Chemistry 324, 2008
HW #3, Due W, Feb 20 (**REVISED DATE #2**)

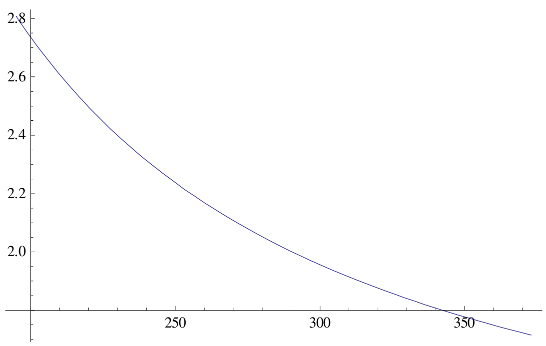
Selected Answers

Problem 1

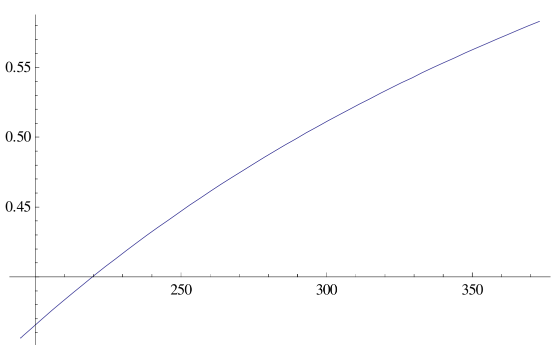
Part A. 0.27, 0.40, and 0.51 kcal/mol for -78, 20, 100 °C, respectively.

Part B. Part A shows that establishing the same degree of selectivity ($k_1/k_2 = 2$) at higher temperature requires a larger $\Delta(\Delta G^{\ddagger})$. To put it another way, for constant $\Delta(\Delta G^{\ddagger})$, there is higher selectivity at low temperature and lower selectivity at high temperature.

The following graph of k_1/k_2 (vertical) vs. T (horizontal) for $\Delta(\Delta G^{\ddagger}) = -0.4$ kcal/mol shows how selectivity falls with increasing T



By the way, it might seem like choosing $\Delta(\Delta G^{\ddagger}) < 0$ was arbitrary. The following graph shows the same temperature range for $\Delta(\Delta G^{\ddagger}) = +0.4$ kcal/mol. You can see that, here too, the reaction becomes less selective ($k_1/k_2 \rightarrow 1$) as T rises.



Part C. Since selectivity can usually be increased by performing a synthesis at lower T, why not always do this? The reaction will slow down. This can be overcome sometimes by using a catalyst.

Problem 2. Comparison of the acrolein and butadiene rotation energy profiles shows the following differences:

1. Acrolein is equally stable in the *cis* and *trans* forms
2. The *cis* form is a rotation transition state for butadiene but it is a stable structure for acrolein

3. The barrier to rotation is much higher in *acrolein* (9 kcal/mol), but no so high as to prevent fast internal rotation

The first and second points can be explained in two ways (and both may be important):

- Steric repulsion between hydrogens destabilizes the *cis* form of butadiene. This is not a problem with acrolein.
- Electrical attraction between oxygen and hydrogen stabilizes the *cis* form of acrolein.

I don't have an explanation for the higher barrier in acrolein (point #3), but it's worth thinking about.

Problem 3. There are many structural motifs that one might look for. Everyone noticed some important motifs and overlooked others (perhaps you were too worried about explaining energy differences?). I was tempted to say, "go back and look for more," but I won't do that to you. Here are some motifs worth noticing:

- Diene planarity
- Diene cis or trans
- Enone planarity **(remember problem #2?)**
- Enone cis or trans **(remember problem #2?)**
- Exo or endo **(remember previous HW?)**
- Lengths of forming CC single bonds (roughly equal or unequal? Short or long?)
- 6-membered ring conformation (chair? boat?)
- Staggered vs. eclipsed bonds
- Steric repulsions

There are also a host of quantitative measurements that can be made. One would be the lengths of the forming CC single bonds. Other nonbonded distances, angles, etc., might be interesting, but then you should provide a point of reference.