Chem 220 - Organic Chemistry

Problem Set 3

Chapter 4, Chemical Reactions

Due: Monday, February 11, 2013

Solution Set

Dualism vs. Substitution Theory

The prevailing theory of organic structure in the early 19th century was Dualism or the Electrochemical Theory, principally championed by <u>Berzelius</u>. 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. <u>Liebig</u> (German) and Dumas (French), influential chemists of the day, published a joint paper (1837), *<u>On the Present State of Organic Chemistry</u>*, 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 <u>Tuileries</u> 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 <u>here</u>. For the history of this composition and background music, go <u>here</u>.(<u>On YouTube, try this</u>.)*] 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 <u>August Hofmann</u> 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 <u>Liebig</u> and <u>Wöhler</u> had done precisely this in 1832 during their work on the benzoyl radical (C_7H_5O). <u>They</u> 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 three of the four hydrogens of acetic acid for chlorine to form <u>trichloroacetic acid</u>, which had properties to acetic acid. The recognition of these similar
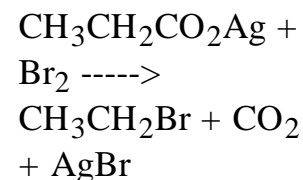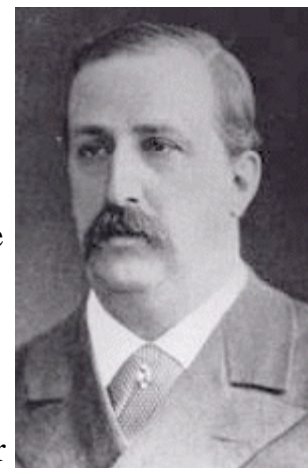
properties led to early Type Theory. In 1842, Melsen, a student of Dumas, reversed Dumas's experiment by reducing trichloroacetic acid to acetic acid by the action of zinc metal. The promulgation of Substitution Theory gave the wry wit of Wöhler, a.k.a., S. C. H. Windler, an opportunity to shine. At 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.

Jean-Baptiste-Andrè Dumas (1800-1884)

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

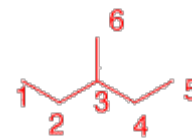Alexander Borodin (1833-1887), the accomplished Russian composer, did not quit his day job. He was a Professor of Organic Chemistry in St. Petersburg although he is more famous as a composer. He unknowingly discovered a method for the decarboxylation of carboxylic acids (via their silver salts) in the 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 eponomously 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.

C_1 and C_5 are equivalent primary carbons. Substitution of any one of these 6 hydrogens with chlorine will lead to 1-chloro-3-methylpentane. C_6 is primary but different from C_1

and C_5. Why? There are four equivalent secondary hydrogens (C_2, C_4) and one tertiary hydrogen at C_3.

Carbon Atom	# of Hydrogens	Relative Reactivity	Product	Fraction x 100
$C_{1(5)}$ primary (1-chloro-3-methylpentane)	6	1	6	18.5%
C_6 primary (1-chloro-2-ethylbutane)	3	1	3	9.2%
$C_{2(4)}$ secondary (2-chloro-3-methylpentane)	4	4.5	18	55.5%
C_3 tertiary (3-chloro-3-methypentane)	1	5.5	5.5	16.9%
Sum of Product column			32.5	100%

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

a) Using Bond Dissociation Energies (BDEs), calculate the ΔH^o for each relevant step and for the overall reaction. Show work. *The initiation step is not included in 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 -8 kcal/mol. The second propagation step is treated the same way. Summing the two reactions gives -30 kcal/mol for the overall reaction.*

b) Calculate the heat of formation ($\Delta H_f{}^o$) of chlorocycloheptane. Use Heat of Formation Tables. Show work.
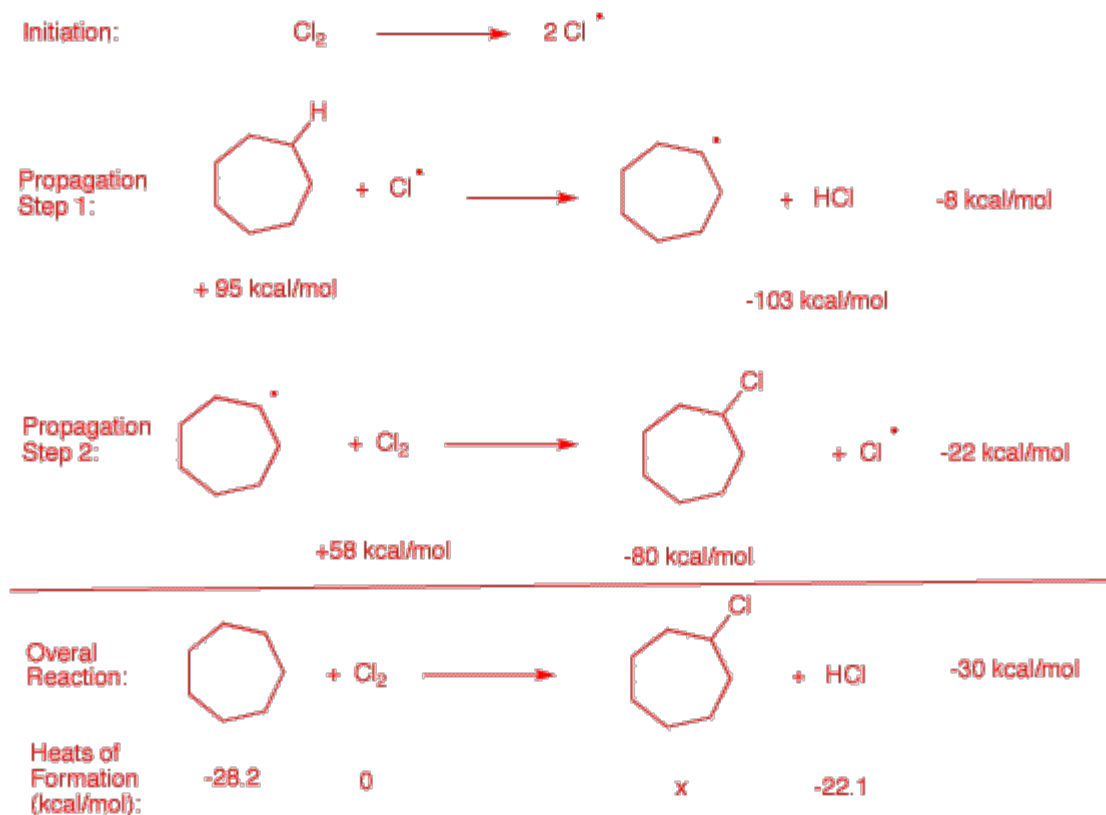
Using heats of formation one can get a value for cycloheptane, chlorine and HCl. The overall heat of the reaction was determined previously. Thus, the heat of formation of chlorocycloctane may be calculated.

$\Delta H^o{}_{rxn} = \Delta H^o{}_{products} - \Delta H^o{}_{reactants}$

$-30 = (x - 22.1) - (-28.2 + 0)$

$-30 = x + 6.1$

$x = -36.1$ kcal/mol for the

Initiation: $Cl_2 \longrightarrow 2\, Cl\, ^\bullet$

Propagation Step 1:

$+\ Cl\,^\bullet \longrightarrow$ + HCl   -8 kcal/mol

+ 95 kcal/mol   -103 kcal/mol

Propagation Step 2:

$+\ Cl_2 \longrightarrow$ + Cl $^\bullet$ -22 kcal/mol

+58 kcal/mol   -80 kcal/mol

Overall Reaction:

$+\ Cl_2 \longrightarrow$ + HCl   -30 kcal/mol

Heats of Formation (kcal/mol):   -28.2   0   x   -22.1
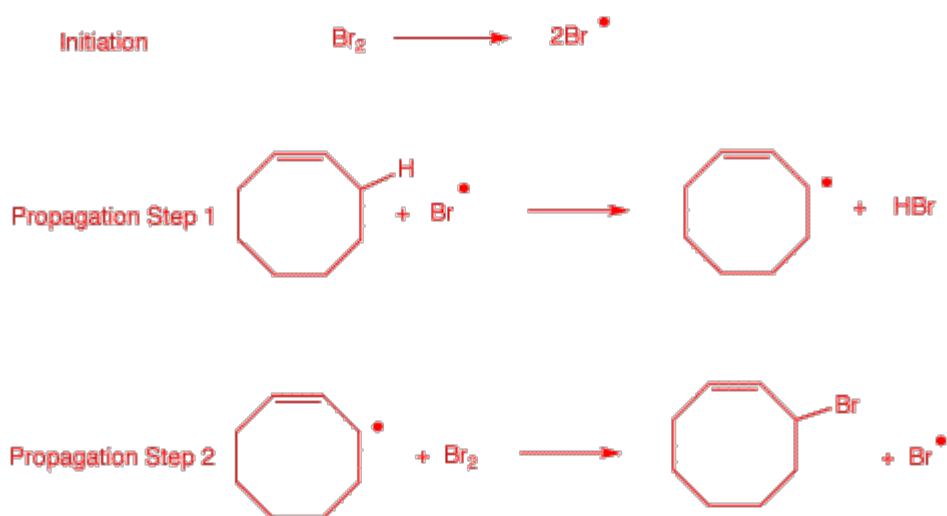
heat of formation of chlorocycloheptane..

3. When cis-cyclooctene undergoes radical chain bromination, only one monobromination product is isolated.
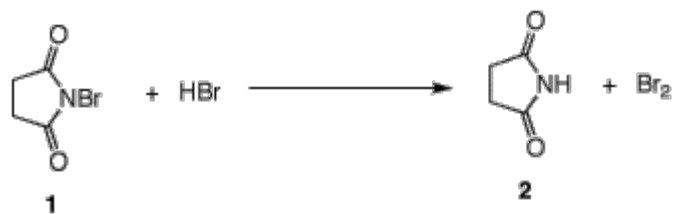
a) Draw the structures of the possible monobromination products. Using [BDEs](#), explain which one is formed. *The weakest C-H bond is the one that is allylic. It overlaps with the with the π-bond. Only the circled bromide will form.*

b) Write a radical chain mechanism for this reaction.

Initiation $Br_2 \longrightarrow 2Br\,^\bullet$

Propagation Step 1

$+\ Br\,^\bullet \longrightarrow$ + HBr

Propagation Step 2

$+\ Br_2 \longrightarrow$ + Br $^\bullet$

For this reaction to be successful, bromine must be present in low concentration. N-Bromosuccinimide (**1,**

NBS) is often used for this purpose (Wohl-Ziegler) reaction). Traces of HBr cause the formation of succinimide **2** and bromine as shown.
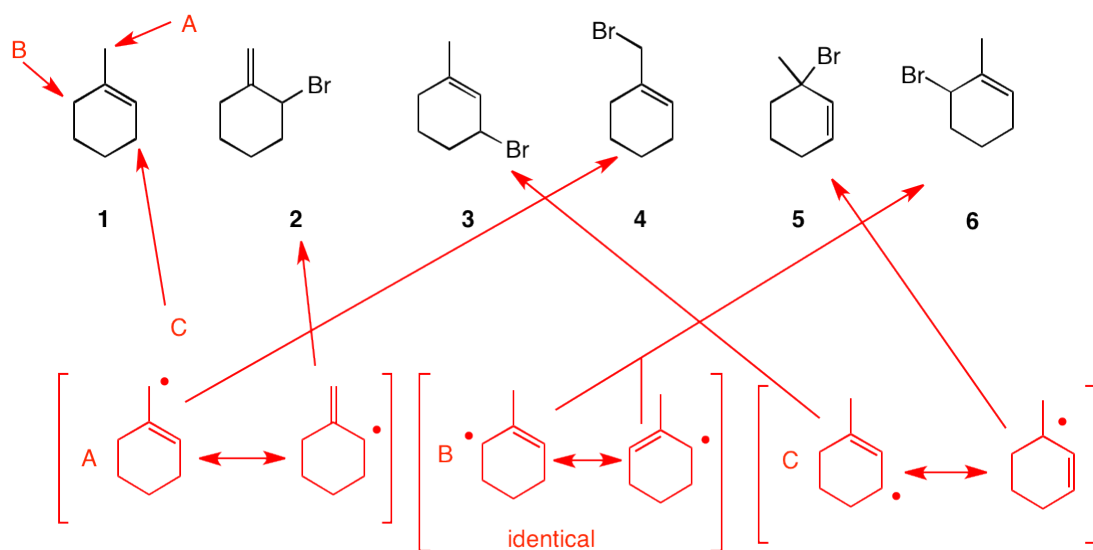

c) Carbon tetrachloride is the classic solvent for this reaction. Benzene may also be used as a solvent but not toluene (methylbenzene). Explain why carbon tetrachloride and benzene are acceptable solvents but not toluene. *CCl_4 has no CH bonds and the CH bonds in benzene, like the vinylic CH bonds 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? *Karl Ziegler recognized early on that allylic methyl groups are less reactive than allylic*
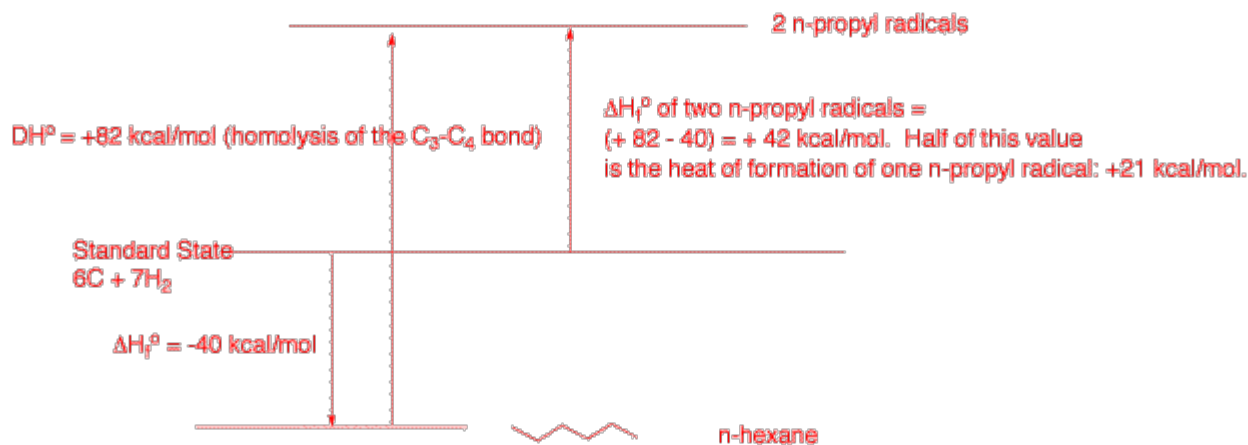
methylene groups. Generally, the bromide with the more substituted double bond is preferred: Excluding path A, C prefers 3 and not 5.

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.

b) How does your answer in a) compare with the value in the Heats of Formation table?

You will notice that an n-propyl radical is not listed but an ethyl radical has a heat of formation of +26 kcal/mol. Since an n-propyl radical has one more -CH$_2$- than an ethyl radical,the heat of formation of the n-propyl radical should be -5 kcal/mol less than an ethyl radical or ΔH_f^o = +21 kcal/mol. On the money!

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:*

$\Delta H_f^o(R\text{-}R) + \Delta H^o(R\text{-}R) = 2 \times \Delta H_f^o(R\cdot)$, therefore

$\Delta H^o(R\text{-}R) = [2 \times \Delta H_f^o(R\cdot)] - \Delta H_f^o(R\text{-}R)$

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

PS3