

## Chem 220 - Organic Chemistry

### Problem Set 3 -Solution Set

#### Chapter 4, Chemical Reactions

Due: Monday, September 28, 2009

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### 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  $\text{Na}^+\text{Cl}^-$ , then an alkyl halide such as  $\text{RCl}$  could be thought of as  $\text{R}^+\text{Cl}^-$ . 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 Tuileries Gardens was one of the images in Mussorgsky's "Pictures at 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 ( $\text{C}_7\text{H}_5\text{O}$ ). [They](#) had converted benzaldehyde [ $(\text{C}_7\text{H}_5\text{O})\text{H}$ ] into benzoyl chloride [ $(\text{C}_7\text{H}_5\text{O})\text{Cl}$ ] 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



**Jean-Baptiste-Andr  Dumas (1800-1884)**

exchange. Thus, Substitution Theory. Moreover, Dumas (1838) was able to substitute 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 [W hler](#), 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).

1. Determine the percent of each of the constitutional monochloro isomers expected from the chlorination of 2-methylpentane. Show work.

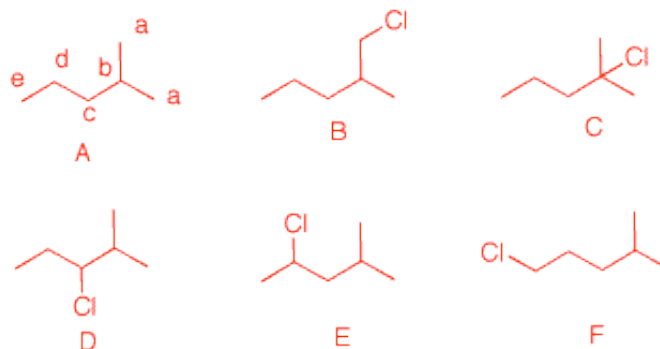
*2-Methylpentane (A) has five constitutional isomers. Positions a-e are labeled in A. The monochloro compounds are B-F. Relative reactivity for chlorination:  $1^\circ = 1$ ;  $2^\circ = 4.5$ ;  $3^\circ = 5.5$ . Multiply the number of hydrogens at each, primary, secondary or tertiary site by its relative reactivity. Add these values to obtain 32.5. Divide each product to obtain a fractional part. Convert to a percentage. Although a and e are methyl groups, they are considered separately because they lead to different products:*

*a ---> B*

*b ---> C*

*c ---> D*

*d ---> E*



| Position | #H's | Rel. React. | #H's x Rel. React. | (#H's x Rel. React.)/32.5 | %    |
|----------|------|-------------|--------------------|---------------------------|------|
| a        | 6    | 1           | 6                  | 0.185                     | 18.5 |
| b        | 1    | 5.5         | 5.5                | 0.169                     | 16.9 |
| c        | 2    | 4.5         | 9                  | 0.277                     | 27.7 |
| d        | 2    | 4.5         | 9                  | 0.277                     | 27.7 |
| e        | 3    | 1           | 3                  | 0.092                     | 9.2  |

$e \rightarrow F$

|  |  |     |      |       |     |
|--|--|-----|------|-------|-----|
|  |  |     |      | 0.002 | 0.2 |
|  |  | Sum | 32.5 | 1.000 | 100 |

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

a) Using Bond Dissociation Energies (BDEs), calculate the  $\Delta H^\circ$  for each relevant step and for the overall reaction. Show work.

b) Calculate the heat of formation ( $\Delta H_f^\circ$ ) of chlorocycloheptane. Show work.

*The initiation step does not contribute to the heat of the reaction.*

*Low concentrations of radicals are produced.*

*BDEs are from the table. Representative examples are used.*

*Breaking bonds: think uphill, positive; breaking bonds: think downhill, negative.*

*Both propagation steps are exothermic, the second more so than the first. Adding the two propagation steps gives -30 kcal/mol for the reaction.*

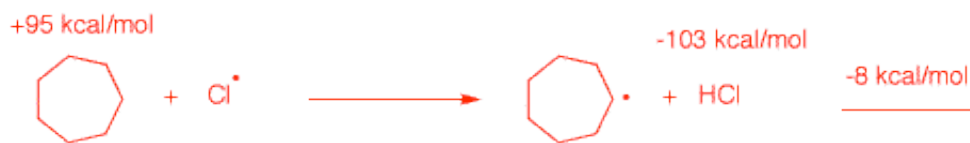
*The  $\Delta H_f^\circ$  of chlorocycloheptane can be determined using heats of formation found in the  $\Delta H_f^\circ$  table.*

$$\begin{aligned} \Delta H^\circ(\text{reaction}) &= \\ \Delta H^\circ(\text{products}) &- \\ \Delta H^\circ(\text{reactants}) & \\ -30 &= [x + (-22.1)] - \\ &[(-28.1) + 0] \end{aligned}$$

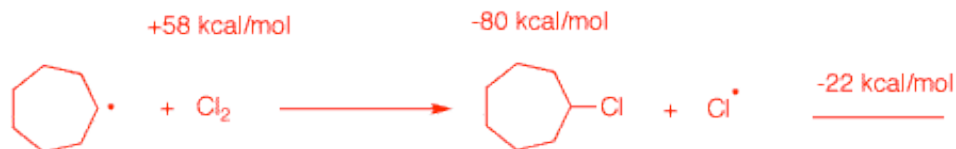
Initiation Step



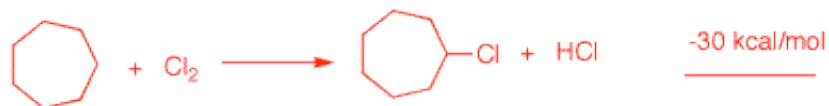
Propagation Step 1



Propagation Step 2



Overall Reaction



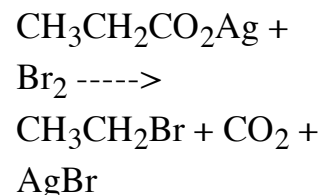
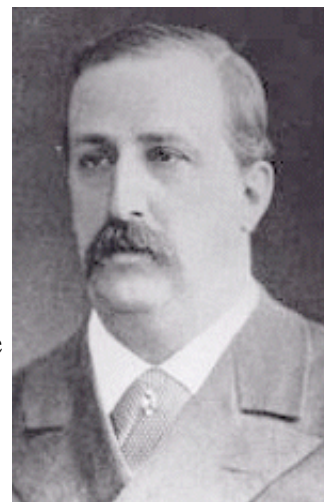
|                               |       |   |   |       |
|-------------------------------|-------|---|---|-------|
| $\Delta H_f^\circ$ (kcal/mol) | -28.2 | 0 | x | -22.1 |
|-------------------------------|-------|---|---|-------|

$$x = (-30) - (-22.1) + (-28.1)$$

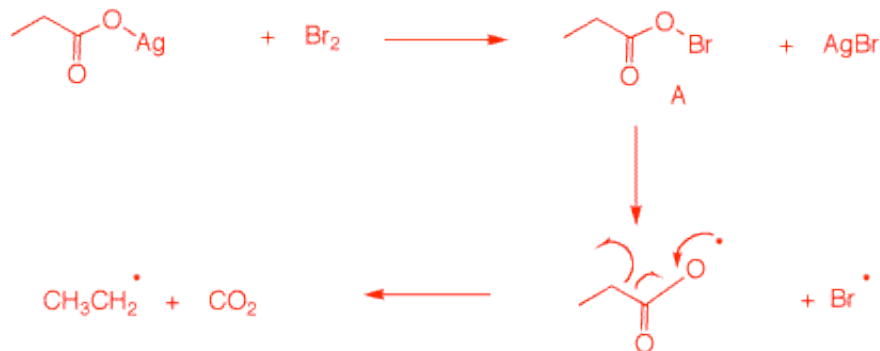
$$x = \Delta H_f^\circ$$

(chlorocycloheptane) =  
-36 kcal/mol

3. [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<sub>2</sub>. 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. The silver carboxylate and bromine form AgBr and **A** before the free radical chain begins. What is **A**? Write the initiation and propagation steps for this reaction.



## Initiation Steps



Structure **A** has the silver of the reactant replaced by bromine. The O-Br bond cleaves homolytically to generate a little carboxy radical (and a bromine atom), which rapidly loses  $\text{CO}_2$  and generates an ethyl radical. This is the initiation step. The limited amount of ethyl radical reacts with **A**, beginning the chain reaction on the left.

## Propagation Step 1



## Propagation Step 2

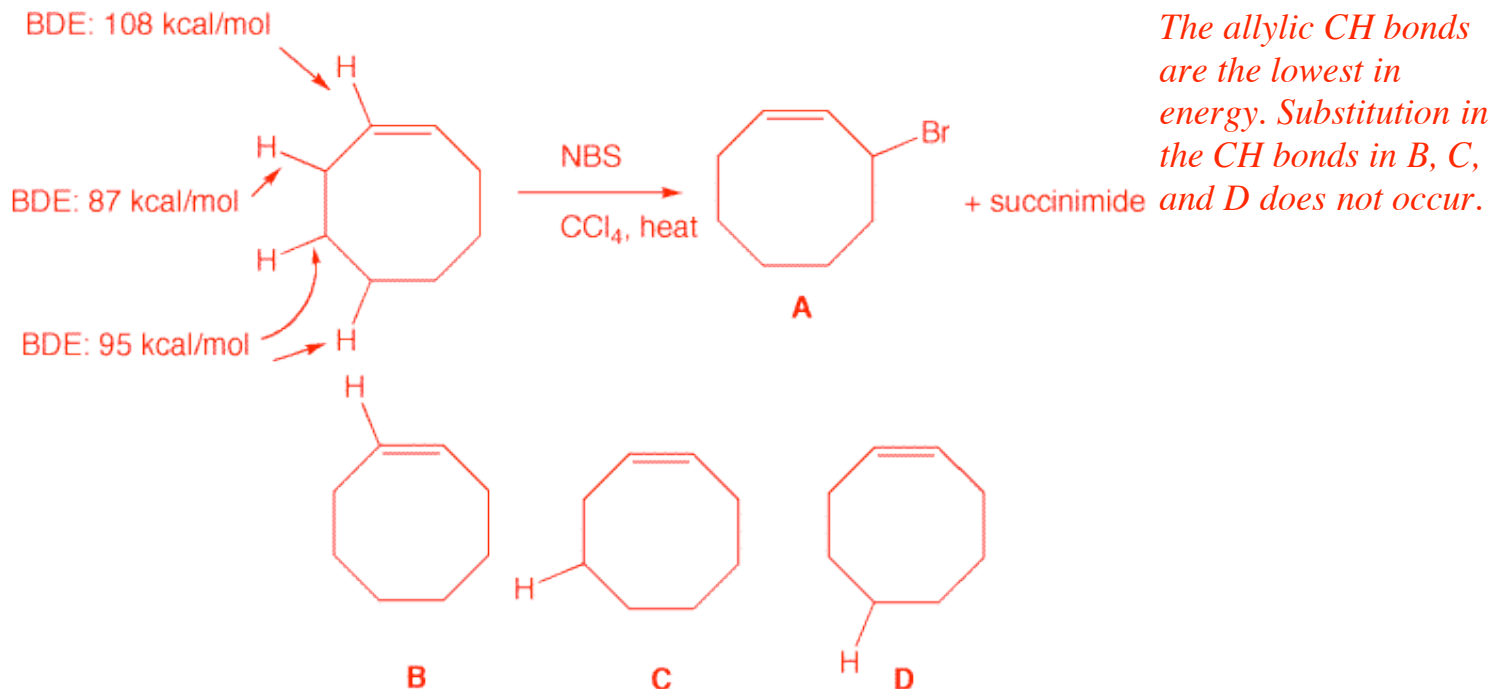


## Overall Reaction



4. 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.



b) Write a radical chain mechanism for this reaction.

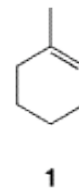
*Use the answer in problem #2 as a guide.*

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 below.



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<sub>4</sub> 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. The benzyl radical is resonance stabilized.*

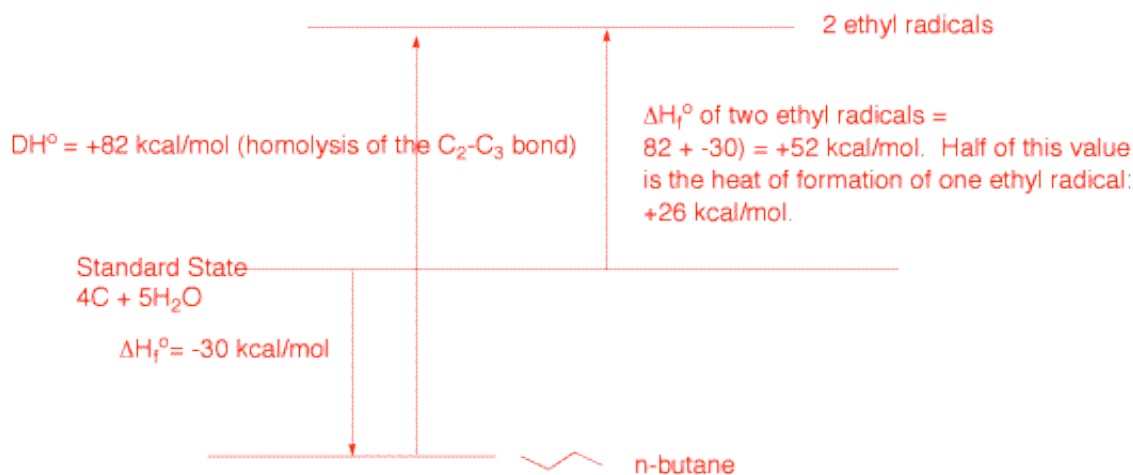
d) From a preparative viewpoint, why is this reaction not suitable for the free radical bromination of 1-methyl-1-cyclohexene **1**. *There are too many allylic positions leading to five possible constitutional isomers.*



5. 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  $\Delta H_f^\circ$  of an ethyl radical. Make use of the [BDEs](#) and [Heats of Formation](#) Tables.



*The value of 82 kcal/mol comes from the BDE Table. The heat of formation of butane is from the Heats of Formation Table.*

b) How does your answer in a) compare with the value in the [BDEs](#) table?

*The calculated heat of formation of an ethyl radical is the same as in the table.*

c) Using the value obtained in a), illustrate and calculate the C<sub>2</sub>-C<sub>3</sub> bond energy in n-butane.

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

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

$$DH^\circ(R-R) = [2 \times DH_f^\circ(R\cdot)] - DH_f^\circ(R-R)$$

$$DH^\circ(R-R) = [2 \times 26] - (-30) = 82 \text{ kcal/mole}$$

