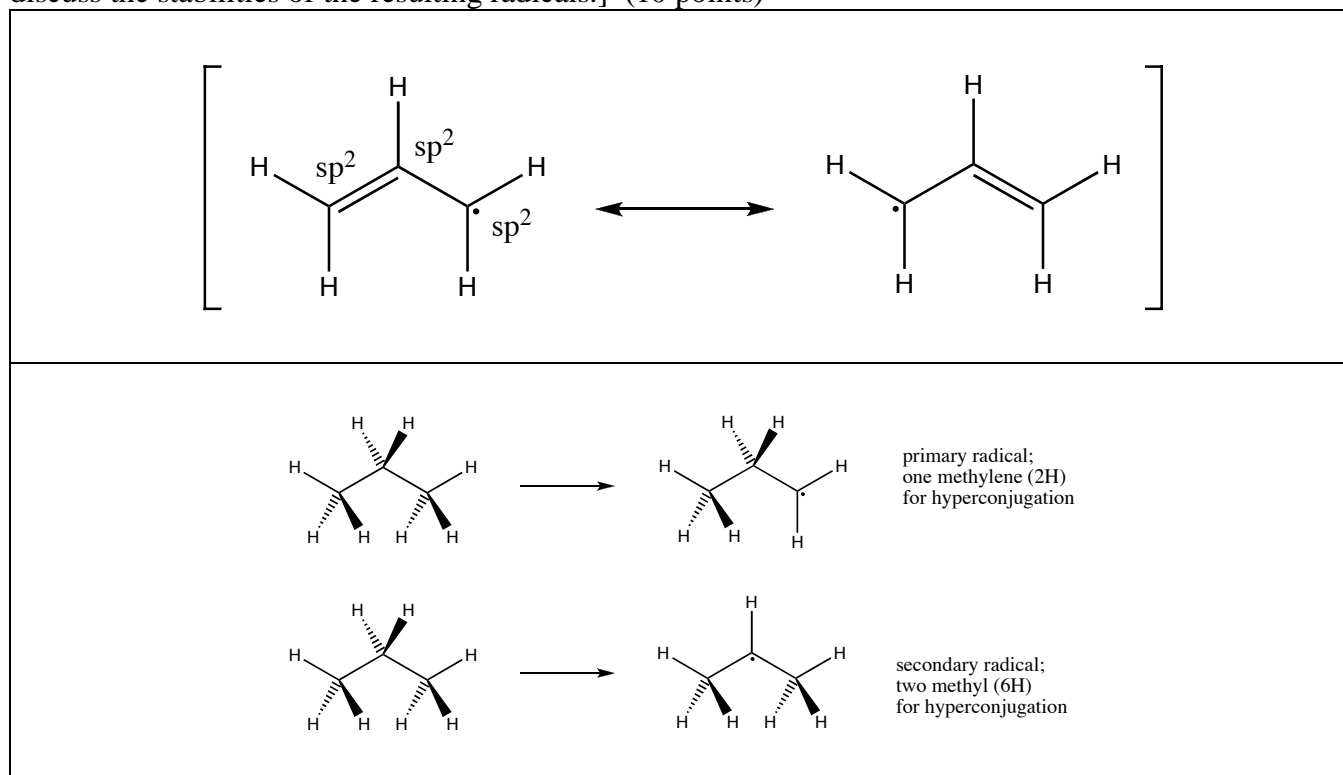
(a) Baseline knowledge on bond dissociation energies. (10 points)

Homolysis $X_2 \rightarrow 2 X^\bullet$ is the most facile for which halogen? (F, Cl, Br, I)	I
Homolysis $X_2 \rightarrow 2 X^\bullet$ is the most endothermic for which halogen? (F, Cl, Br, I)	Cl
Bond dissociation energy (BDE) for methane , $CH_4 \rightarrow CH_3^\bullet + H^\bullet$, in kcal/mol?	104
Is the BDE for fluoromethane , $FCH_3 \rightarrow FCH_2^\bullet + H^\bullet$, smaller, larger, or about the same as compared to the BDE for methane , $CH_4 \rightarrow CH_3^\bullet + H^\bullet$?	Larger
Is the BDE for HCl , $HCl \rightarrow H^\bullet + Cl^\bullet$, smaller, larger, or about the same compared to the BDE for HBr , $HBr \rightarrow H^\bullet + Br^\bullet$?	Larger

(b) Allyl radical is formed by H-abstraction of one methyl H-atom from **propene**.

IN THE FIRST BOX: Draw the structure of allyl radical and indicate the hybridization of every C-atom.

IN THE SECOND BOX: Explain why the H-abstraction from propene's methyl group is much easier than any H-abstraction from **propane**. [Hint: Write down the equations for H-abstraction from propane and discuss the stabilities of the resulting radicals.] (10 points)



Question 2. Radical Halogenation I: Products. (20 points)

(a) Draw the structures and provide the names of the **four** products of the **chlorination of methane**. (8 points)

CH_3Cl , chloromethane; CH_2Cl_2 , dichloromethane or methylenechloride;
 CHCl_3 , trichloromethane or chloroform; CCl_4 , tetrachloromethane.

(b) Consider the **chlorination of ethane** and assume that the reaction is carried out with a **very large excess of ethane** (i.e. 1 Cl_2 molecule for every 1,000 ethanes). Draw the structure(s) of the major product(s). Briefly explain why other possible products are not formed in high yield. (4 points)

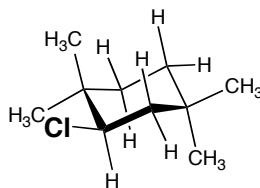
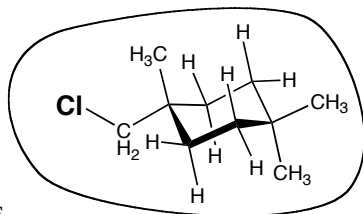
$\text{H}_3\text{C}-\text{CH}_2\text{Cl}$, chloroethane

To form a dichloroethane molecule requires the collision of a Cl radical with a chloroethane. The chances for that event to happen are very small because of the huge ethane excess. Once all the Cl_2 has been used, the ratio ethane : chloroethane will still be close to 1000.

(c) Consider the **monochlorination of 1,1,4,4-tetramethylcyclohexane**. (8 points)

IN THE FIRST BOX: Draw the structures of the **two** products, each in its best conformation. Circle the one product that is **statistically** most likely to be formed.

IN THE SECOND BOX: Considering selectivities of 1 : 4 : 5, respectively, for 1°, 2° and 3° carbons, respectively, compute the **approximate** yields of the two products of monochlorination. Show your work.



$$12x \cdot 1 + 8x \cdot 4 = 100\%$$

$$12x + 32x = 44x = 100\% \rightarrow x \approx 2.3$$

27.6% chlorination of methyl

73.6% chlorination of the methylene

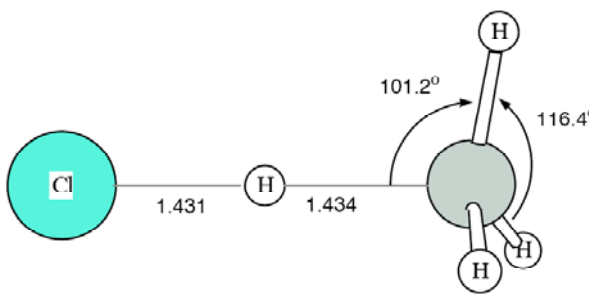
Question 3. Radical Halogenation II: Mechanisms. (20 points)

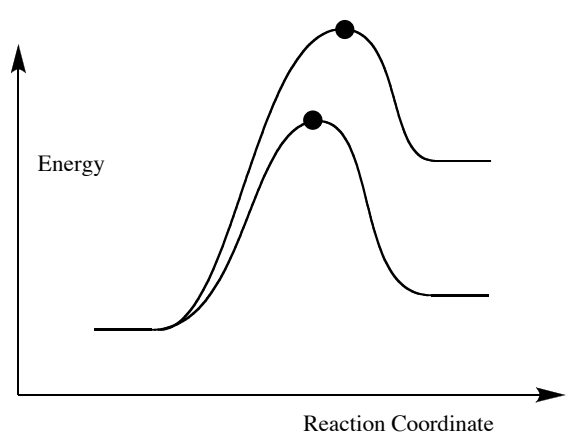
(a) Baseline knowledge on radical chain mechanism for chlorination of methane. (10 points)

What is needed to start the initiation reaction?	Heat, light, or initiator.
Reaction of the first chain propagation step?	$\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{Cl-H} + \cdot\text{CH}_3$
Reaction in the second chain propagation step?	$\text{Cl-Cl} + \cdot\text{CH}_3 \rightarrow \text{Cl}\cdot + \text{Cl-CH}_3$
Which chain propagation step is rate-limiting?	Step 1
Provide one termination reaction that will take a methyl radical away.	$\text{Cl}\cdot + \cdot\text{CH}_3 \rightarrow \text{Cl-CH}_3$

(b) ON THE LEFT, the transition state structure is shown for the **H-atom abstraction by chlorine from methane**. For every value provided for the chlorine reaction, indicate whether the respective value would be “**smaller**” or “**larger**” for the case of the bromine reaction. **ON THE RIGHT**, the reaction diagram is shown for the first step of the radical chain chlorination of methane. Include the respective diagram for the bromination reaction. (10 points)

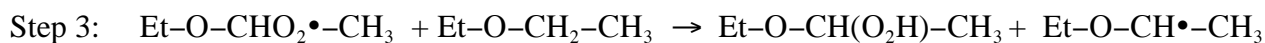
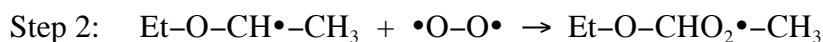
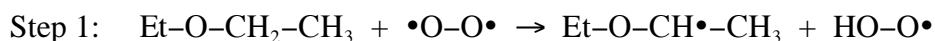
Larger: $d(\text{Br-H})$, $d(\text{H-C})$, $\angle(\text{H-C-H})$
 Smaller: $\angle(\text{X}\cdots\text{H-C-H})$



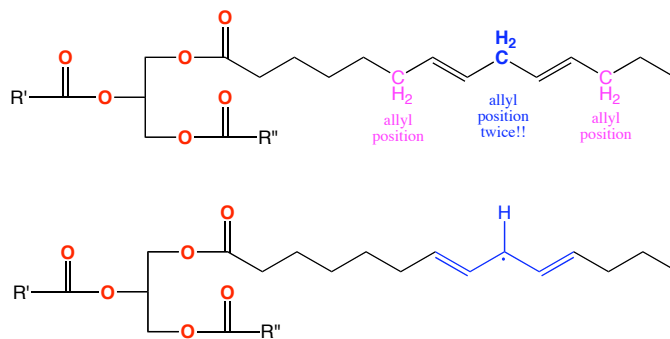


Question 4. Autoxidation. (20 points)

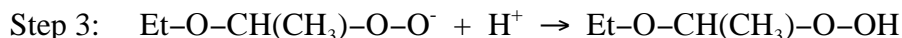
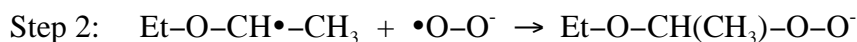
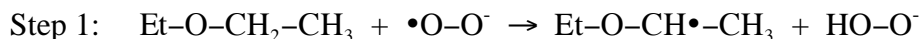
(a) **Diethyl ether**, $\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$, is slowly oxidized by air. Oxygen molecules are diradicals and they can initiate radical reactions. Show the **three reaction steps** involved in the formation of $\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}(\text{CH}_3)-\text{O}-\text{O}-\text{H}$ from $\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ and O_2 . (9 points)



(b) The fat molecule shown below contains one **unsaturated fatty acid** and the two other fatty acid moieties are abbreviated as R' and R'' . The slow oxidation of this fat molecule by O_2 *in vivo* (i.e. in the living body) is initiated by abstraction of one H-atom by O_2 . With your knowledge about radical stabilities and radical chain reactions decide which H-atom is most likely to be abstracted. Draw the resulting radical and justify your decision with a few good words. (6 points)



(c) **Superoxide** is the radical anion O_2^- . Superoxide reacts fast with hydrocarbons by H-abstraction. Consider the reaction of $\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3$ with superoxide. Can you suggest a plausible mechanism for the formation of $\text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}(\text{CH}_3)-\text{O}-\text{O}-\text{H}$? [Hint: This mechanism contains radical reactions but it does not have to be a radical chain mechanism.] (5 points)

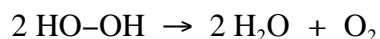


Question 5. Initiation & Inhibition. (20 points)

(a) Hydrogen peroxide slowly reacts to form water and O₂. The first step of this reaction is the dissociation of O₂H₂ into two hydroxyl radicals.

IN THE FIRST BOX: Provide a balanced equation for the overall reaction. (2 points)

IN THE SECOND BOX: Heating accelerates the OO bond dissociation of O₂H₂. Explain based on your knowledge about Boltzmann distributions. [Hint: Draw two Boltzmann distributions for low and high temperatures.] (8 points)



See notes for Boltzmann distributions.

If $T_1 < T_2$: (a) $\text{Max}(T_2)$ is to the right of $\text{Max}(T_1)$, (b) $\text{Max}(T_2)$ lower than $\text{Max}(T_1)$, and (c) the Boltzmann tail covers a larger area at T_2 compared to T_1 .

(b) Suppose some superoxide was formed in your body. Do not panic! Your body has ways to get rid of superoxide either with radical chemistry or with reduction chemistry. In your answers, use complete structures (all atoms, all bonds, all lone pairs and unpaired electrons, charges).

IN THE FIRST BOX: The radical way to scavenge superoxide involves a "radical trap." Show this reaction using phenol as the trap. (6 points)

IN THE SECOND BOX: The reduction chemistry involves the enzymatic conversion to hydroxide ion. Show the balanced equation for the reduction of superoxide with electrons to hydroxide ions. [Hint: Use protons to balance the equation.] (4 points)

