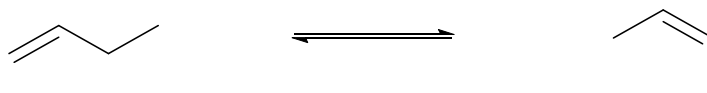


CHEM 267. Alkenes From Alcohols. Labnotes (revised 7/14).

Include the Prelab Exercise on p. 205 of the lab text in your prelab outline. Answer the same for 2-butanol. Review Wade, Section 7-7 (A-C). **Although the lab experiment is short and straightforward, you will need to put additional effort into the report. It is expected that such additional effort will be expended. Note also that unlike previous experiments, in which the procedure was spelled out quite exactly in the handout, this experiment and others to follow will rely more on the procedures given in the lab text.**

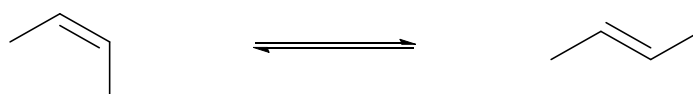
Experiment Notes: **Be extremely careful in using concentrated sulfuric acid.** Instead of the 10 cm column/collection tube described in the book, use the longer chromatography column to collect the product. Much of the first slow bubbling that occurs is simply displaced air from the heated reaction tube. Once product formation begins, the bubbling becomes rapid. To ensure that the butenes, and not just air is being collected, allow the reaction to proceed until the tube is at least about 3/4 full.

Calculations: From the GC analysis, determine the relative amounts of the three isomers produced in the reaction. These will be used to compute energies which will be compared with calculated and other experimental values. Note that the assumption that peak area is directly proportional to molar amount is not necessarily correct. The detector responds differently to different compounds. Usually however, for structurally similar compounds, as in this case, the assumption is valid. Air will elute first, followed by the butenes in order of boiling point.



For the equilibrium as drawn above, calculate ΔG° , using the relationship, $\Delta G^\circ = -RT \ln K_{eq}$, where $R = 1.99 \text{ cal/mol} \cdot \text{Kelvin}$, $T = 373 \text{ K}$, and $K_{eq} = N_{(cis-2-butene)} / N_{(1-butene)}$, and $N_{(1-butene)}$ = mol fraction of 1-butene and $N_{(cis-2-butene)}$ = mol fraction of *cis* -2-butene. (Why is $T = 373 \text{ K}$ used?) Be careful to use the correct sign for ΔG° for the equilibrium, and do not mix units (cal vs kcal).

In the same way, calculate ΔG° for the following equilibrium:



Other experimental data - heats of hydrogenation: use the heat of hydrogenation data given in Wade, Table 7-1 (for example, $\Delta H^\circ = -1.0 \text{ kcal/mol}$ for the equilibrium *cis* to *trans* 2-butene). (Heats of combustion, if available could also be compared and would provide the same qualitative results, within experimental error.) As stated in the other handout for this experiment, "An Experimental and Computational Investigation of the Dehydration of 2-Butene", you will find additional experimental heat of formation data from the web.

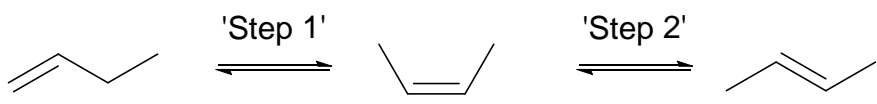
As part of the report, construct a table (see sample data table at end) which allows for a clear comparison of all experimental energy differences. Concentrate on the predicted direction of

equilibrium and order of magnitude of the energies. Remember that the sign for ΔG° and ΔH° is absolutely crucial and depends upon the way in which the equilibrium is drawn.

Summary: for the three isomeric butenes produced in the dehydration of 2-butanol do the following:

- 1) Determine product distributions using GC, and from those, free energies.
- 2) Compare your experimental values with hydrogenation energies from Wade.
- 4) Compare your experimental data with the experimental values from the NIST website (see other handout) and comment on the correlations or lack thereof.
- 5) Draw the mechanism and energy diagram for the reaction and discuss results found in terms of transition state energies and structures, how structures of transition states correspond to structures of products and therefore energies of products.
- 6.) Comment on the product distribution predicted from statistical considerations only vs. what you found.

Sample Data Table



ΔG° (Your experiment)	Step 1	Step 2
ΔH° (hydrog)		
ΔH° (NIST)		