

Chem 220a - Organic Chemistry

Problem Set 3

Chapter 4

Due: Monday, September, 30, 2002

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 discomfited 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. Study the Alkane Module in [Organic Reactions Go Online](#) (ORGO).
2. Consider 2,3-dimethylbutane.
 - a) What is the difference in energy between the two lowest energy conformations viewing along the C_2-C_3 axis? [Draw Newman projections of both and show calculations.]
 - b) How many monochlorination products of this hexane are possible? How much of each? Show work.
- 3) Why is monochlorination of cyclohexane a more effective preparative reaction than monochlorination of its constitutional isomer, methylcyclopentane?

4) Determine the heat of reaction for each of the propagation steps and for the overall reaction in the bromination of cyclohexane. Show work. Draw a reaction coordinate diagram for the reaction (Cf., Fig.4-4, pg. 149)

5) The heat of combustion of cyclopropane is -499.8 kcal/mol [pg.109]. The combustion of H_2 at 25 °C liberates -68.3 kcal/mol while the combustion of graphite liberates -94.05 kcal/mol. From these data cyclopropane can be shown to be less stable (+12 to 13 kcal/mol) than the elements from which it is formed. a) Explain and show work. [The [thermochemistry](#) module will be of assistance to you.]. display the data graphically. See [here](#).

6) Given information in Table 3-4, pg. 109, estimate the heat of combustion of n-decane if the heat of combustion of n-octane = 1302.7 kcal/mol.

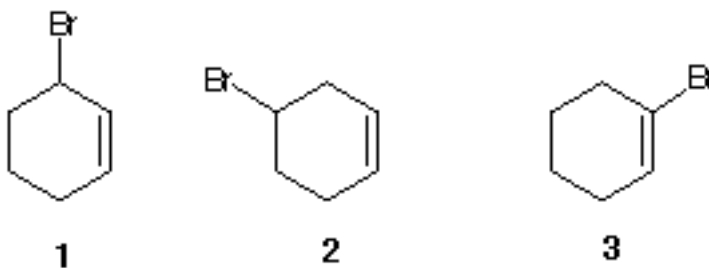
7) [Examine](#) the difference in the heat of formation of a series of n-alkanes.

a) What is the average difference in the heat of formation of a series of n-alkanes? Show work.

b) Using the value in **7a**, calculate the value from Table 3-4 that you used in problem #6 with the aid of the hypothetical reaction $CH_2 + 3/2 O_2 \rightarrow CO_2 + H_2O$.

c) Using the heats of formation of cyclopentane and cyclohexane ([click here](#)) and the answer from parts a) and b) above, make an argument for the relative stability of these two cycloalkanes. Show work.

8) The free radical bromination of cyclohexene produces **only one** of the structures below.



a) Explain with the aid of bond dissociation energies ([BDEs](#)).

b) What complication might arise when this reaction is applied to trans-3-hexene (**4**)? Resonance plays a role here. Explain and illustrate



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