Chem 220 - Organic Chemistry

Problem Set 3

Solution Set

Chapter 4, Chemical Reactions

Due: Monday, September 27, 2010

Dualism vs. Substitution Theory

The prevailing theory of organic structure in the early 19th century was Dualism or the Electrochemical Theory, principally championed by Berzelius. Since inorganic sodium chloride could be considered as Na^+Cl^-, then an alkyl halide such as RCl could be thought of as R^+Cl^-. The R group or "radical" of its day, was thought to be immutable, the carbons and hydrogens behaving as though they were an element. Liebig (German) and Dumas (French), influential chemists of the day, published a joint paper (1837), *On the Present State of Organic Chemistry*, extolling the concept and claiming all that was left to do in organic chemistry was to identify these immutable radicals (benzoyl, ethyl, acetyl, etc.) As the story goes, a Parisian reception at the Tuileries was to change all of this. [*The Tuilerie Gardens was one of the images in Mussorgsky's "Pictures at an an Exhibition", composed in 1874 for piano and later orchestrated by Ravel. The Tuileries selection is here. For the history of this composition and background music, go here. (At Yale, try this.*] The guests were discomforted by fumes from the burning candles. Dumas was called in as a consultant. He found that the waxes (fatty esters) had exchanged chlorine for hydrogen, the culprit being the by-product hydrogen chloride. [*This story is likely apocryphal. It was told by August Hofmann at a eulogy for Dumas (1884). If the event did occur, it is more likely that the bleaching of candle wax involved addition of chlorine to double bonds. Nonetheless, Dumas did investigate substitution reactions.*]

The concept of exchanging electropositive hydrogen for electronegative chlorine was anathema to dualism. Liebig was not enamored with substitution. Why shouldn't he be? After all Liebig and Wöhler had done precisely this in 1832 during their work on the benzoyl radical (C_7H_5O). They had converted benzaldehyde [$(C_7H_5O)H$] into benzoyl chloride [$(C_7H_5O)Cl$] by the action of chlorine. So disenchanted was Liebig with the controversies regarding theory in organic chemistry, by 1840 he turned his attention to the practical applications of agricultural chemistry. Thus arose Liebig's beef extract.

Dumas's student, Laurent, not one to shirk from controversy, was bold enough to call the process substitution rather than exchange. Thus, Substitution Theory. Moreover, Dumas (1838) was able to substitute

Jean-Baptiste-Andrè Dumas (1800-1884)

three of the four hydrogens of acetic acid for chlorine to form trichloroacetic acid, which had properties to acetic acid. The recognition of these similar properties led to early Type Theory. In 1842, Melsen, a student of Dumas, reversed Dumas's experiment by reducing trichloroacetic acid to acetic acid by the action of zinc metal. The promulgation of Substitution Theory gave the wry wit of Wöhler, a.k.a., S. C. H. Windler, an opportunity to shine. At the beginning of the 20th century free radicals were detected and named free radicals to distinguish them from the older radicals of Radical Theory of the early 19th century. During the 19th century chemists tried to isolate the older radicals to no avail. When Kolbe and Frankland thought they had isolated methyl, they actually had made the dimer of methyl, ethane. The very process of substituting chlorine for hydrogen is a free radical reaction.


Study the Alkane Module in Organic Reactions Go Online (ORGO).

Alexander Borodin (1833-1887), the accomplished Russian composer, did not quit his day job. He was a Professor of Organic Chemistry at St. Petersburg although he is more famous as a composer. He unknowingly discovered a method for the decarboxylation of carboxylic acids (via their silver salts) in the presence of bromine to afford an alkyl bromide with the liberation of CO_2. The reaction proceeds through a free radical chain mechanism. Borodin did not isolate the alkyl bromide. That accomplishment rested with Herr und Frau Hunsdiecker (1942), after whom the reaction is named.

$CH_3CH_2CO_2Ag + Br_2$ -----> $CH_3CH_2Br + CO_2 + AgBr$
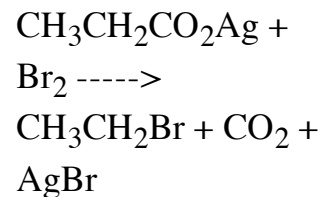
1. Determine the percent of each of the constitutional monochloro isomers expected from the chlorination of 2-methylbutane. Show work.

There are four different carbons in the structure. Multiply the number of hydrogens by the relative reactivity (for chloination) of the type of C-H bond. divide the product by the sum of products (23.5) to get the percentages.
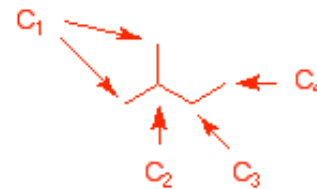
Carbon Atom	# of Hydrogens	Relative Reactivity	Product	Fraction x 100
C1 primary (1-chloro-2-methylbutane)	6	1	6	25.5%
C2 tertiary (2-chloro-2-methylbutane	1	5.5	5.5	23.4%
C3 secondary (2-chloro-3-methylbutane)	2	4.5	9	38.2%
C4 primary (1-chloro-3-methylbutane)	3	1	3	12.8%

2. Show the initiation and propagation steps for the free radical chlorination of cyclooctane. *See 2b.*

a) Using Bond Dissociation Energies (BDEs), calculate the ΔH° for each relevant step and for the overall reaction. Show work. *The initiation step is not included in the the heat of the reaction. It is catalytic. It gets things going. In the 1st propagation step a secondary C-H bond is broken (+95 kcal/mol) while H-Cl is formed (-103 kcal/mol). The difference is -5 kcal/mol. The second propagation step is treated the same way. summing the two reactions gives -27kcal/mol for the overall reaction.*

b) Calculate the heat of formation (ΔH$_f$°) of chlorocyclooctane. Use Heat of Formation Tables. Show work.

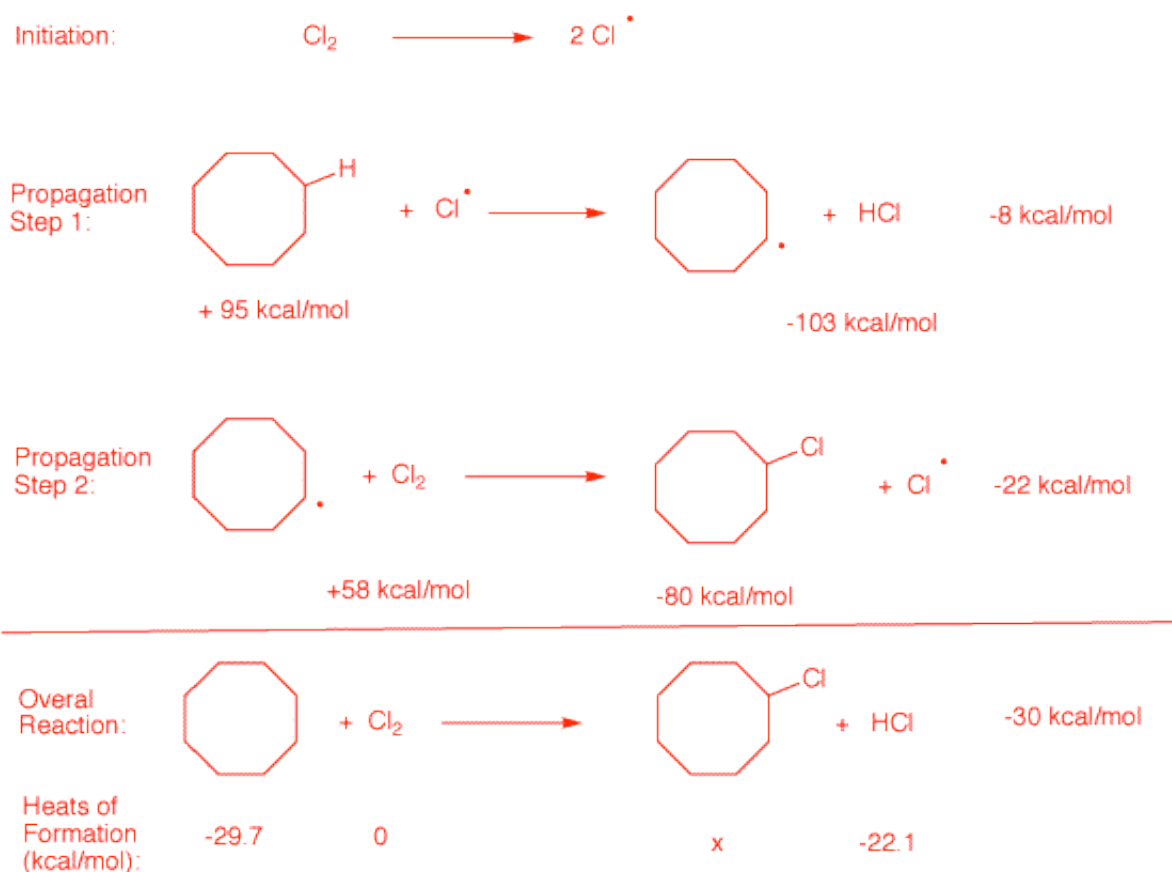*Using heats of formation one can get a value for cyclooctane.*

chlorine and HCl. The overall heat of the reaction was determined previously. Thus, the heat of formation of chlorocycloctane may be calculated.

$\Delta H^o{}_{rxn} =$

$\Delta H^o{}_{products}$ −

$\Delta H^o{}_{reactants}$

−30 = (x −22.1) − (−29.7 + 0)

−30 = x + 7.6

x = −37.6 kcal/mol for the heat of formation of chlorocyclooctane.

Initiation: Cl$_2$ → 2 Cl•

Propagation Step 1: [octane ring with H] + Cl• → [octane ring radical] + HCl −8 kcal/mol

+ 95 kcal/mol   −103 kcal/mol

Propagation Step 2: [octane ring radical] + Cl$_2$ → [octane ring with Cl] + Cl• −22 kcal/mol

+58 kcal/mol   −80 kcal/mol

Overal Reaction: [octane ring] + Cl$_2$ → [octane ring with Cl] + HCl −30 kcal/mol

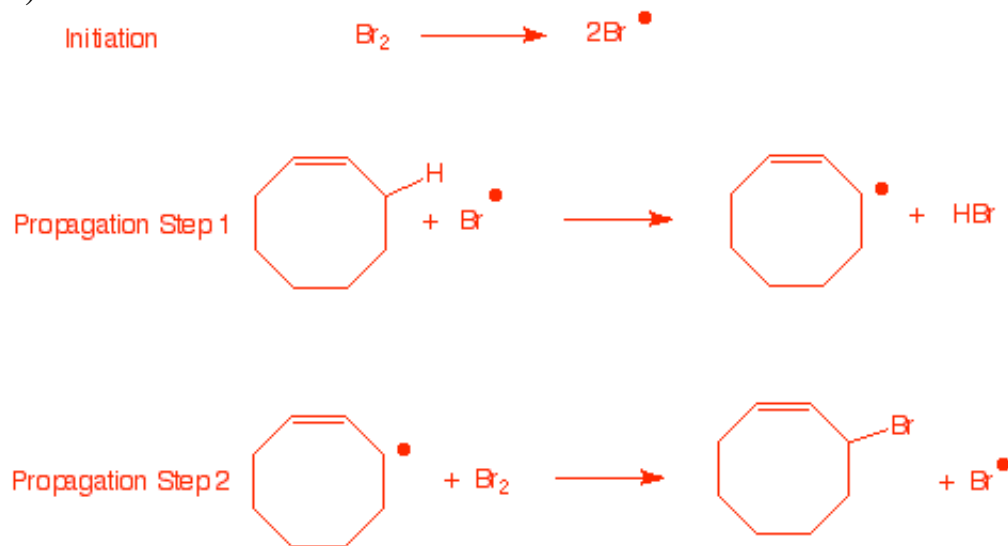Heats of Formation (kcal/mol): −29.7   0   x   −22.1

3. When cis-cyclooctene undergoes radical chain bromination, only one monobromination product is isolated.

a) Draw the structures of the possible monobromination products. Using [BDEs](), explain which one is formed. *The weakest C-H bond is the one that is allylic. It overlaps with the with the π-bond. Only the circled bromide will form.*

BDE = 108 kcal/mol

BDE = 87 kcal/mol

BDE = 95 kcal/mol
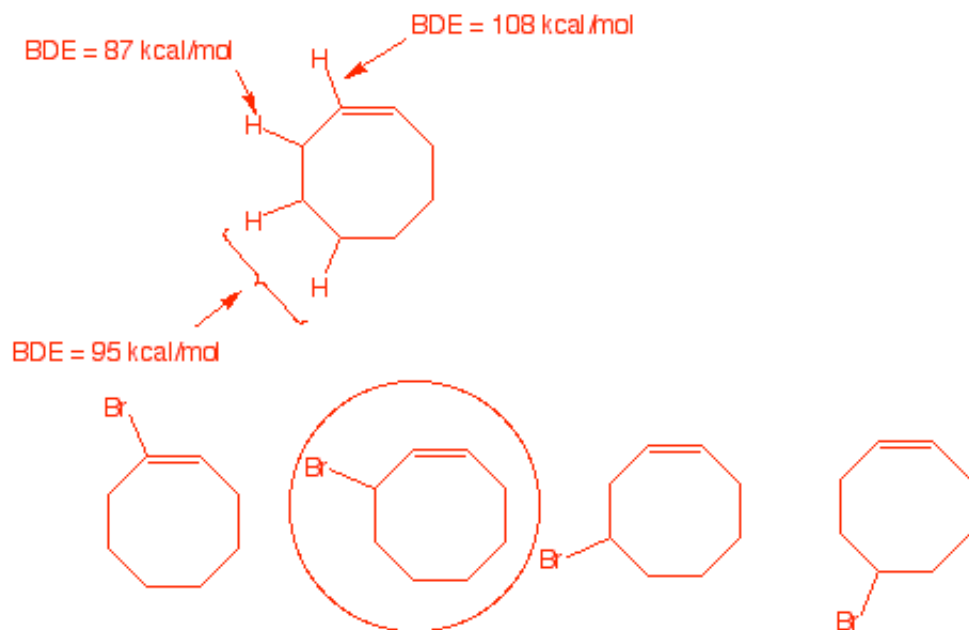
b) Write a radical chain mechanism for this reaction.

Initiation Br_2 ⟶ 2 Br •

Propagation Step 1

Propagation Step 2

For this reaction to be successful, bromine must be present in low concentration. <u>N</u>-<u>B</u>romo<u>s</u>uccinimide (**1**, NBS) is often used for this purpose (Wohl-<u>Ziegler</u> reaction). Traces of HBr cause the formation of succinimide **2** and bromine as shown.

c) Carbon tetrachloride is the classic solvent for this reaction. Benzene may also be used as a solvent but not toluene (methylbenzene). Explain why carbon tetrachloride and benzene are acceptable solvents but not toluene. *CCl₄ has no CH bonds and the CH bonds in benzene, like the vinylic CH bonds of an alkene, have a BDE = 108 kcal/mol. The methyl hydrogens of toluene are benzylic CH*

bonds: BDE = 85 kcal/mol. They are too reactive. The benzyl radical is resonance stabilized.

d) The NBS free radical allylic bromination of 1-methyl-1-cyclohexene (**1**) is not a good preparative reaction. Although the five allylic bromides **2-6** are the possible products, only bromides **3** and **6** are formed. Still, this is a difficult separation.
i) How many unique allylic sites are there in alkene **1**? Show them. *There are three: A = methyl; B = methylene; C = methylene.*
ii) Which bromides are formed from each of the sites in part i)? *The bromides are formed in the second propagation step. The resonance structures of the radicals are shown along with the bromides that form.*
iii) What does the fact that only **3** and **6** are formed tell you about the allylic methylene group vs. the allylic methyl group? *Ziegler*
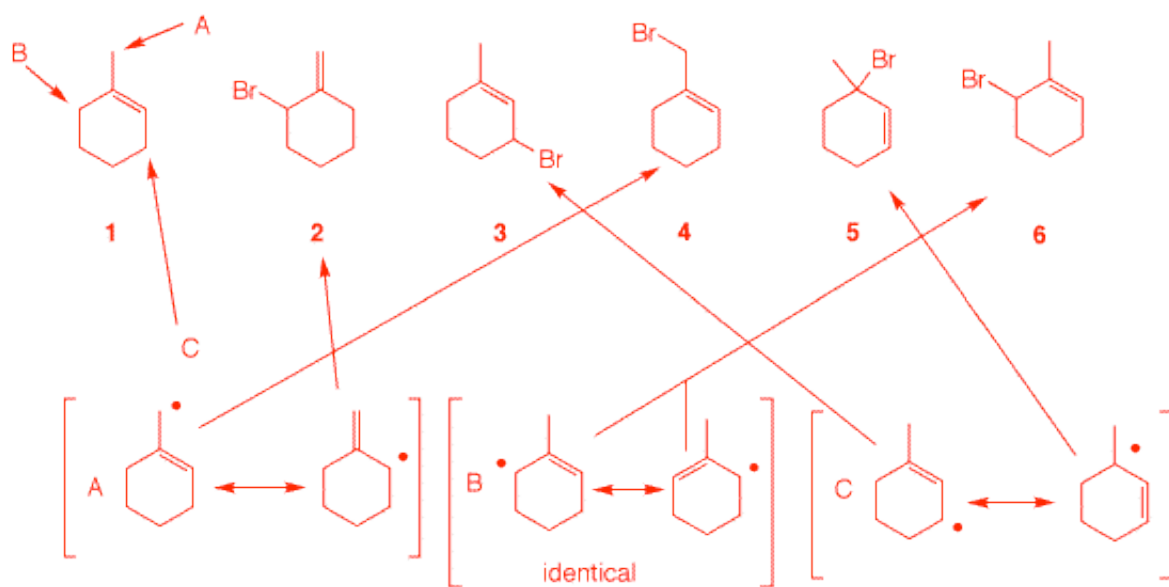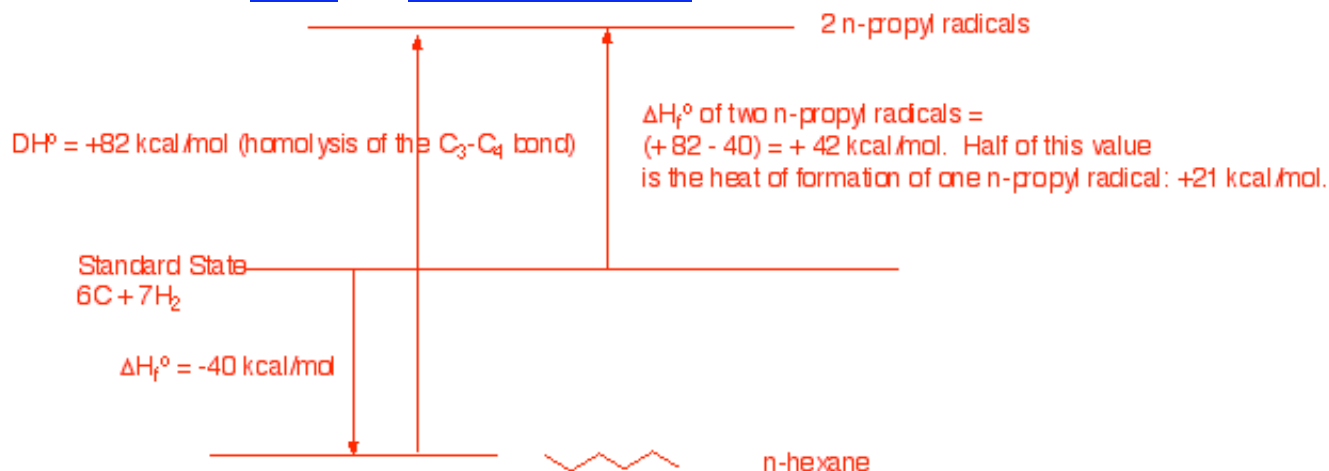
*recognized early on that allylic methyl groups are less reactive than allylic methylene groups. Generally, the bromide with the more substituted double bond is preferred: Excluding path **A**, **C** prefers **3** and not **5**.*

iv) How could you have anticipated this relative reactivity?

Non-allylic methylenes are also more reactive than non-allylic methyl groups.

4. After reading "Hess's Law of Constant Heat Summation" and/or "Heats of Combustion, Heats of Formation, and Bond Dissociation Energies (Powerpoint)" in the Thermochemistry Module, answer the following :

a) Draw a Standard State diagram that illustrates how to calculate the ΔH_f^o of an n-propyl radical. Make use of the BDEs and Heats of Formation Tables.

DH° = +82 kcal/mol (homolysis of the C_3-C_4 bond)

2 n-propyl radicals

ΔH_f^o of two n-propyl radicals = (+ 82 - 40) = + 42 kcal/mol. Half of this value is the heat of formation of one n-propyl radical: +21 kcal/mol.

Standard State
$6C + 7H_2$

ΔH_f^o = -40 kcal/mol

n-hexane

b) How does your answer in a) compare with the value in the BDEs table?

Oops! n-Propyl radical is not in the BDE Table. It should have read in the Heats of Formation Table. It is not there either. But ethyl radical is at +26 kcal/mol. Using the rule of -5 kcal/mol/CH2, that

woulf give +21 kcal/mol for n-propyl radical. good agreement.

c) Using the value obtained in a), illustrate and calculate the C_3-C_4 bond energy in n-hexane.

Here we work the problem in reverse. In a) we see that

$DH_f^o(R\text{-}R) + DH^o(R\text{-}R) = 2 \times DH_f^o(R\cdot)$, therefore

$DH^o(R\text{-}R) = [2 \times DH_f^o(R\cdot)] - DH_f^o(R\text{-}R)$

$DH^o(R\text{-}R) = [2 \times 21] - (-40) = 82$ kcal/mole