Chem 220 - Organic Chemistry

Solution Set

Problem Set 2

Chapter 3, Alkanes

Due: Monday, September 20, 2010

The Baeyer Laboratory, Munich, 1893

(This photograph is in the hallway across from 110 SCL)

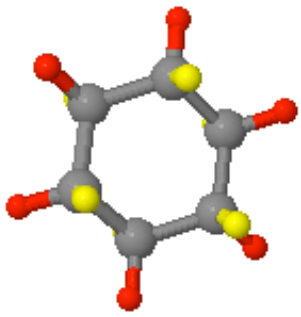
Adolf von Baeyer (1835-1917); Nobel Prize 1905. (center, seated with derby), who was a student of Kekulé, succeeded Liebig at Munich. In the photograph (second row; third from right) is Henry Lord Wheeler (1867-1914); Yale Faculty 1896-1911. As was the custom in the 19th century, many Americans, such as Wheeler, did advanced study in chemistry in Europe. Karl is the laboratory assistant. (The only person wearing an apron and no tie; upper left.)

In 1885, as an addendum to a paper on acetylenic compounds, Baeyer proposed that cyclopentane was the least strained of the cycloalkanes. While he accepted the idea that the carbon atoms in cycloalkanes were tetrahedral, he treated the cycloalkanes as though they were flat. He argued that there is only one cyclohexane carboxylic acid, not two (axial and equatorial) as was predicted by a chair cyclohexane.

Sir Derek H. R. Barton (1918-1998)

1969 Nobel Prize with Odd Hassel for their work on conformational analysis

For a video of Barton talking about conformational analysis, click here.



- Equatorial is frequently misspelled.

- A Projection of Melvin Newman (Son of Yale: 1929, BS; 1932, PhD)

Cyclohexane in the chair conformation

(How to manipulate Jmol structures)

Reading and Enrichment Assignments:

a. Work through How to Draw Cyclohexanes (PowerPoint)

b. The Conformation Module in the Study Aids will give you a good overview of the subject of conformation.

c. View The Evolution of Formulas and Structure in Organic Chemistry During the 19th Century (PowerPoint).

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1. Redraw (line angle formula) and name (IUPAC) the hydrocarbon in this problem. For a dynamic view click here. For a static view click here. How to manipulate Jmol structures. [What if there are two different longest chains? Check here.] *4-Isopropyl-2,6-dimethyloctane*

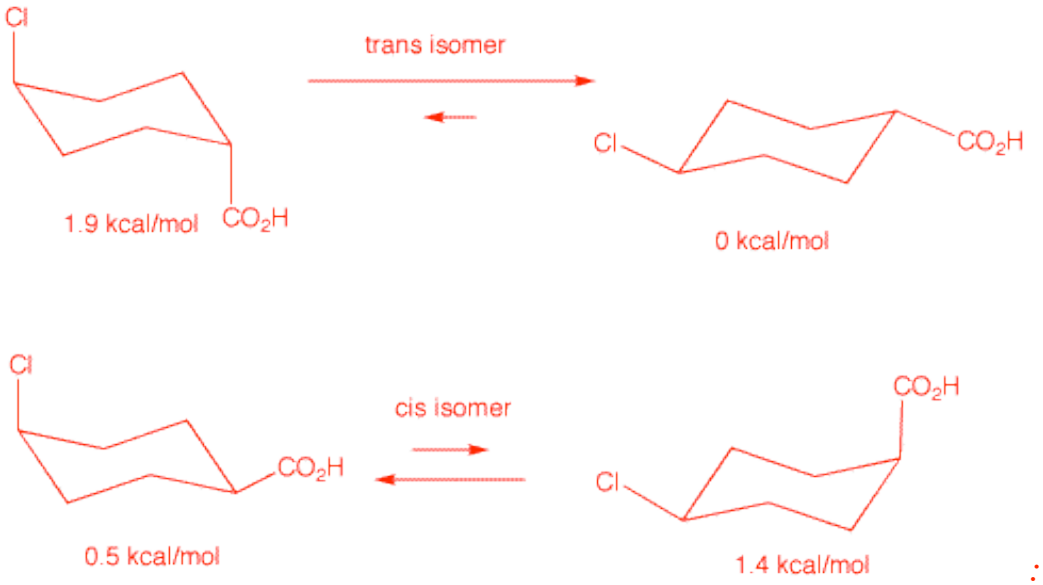
2. Compound **A** (MW=162.61), a 1,4-disubstituted cyclohexane, has the following composition: C, 51.70%; H, 6.82%; Cl, 21.80%. The difference in conformational energy for the two chair conformations of **A** is 1.9 kcal/mol. Using the A-value data (Energy Differences Between ..... Cyclohexanes), determine the structure of **A**. Illustrate and explain. What is the conformational energy difference for the stereoisomer of **A**, ---namely **A'**. Explain and illustrate. Show the chair comformations of **A** and **A'** with the appropriate equilibrium arrows to illustrate the major and minor conformations. Label each conformation with its energy.

The first order of business is to determine the molecular formula of the compound. Does compound A contain only C, H and N? No! The sum of the percentages adds up to 80.32%. Since oxygen is determined by difference it must constitute 19.68% of the remaining matter. For the calculation:

Atom	*At. Wt.*	*%/At. Wt.*	*%/At. Wt./0.61*	*Rounding*
C	*12.01*	*4.30*	*7.05*	*7*
H	*1.008*	*6.76*	*11.08*	*11*
Cl	*35.45*	*0.61*	*1*	*1*
O	*16*	*1.23*	*2.02*	*2*

The formula is $C_7H_{11}ClO_2$. M.W. calculated: 162.61, which agrees with the given value. [Note: A

*compound composed of these four elements must, if it has an odd number of halogens,, must have an odd number of hydrogens. Check here.] Compound **A** is a 1,4-disubstituted cyclohexane. Cyclohexane is C_6H_{12}. Subtracting two hydrogens for the positions of the two substituents leaves a cyclohexane nucleus of C_6H_{10}. Subtracting: $C_7H_{11}ClO_2 - C_6H_{10} = CHClO_2$ for the sum of the composition of the two substituents. Although there are several permutations for these groups, there is only one chlorine containing group --- chlorine (0.5 kcal/mol) itself. Therefore, the other group must be CO_2H (1.4 kcal/mol). Since the energy difference between the two chair conformations of A is the sum of the two groups, both groups must be axial (1.9 kcal/mol) in one conformation and diequatorial (0 kcal/mol) in the other conformation. A is trans-4-chlorocyclohexanecarboxylic acid. Stereoisomer A' is the cis isomer whose energy difference between the two chair conformations is 1.4 - 0.5 = 0.9 kcal/mol. See below:*



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3. Predict the heat of formation of 2-methyloctane using the data presented here. Explain.

There are several 2-substituted alkanes listed: 2-methylbutane (-36.7 kcal/mol), 2-methylpentane (-41.7 kcal/mol), 2-methylhexane

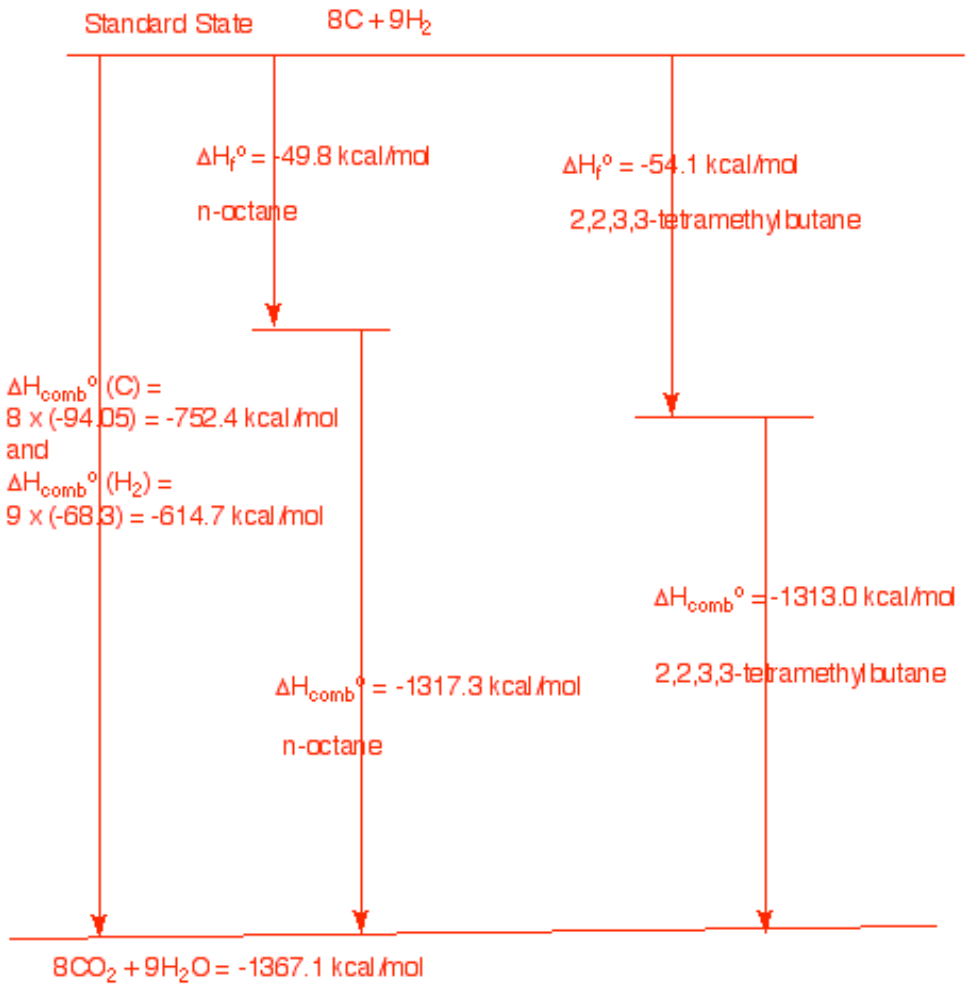
(-46.6 kcal/mol) and 2-methylheptane (-51.1 kcal/mol). This series adds one $-CH_2-$ group at an average value of -5 kcal/mol/CH_2. Thus, 2-methyloctane's heat of combustion can be estimated as -51.5 -5 = -56.5 kcal/mol.

4. Examine the heats of formation of the four octanes listed in the heats of formation tables.

	octane	ΔH_f^o (kcal/mol)
	n-octane	-49.8
	2-methylheptane	-51.5
	2,2-dimethylhexane	-53.7
	2,2,3,3-tetramethylbutane	-54.1

a)What trend do you notice? *Branching gives a more negative heat of formation.*

b) Draw a diagram that shows the heat of formation and heat of combustion of the two extreme cases: n-octane and 2,2,3,3-tetramethylbutane. *Show calculations. In ractice the heats of formation are determined by combusting the appropriate amounts of graphite and hydrogen to et the heat of combustions from the the elements (ΔH_f^o = 0 kcal/mole). Combustion of the compounds gives a value whose difference from the elements determines the heat of formation. In this instance we are calculating the heat of combustion of two isomers knowing the heats of formation. clearly, the difference in the heat of combustion for a compound equals the difference in the heat of formation.(Chart not to scale.)*



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5. a) Calculate the heat of combustion of cyclobutane using the data (ΔH_f^o of cyclobutane, CO_2 and H_2O) in the heats of formation tables. Compare your value with the value in Table 3-5 in your text.

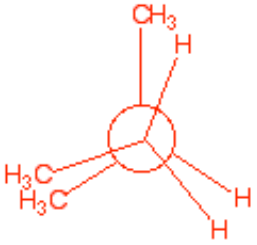
Cyclobutane has the formula C_4H_8 (ΔH_f^o = +6.6 kcal/mol). The heat of combustion of four moles of graphite and four moles of hydrogen is 4 x [(-94.05) + (-68.3)] = -649.4 kcal/mol. The heat of combustion of cyclobutane = -649.4 - (+6.6) = -656 kcal/mol. compares well with the table. Note that cyclobutane is less stable than the atoms from which it is formed.

b) Calculate the strain energy in cyclobutane given the heat of combustion of cyclohexane (Table 3-5 in your text) and the knowledge that cyclohexane is strain-free.

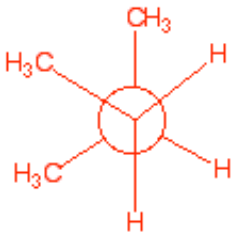
Cyclobutane has 2/3 as many methylene groups as cyclohexane. Therefore, its heat of combustion should be 2/3 the heat of combustion of cyclohexane or 2/3 x (-944.4) = -629.6 kcal/mol for strain-free cyclobutane. But cyclobutane has a heat of combustion of -655.8 kcal/mol. The difference between these numbers is the strain energy: 26.2 kcal/mol.

6. Draw Newman projections for the eclipsed and staggered conformations of 2-methylbutane viewed

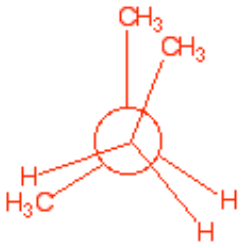
along the C_2-C_3 axis. Calculate the energy of each conformation, both staggered and eclipsed. *It is irrelevant which eclipsed conformation is taken as 0°.*



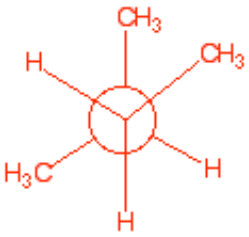
0°
5.3 Kcal/mol



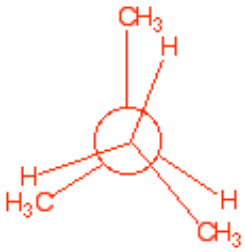
60°
1.8 Kcal/mol



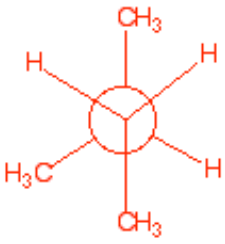
120°
5.3 Kcal/mol



180°
0.9 Kcal/mol



240°
3.9 Kcal/mol



300°
0.9 Kcal/mol