Comprehensive Organic Chemistry - Chem 225b

Problem Set 2

Chapters 2 and 3

Due: Monday, February 4, 2008

The Conformation Module in the Study Aids will give you a good overview of the subject of conformation. Work your way through ethane, propane, and butane.

The alkane module in ORGO will be of assistance in solving some of these problems.

The Heats of Reaction module (StudyAids/thermochemistry) will be of assistance.

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 and Dumas, 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 was to identify these immutable radicals (benzoyl, ethyl, acetyl, etc.) A Parisian reception was to change all of this. The guests were discomforted by fumes from the 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.

Jean-Baptiste-André Dumas (1800-1884)

The concept of exchanging electropositive hydrogen for electronegative chlorine was anathema to dualism, although Liebig and Wöhler had done precisely this in 1832 on their work on the benzoyl radical (C_7H_5O). 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. As Radical Theory of the early 19th century waned, at the turn of the 20th century free radicals, to distinguish them from the older radicals, were detected and investigated. The very process of substituting chlorine for hydrogen is a free radical reaction.

1. Calculate the energy of the three staggered and three eclipsed conformations of 2-methylbutane about the C_2-C_3 bond.

2. 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 ^oC. 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, respectively ---, calculate the expected percentage of each of the four monochloro constitutional (structural) isomers formed during the chloination of the mixture. Draw their structures and name them.

3. What is the major monobromination product formed by free radical bromination of 2-methylbutane?

a) Illustrate the initiation and propagation steps.

b) Provide the enthalpies of the propagation steps and the heat of the overall reaction. BDEs are here.

c) Why was the enthalpy of the initiation step ignored?

d) Draw a reaction coordinate diagram (energy vs. reaction coordinate) for this process. Label the enthalpies and activation energies. Which of the two activation energies is lower. [Does your diagram comply with the Hammond Postulate?]

e) Determine the heat of formation of the gaseous alkyl halide using heats of formation located here.

4. In problem 2, our chemist ran the free radical chlorination of the gaseous mixture under the two sets of conditions shown below:

a) Equal volumes of the alkane mixture and chlorine were allowed to react.

b) Five volumes of the alkane mixture were allowed to react with one volume of chlorine.

i) Which set of conditions gives more dichloro compounds? Why?

ii) Which set of conditions maximizes monochloro compounds? Why?

5. There is a regular increment in the heats of combustion and the heats of formation in the gas phase of the straight chain alkanes. Look here.

a) Determine these two increments. Show work.

b) Show how these increments agree with the combustion of a methylene group, -CH_2-.

c) Estimate the heat of combustion and heat of formation of nonadecane.