

Chem 225b - Comprehensive Organic Chemistry

Problem Set 3

Chapter 4, Chemical Reactions

Due: Monday, February 11, 2008

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 Tuileries Gardens was one of the images in Mussorgsky's "Pictures at an Exhibition", composed in 1874 for piano and later orchestrated by Ravel. Select item 6 [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 should 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 was born Liebig's beef extract.



**Jean-Baptiste-André
Dumas (1800-1884)**

Dumas's student, Laurent, not one to shirk from controversy, was bold enough to call the process substitution rather than exchange. Thus was Substitution Theory born. Moreover, Dumas (1838) was able to substitute three of the four hydrogens of acetic acid for chlorine to form trichloroacetic acid, having similar 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) turn 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 they (Kolbe and Frankland) thought they had isolated methyl, they actually had 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).

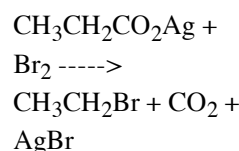
1. Determine the percent of each of the constitutional monochloro isomers expected from the chlorination of 3-methylpentane. Show work.

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

a) Using Bond Dissociation Energies (BDEs), calculate the ΔH° for each relevant step and for the overall reaction. Show work.

b) Calculate the heat of formation (ΔH_f°) of chlorocyclooctane. Show work.

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) to afford an alkyl halide with the liberation of CO_2 . The reaction proceeds through a free radical chain mechanism. Borodin did not isolate the alkyl halide. That accomplishment rests 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.

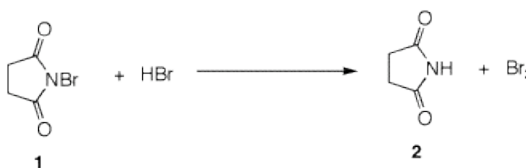


4. When cis-cyclooctene undergoes radical chain bromination, only one monobromination product is isolated.

a) Draw the structures of the possible monobromination products. Using BDEs, explain which one is formed.

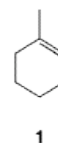
b) Write a radical chain mechanism for this reaction.

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.

d) From a preparative viewpoint, why is this reaction not suitable for 1-methyl-1-cyclohexene **1**.



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 ΔH_f° of a methyl radical. Make use of the [BDEs](#) and [Heats of Formation](#) Tables.
- b) How does your answer in a) compare with the value in the [BDEs](#) table?
- c) Using the value obtained in a), illustrate and calculate the C-C bond energy in ethane.
- d) How does your answer in a) compare with the value in the [BDEs](#) table?

6. A chemist desires samples of all of the monochlorination products of propane and isobutane. Her only source of these gaseous hydrocarbons is a gas cylinder containing both of these hydrocarbons. She determines that the vapor density of the mixture is 1.99 g/L at 1 atm and 27 °C. Determine the composition of the mixture. Using the values for the relative reactivity of primary (methyl), secondary (methylene) and tertiary (methine) hydrogens with chlorine --- 1:4.5:5.5, respectively ---, calculate the expected percentage of each of the four monochloro constitutional (structural) isomers formed during the chlorination of the mixture. Draw their structures and name them.