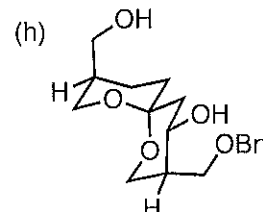
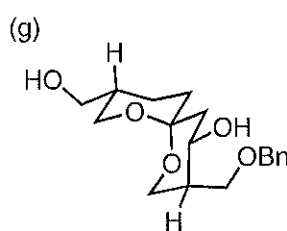
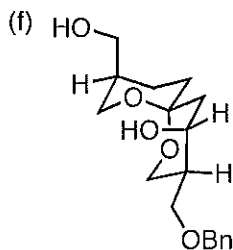
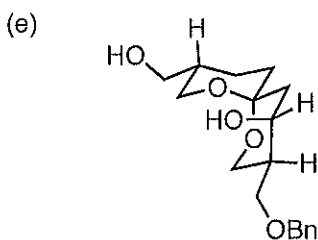
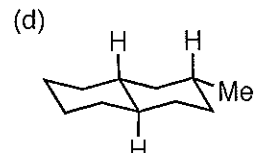
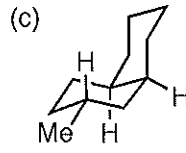
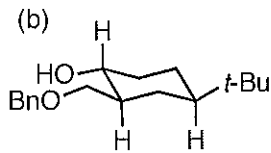
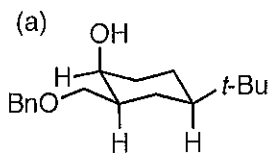
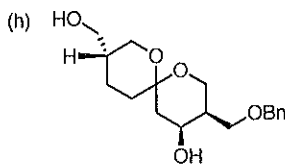
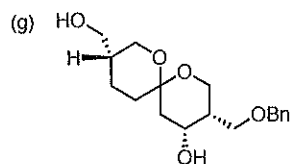
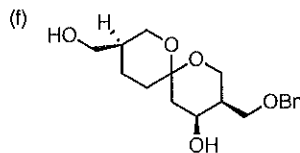
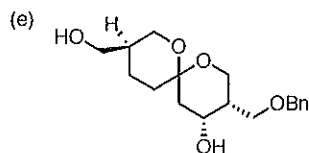
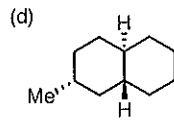
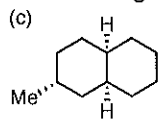
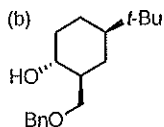
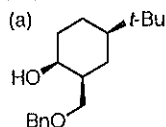


CHEM 633: Advanced Organic Chem: Physical
Problem Set 5 Answer Key
Due on 10/13/09

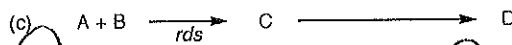
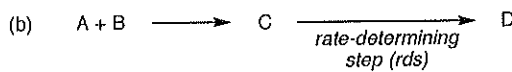
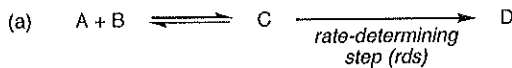
For the following problems, please use Excel (or another graphing program), when necessary. Please submit your graphs with your problem set.

1. Please draw the most stable conformation of each of the following molecules.

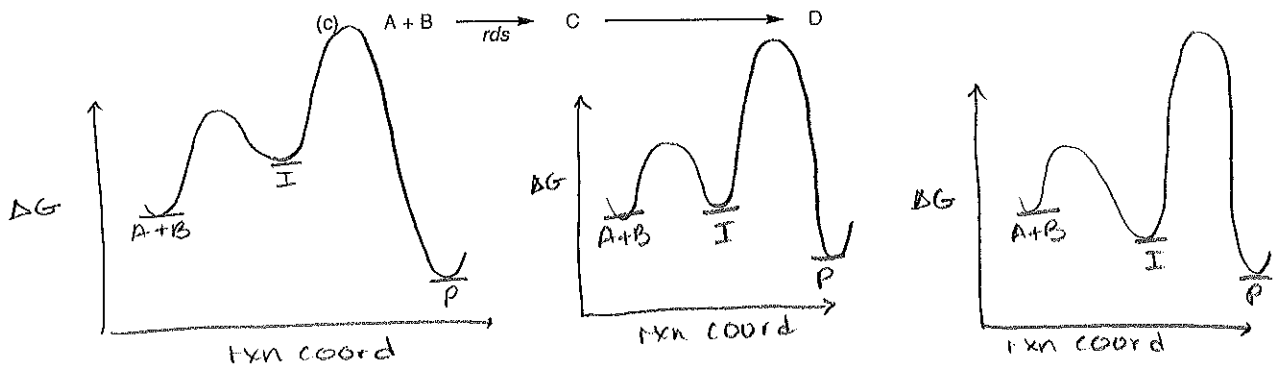


2. Please draw reaction coordinate diagrams, which illustrate the following scenarios. If more than one reaction coordinate is possible, please draw all possibilities.

Assume all are exothermic.

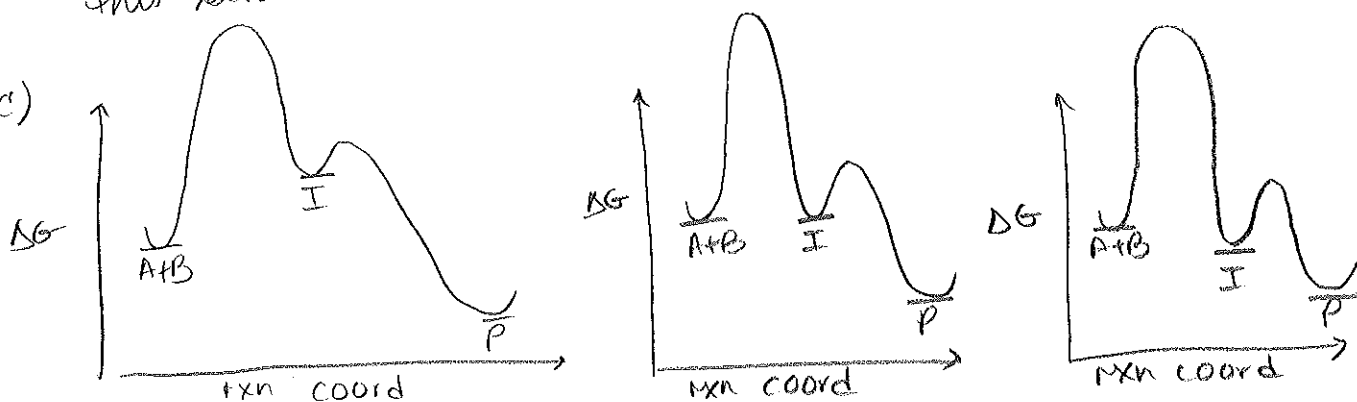


(a)



(b) Unless you are under special conditions, this situation is not possible.

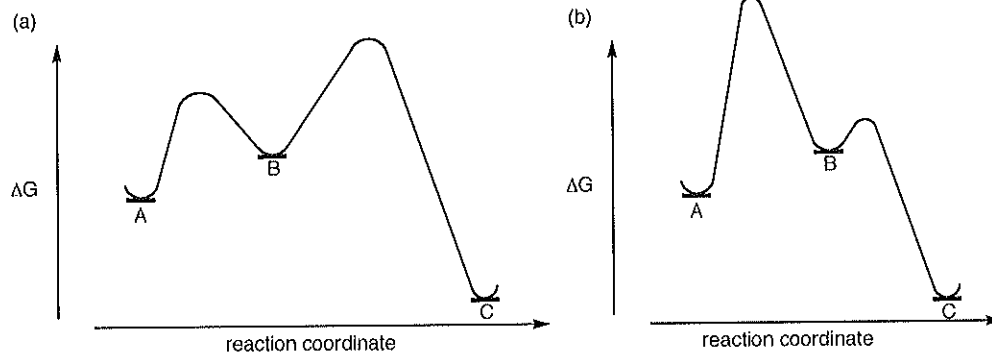
(c)



3. Consider the following theoretical reaction coordinate diagrams, describing the transformation of starting material **A** into product **C** via intermediate **B**. For each reaction coordinate diagram, please answer the following questions:

(1) Is there a possibility that intermediate **B** may be observable using standard spectroscopic methods, such as NMR spectroscopy?

(2) If there is the possibility that **B** may be observable, what is the maximum possible energy difference between **A** and **B** to allow observation of **B** by NMR spectroscopy? Please explain your reasoning.



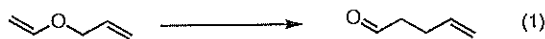
(a) B may be observed. ⁺²
 By NMR, (largest K_{eq} for $A \rightleftharpoons B \approx 100:1$)

$$\times 3 \quad \Delta G^\circ = -RT \ln K_{eq}$$

$$\Delta G_{298}^\circ = +2.72 \text{ kcal/mol}$$

⁺⁵ (b) B will not be observed.

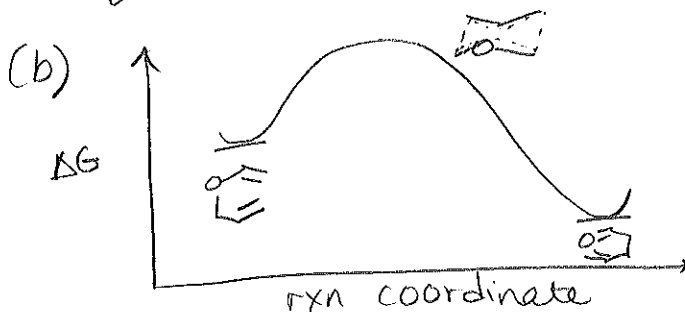
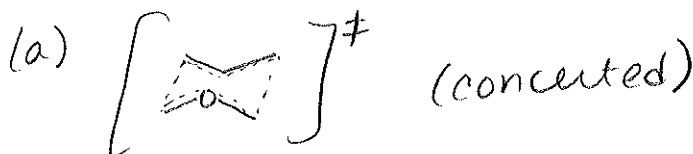
3. The temperature-dependent rates of rearrangement of allyl vinyl ether (eq 1) was studied in the gas phase.



Temp (K)	k (s ⁻¹)
469.1	2.875×10^{-3}
469.4	3.021×10^{-3}
473.7	3.838×10^{-3}
427.7	0.120×10^{-3}
456.7	1.166×10^{-3}
451.6	0.788×10^{-3}
440.2	0.341×10^{-3}

Ref: JACS 1950,
72, 3155

- Based on your prior knowledge, provide a depiction of the transition structure for this transformation.
- Draw a reaction coordinate diagram for this transformation, clearly labeling all intermediates and transition states.
- Determine ΔH^\ddagger and ΔS^\ddagger from the data (in kcal/mol and eu, respectively).
- Compare the value of ΔS^\ddagger for this transformation with those of reactions reported in the chemical literature that proceed by related mechanisms, and explain whether your proposed transition structure is consistent with the experimentally measured value of ΔS^\ddagger .



(c) See attached excel data & graph.

Plotted $\ln\left(\frac{k_h}{k_B T}\right)$ vs $1/T$

$$y = -29.490x - 7.9536$$

slope = $-\Delta H^\ddagger$
(in cal/mol)

y-intercept = ΔS^\ddagger
in cal/mol.K = eu

$$\Delta H^\ddagger = +29.5 \text{ kcal/mol}$$

$$\Delta S^\ddagger = -8.0 \text{ eu}$$

(d) $\ominus \Delta S^\ddagger \Rightarrow$ increased order in TS.

similar in sign & magnitude to other
pericyclic rxns where bond breaking & bond making

both occur:

Rxn
Concerted Cope

ΔS^\ddagger (eu)
-13.8 to -11.7

References

Acc Chem Res 2009, 42, 169

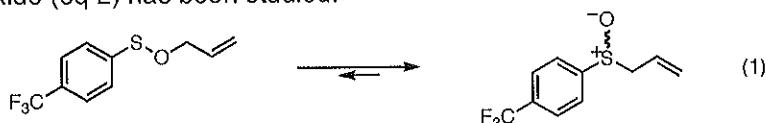
JACS 1964, 86, 899

Allyl methyl
ether fragmentation

-11.6 eu

JACS 1973, 95, 5234

4. The thermal rearrangement of an allyl arenesulfonate (eq 1) and the rate of racemization of the corresponding sulfoxide (eq 2) has been studied.



Temp (°C)	$k_{\text{rearr}} \times 10^4 \text{ (s}^{-1}\text{)}$
6.9	10.8
12.4	20.2
20.1	48.4
25.1	92.3

Ref: JACS 1970,
92, 2100



Temp (°C)	$k_{\text{rac}} \times 10^5 \text{ (s}^{-1}\text{)}$
39.8	20.5
49.6	60.9
58.8	152

- Determine ΔH^\ddagger and ΔS^\ddagger for each process in kcal/mol and eu, respectively.
- The rearrangement reaches equilibrium at 99% conversion at 25 °C. Determine ΔG° .
- Calculate ΔG_{298}^\ddagger for each process.
- Draw a reaction coordinate diagram (with Gibbs free energy as the y-axis) for these processes that is consistent with the data and included accurate depictions of the key intermediates and transition structures.

(a) Rearrangement (Graph attached) | Racemization (Graph Attached)

$$y = -18662x - 4.8954$$

$$+2 \Delta H^\ddagger = 18.7 \text{ kcal/mol}$$

$$+2 \Delta S^\ddagger = -4.9 \text{ eu}$$

$$y = -20930x - 8.1199$$

$$+2 \Delta H^\ddagger = 20.9 \text{ kcal/mol}$$

$$+2 \Delta S^\ddagger = -8.1 \text{ eu}$$

(b) $K_{\text{eq}} = \frac{99}{1}$ $T = 298.15 \text{ K}$ $R = 1.98 \text{ cal/mol}\cdot\text{deg}$

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$\Delta G^\circ = -(1.98 \text{ cal/mol}\cdot\text{deg}) (298.15 \text{ K}) \ln(99) = -2671.6 \text{ cal/mol}$$

$$+2 \Delta G^\circ = -2.7 \text{ kcal/mol}$$

(c) $\Delta G_{298}^\ddagger = \Delta H^\ddagger - (298 \text{ K}) \Delta S^\ddagger$

Rearrangement:

$$\Delta G_{298}^\ddagger = 18.7 \text{ kcal/mol} - (298 \text{ K}) \left(-4.9 \frac{\text{cal}}{\text{mol}\cdot\text{K}} \right) \left(\frac{\text{kcal}}{1000 \text{ cal}} \right) = 18.7 + 1.46 \text{ kcal/mol}$$

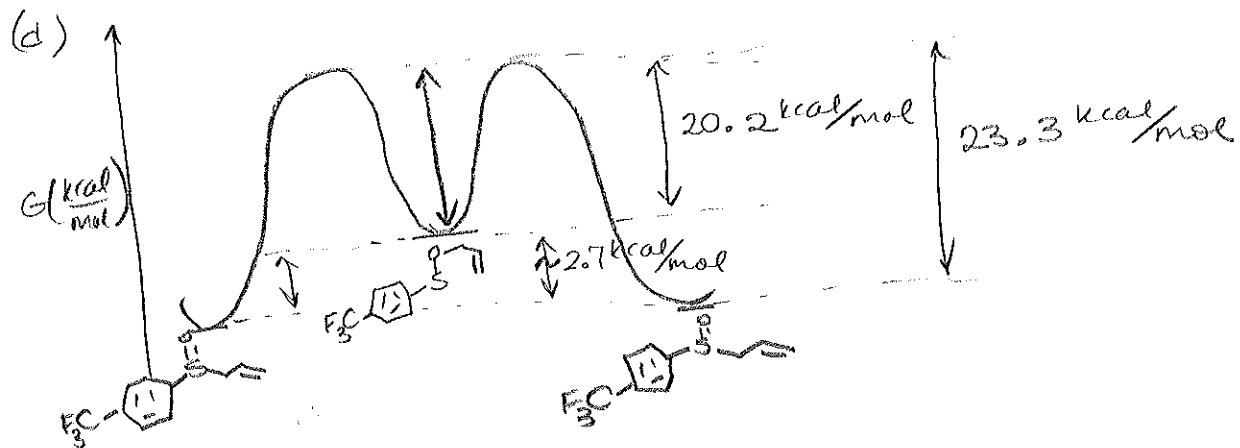
$$\Delta G_{298}^\ddagger = 20.2 \text{ kcal/mol}$$

(4c) - continued

Racemization

$$\Delta G_{298}^{\ddagger} = 20.9 \text{ kcal/mol} - (298 \text{ K})(-8.1 \text{ cal/mol}\cdot\text{K}) \left(\frac{\text{kcal}}{1000 \text{ cal}}\right)$$

$$\Delta G_{298}^{\ddagger} = 23.3 \text{ kcal/mol}$$



Note: The small error (0.4 kcal/mol) can be attributed to difficulty of measuring a large k_{eq} accurately.

5. The thermal rearrangement of a cinnamyl arenesulfonate (eq 1) has been studied. No intermediates could be observed by NMR spectroscopy. Note that some experiments were run in duplicate.



Temp (°C)	k_{rearr} (s^{-1})
40.0	8.2×10^{-6}
40.0	8.3×10^{-6}
65.6	2.7×10^{-4}
76.5	1.0×10^{-3}
76.5	9.1×10^{-4}

Ref: JACS 2000,
122, 3367.

- Determine ΔH^\ddagger and ΔS^\ddagger for each process in kcal/mol and eu, respectively, and compare these values to those in questions 3 and 4.
- Please propose 2 arrow-pushing mechanisms for this transformation. On the basis of the calculated activation parameters, evaluate the plausibility of each of your proposed mechanisms.

(a) graph attached

Plot $\ln\left(\frac{k}{k_{\text{ref}}T}\right)$ vs. $1/T$

$$y = -27443x + 6.3345$$

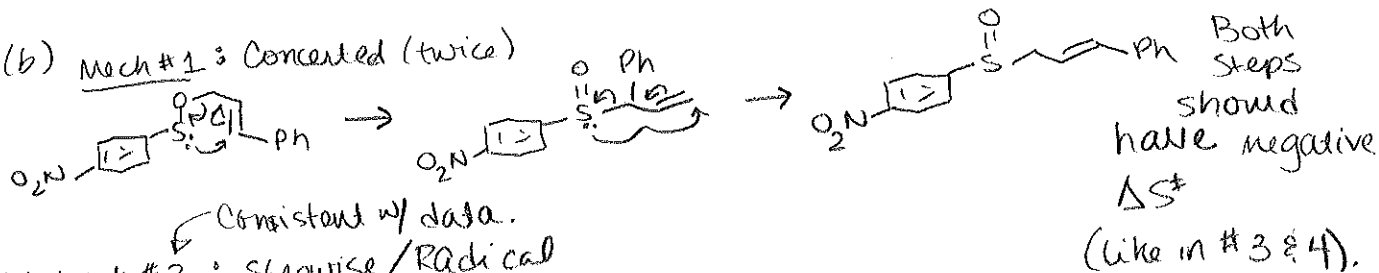
$$\Delta H^\ddagger = +27.4 \text{ kcal/mol}$$

$$\Delta S^\ddagger = +6.3 \text{ eu}$$

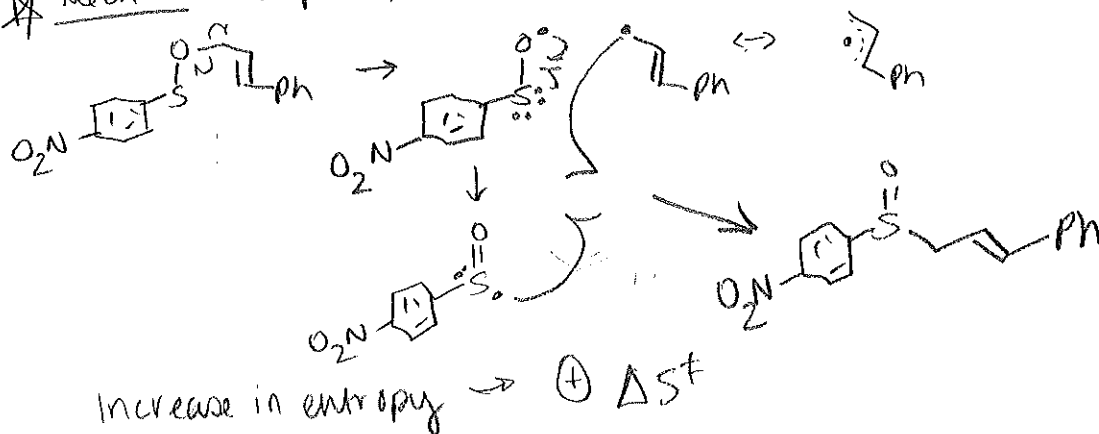
Bigger, ^{enthalpic} activation barrier here than for #4's rxns, but a little smaller than for #3's.

In #3 & 4 $\rightarrow \Delta S^\ddagger$ was negative, so this mechanism goes through more disordered T.S. than the mechanisms in #3 & 4.

(b) Mech #1: Concerted (twice)

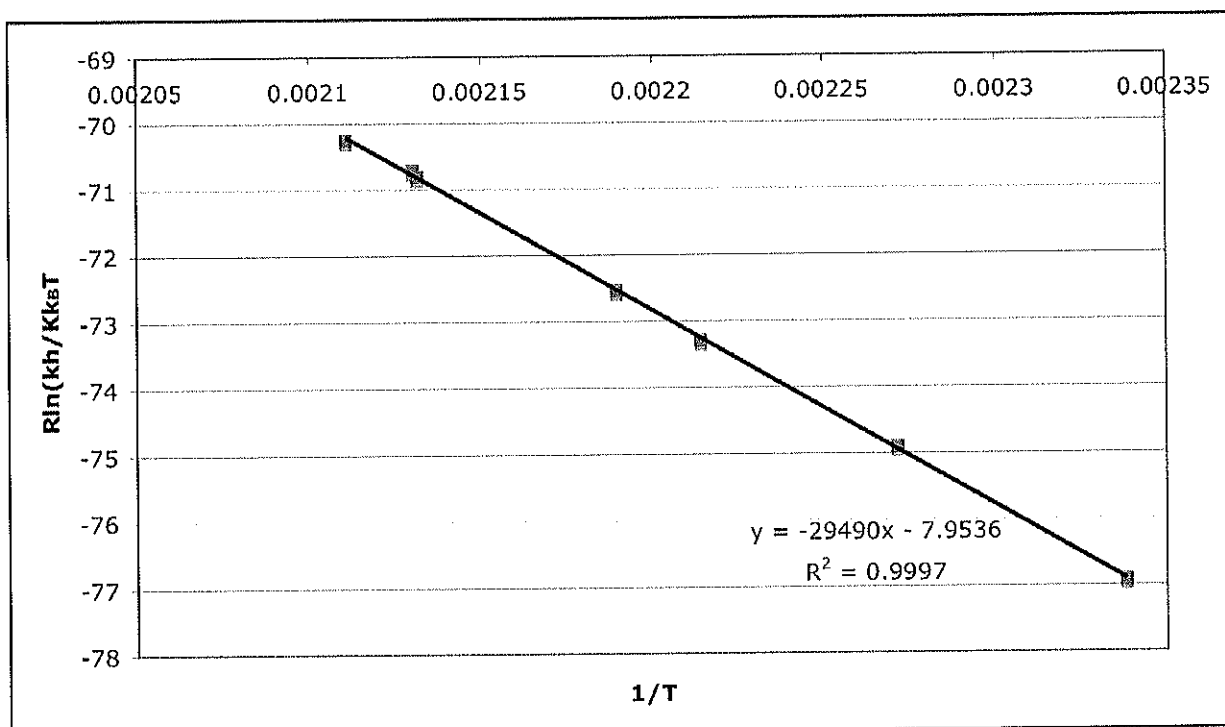


Mech #2: Stepwise/Radical



Supporting Information for #3

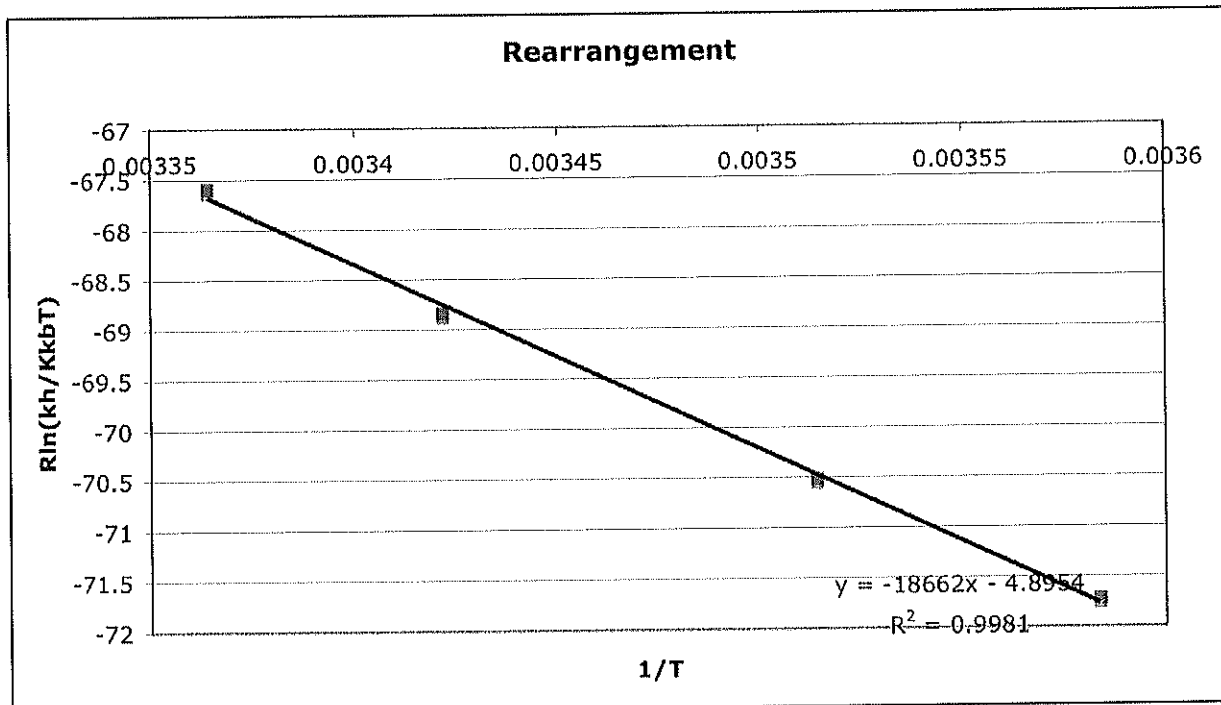
Temp (K)	k (s^{-1})	k (s^{-1})	$1/T$	kh/Kk_bT	$R\ln(kh/Kk_bT)$
469.10	2.875×10^{-3}	0.002875000	0.002131742	2.94228E-16	-70.80911298
469.40	3.021×10^{-3}	0.003021000	0.002130379	3.08972E-16	-70.71229908
473.70	3.838×10^{-3}	0.003838000	0.002111041	3.88967E-16	-70.25641483
427.70	0.120×10^{-3}	0.000120000	0.002338087	1.34695E-17	-76.91527905
456.70	1.166×10^{-3}	0.001166000	0.002189621	1.22568E-16	-72.54296797
451.60	0.788×10^{-3}	0.000788000	0.002214349	8.3769E-17	-73.29656862
440.20	0.341×10^{-3}	0.000341000	0.002271695	3.71891E-17	-74.90442356



Supporting Information for Problem 4

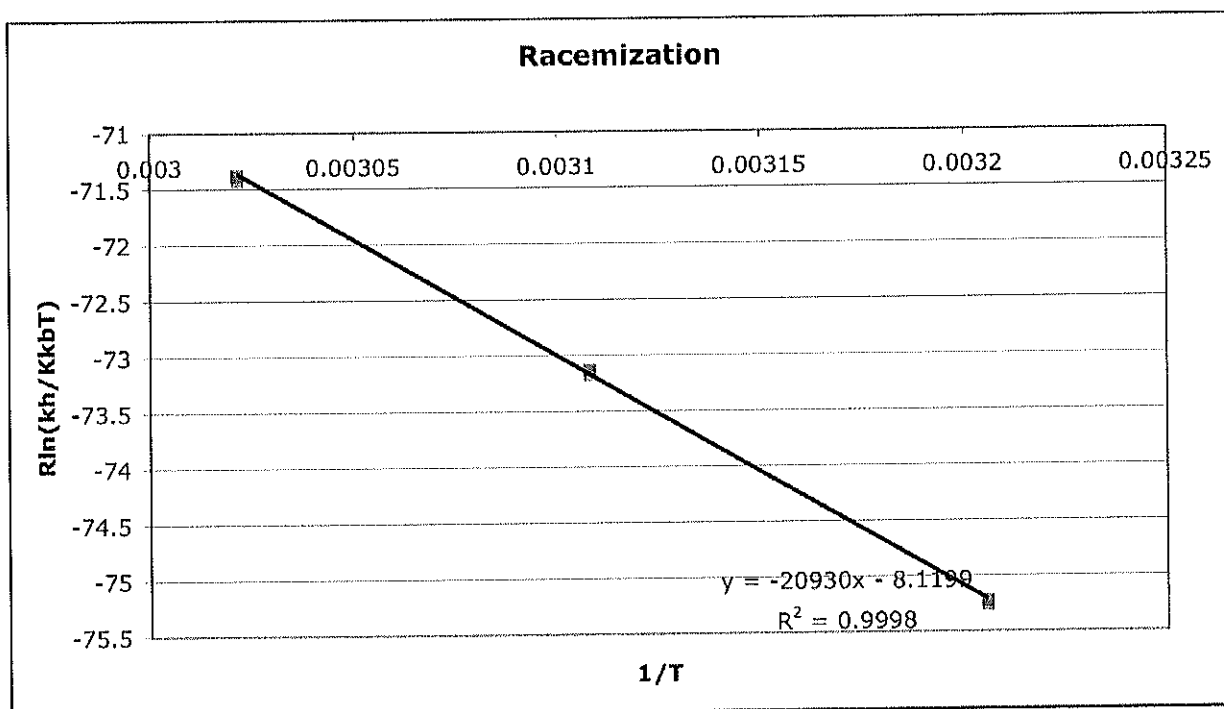
Rearrangement

Temp (K)	$k_{\text{rearr}} \times 10^4$ (s^{-1})	k (s^{-1})	$1/T$	kh/Kk_bT	$R\ln(kh/Kk_bT)$
279.05	10.8	0.001080000	0.003583587	1.85803E-16	-71.71925293
284.55	20.2	0.002020000	0.003514321	3.40803E-16	-70.51814838
292.25	48.4	0.004840000	0.003421728	7.95063E-16	-68.84085752
297.25	92.3	0.009230000	0.003364172	1.4907E-15	-67.59626835



Racemization

Temp (K)	$k_{rac} \times 10^5 (s^{-1})$	$k (s^{-1})$	$1/T$	kh/Kk_bT	$R\ln(kh/Kk_bT)$
311.95	20.5	0.000205000	0.003205642	3.15486E-17	-75.23010633
321.75	60.9	0.000609000	0.003108003	9.08677E-17	-73.13551114
330.95	152	0.001520000	0.003021604	2.20492E-16	-71.38033046



Supporting Information for Problem #5

Temp (K)	$k_{\text{rearr}} (\text{s}^{-1})$	$k (\text{s}^{-1})$	$1/T$	kh/Kk_bT	$R\ln(kh/Kk_bT)$
312.15	8.2×10^{-6}	0.000008200	0.003203588	1.26113E-18	-81.60474949
312.15	8.3×10^{-6}	0.000008300	0.003203588	1.27651E-18	-81.5807492
337.75	2.7×10^{-4}	0.000270000	0.00296077	3.83777E-17	-74.84212747
348.65	1.0×10^{-3}	0.001000000	0.002868206	1.37696E-16	-72.3125374
348.65	9.1×10^{-4}	0.000910000	0.002868206	1.25303E-16	-72.49927254

