Practice Problem Set #1 ANSWER KEY(No credit, no due date)

1. In order to calculate the activation parameters A,E_a, and $\Delta H^{\ddagger}$,$\Delta S^{\ddagger}$ for the first-order thermal decomposition shown below, first prepare the appropriate Arrhenius and Eyring equations in linearized form.

Arrhenius equation $k = Ae^{-E_a/RT}$ $\ln(k) = \ln(A) - \dfrac{E_a}{R}\left(\dfrac{1}{T}\right)$

Eyring equation $k = \hat{e}\,\dfrac{k}{h}e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT}$ $\ln\left(\dfrac{k}{T}\right) = \left(\ln\dfrac{k}{h} + (\dfrac{\Delta S^{\ddagger}}{R})\right) - \dfrac{\Delta H^{\ddagger}}{R}\left(\dfrac{1}{T}\right)$

(assume "fudge factor" $\kappa = 1.0$)

then set up a table of data in appropriate fashion, to make the data plots easier:

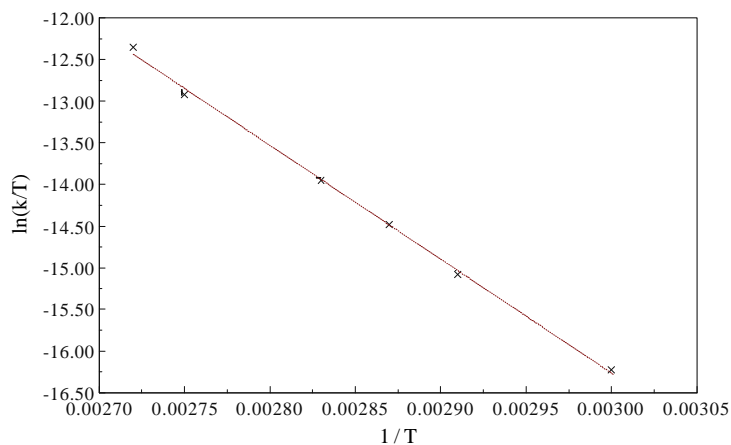| Temp / °C	1/T (K^{-1})	k (0.0001 sec^{-1})	ln(k)	ln(k/T)
60.0	0.00300	0.30	-10.414	-16.223
70.0	0.00291	0.97	-9.241	-15.080
75.0	0.00287	1.79	-8.628	-14.482
80.0	0.00283	3.09	-8.082	-13.950
90.0	0.00275	8.92	-7.022	-12.918
95.0	0.00272	15.90	-6.444	-12.351
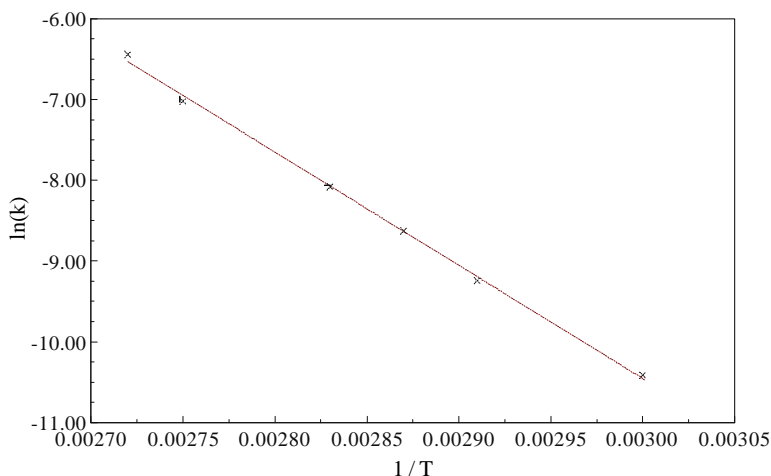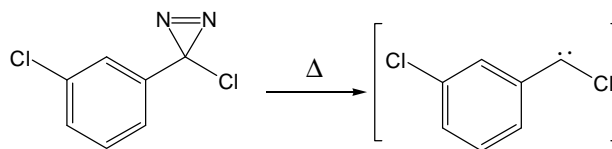
Arrhenius Least Squares Analaysis

Slope =   -14027 K

Intercept = 31.624

Correlation Coeff = 0.998

Using the constant R = 1.987 cal/mol-K, and the above computed slopes and estimates, we get

$A = \exp(\text{intercept}) = \exp(31.624) = 5.4 \times 10^{13}\,\text{s}^{-1}$; $E_a = R \times \text{slope} = 27{,}900$ cal/mol ;

Using the constants R = 1.987 cal/mol-K, k = 1.3806×10^{-23} J-K, h = 6.6262×10^{-34} J-s, κ = 1.0, and the above computed slopes and estimates, we get

$\Delta S^{\ddagger}$ = {intercept – ln(k/h)}R = {24.764 – 23.7595} × 1.987 = 2.0 cal/mol-K

$\Delta H^{\ddagger}$ = (slope) × R $\qquad\qquad\qquad\qquad\qquad$ = 27,200 cal/mol

The small, positive entropy of activation is typical of a unimolecular reaction without major conformational or stereoelectronic constraints. The enthalpy of activation is modest, but large enough to prevent easy decomposition at room temperature (see problems below for some comparisons).

2. The oxy anionic substituent effect (first reported by Evans & Golob, *J. Am. Chem. Soc.*, **1975**, *97*, 4765) accelerates the Cope rearrangement by seventeen orders of magnitude at 298 K.
    (a) If a typical Cope rearrangment activation energy is 30 kcal/mol, how long will a reaction half-life be at room temperature? Show your work. You may assume a typical A-value for a unimolecular reaction.

Assume that A ~ 10^{13} s^{-1}, the low end for a unimolecular process: actually, it is smaller, because a Cope rearrangment is orbital symmetry controlled, but we do not "know that".

Activation enthalpy pretty much is equal to E_a for an Arrhenius model, so at room temperature of 298 K, apply the Arrhenius expression for a rate constant

$$k = \left(10^{13}\, s^{-1}\right) \times e^{(-30,000\, cal/mol)/[(1.987\, cal/mol-K)\cdot(298\,K)]}$$

$$k = 9.9 \times 10^{-10}\, s^{-1}$$

Remember your first order kinetics!   ln[k(t)/k(0)] = -kt

$$\ln(1/2) = -(9.9 \times 10^{-10}) \cdot t$$

So, t (half-life) = 7×10^{8} s, which is roughly 22 years for the half-life of a typical Cope rearrangment at room temperature.

(b) What will be the activation energy of the oxy anionic Cope rearrangment, if its rate enhancement is seventeen orders of magnitude at 298 K? Show your work. You may assume a typical A-value for a unimolecular reaction.

Use the same reasoning as was used in (a) above. The rate enhancement is 17 orders of magnitude, so instead of having k = 9.9×10^{-10} s^{-1} we have k ~ 10^8 s^{-1}.

$$k = 10^8 \text{ s}^{-1} = \left(10^{13} s^{-1}\right) \times e^{(-E_a cal/mol)/[(1.987 cal/mol-K)\cdot(298 K)]}$$

$$\ln(10^8) = [-E\{\text{accelerated}\}]/[(1.987)(298)] + \ln(10^{13})$$

$$E_a(\text{accelerated}) = 6800 \text{ cal/mol (6.8 kcal/mol)}$$

Applying the same logarithmic math as was used in (a) above, we get t (half-life) ~ 7×10^{-9} s, which means that the reaction proceeds on the nanosecond timescale at room temperature, an amazing rate enhancement, and one of the largest discovered for a class of reactions.
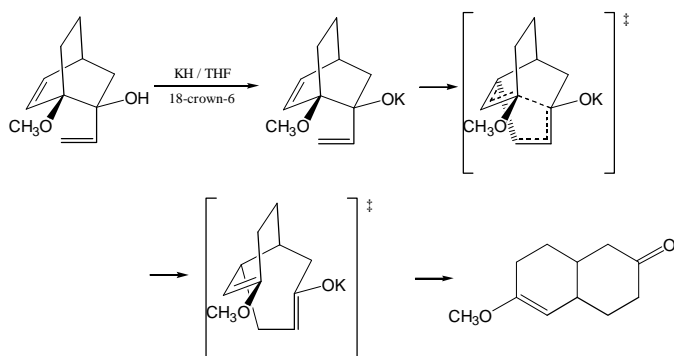

3. This is a typical analysis of a reaction that can proceed through two intermediates. The Benson group enthalpy equivalent data is given to allow an estimate of the relative energies of these two intermediates. Path A is "wrong-bond" cleavage, since it leads to a biradical that has one secondary and one primary radical site, whereas Path B leads through a biradical with two secondary sites. Preliminary analysis therefore favors Path B. Let's find out how much by estimating the enthalpies of the two biradicals

In accord with expectations, the enthalpy of formation predicted for the wrong-bond biradical is higher (+45.4 kcal/mol) than that of the doubly-secondary biradical (+43.4 kcal/mol). The only other way to get these estimates is by NIST thermochemical tables, or by computational chemistry. The computational methods take time, and are not necessarily as effective as the thermochemical estimates.
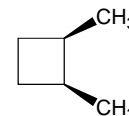The easiest way to figure out the relative
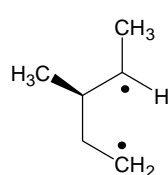
C(H)$_3$(C)	-10.20 kcal/mol
C(H)$_2$(C)(C$\cdot$)	-4.95
C$\cdot$(C)$_2$(H)	37.45
C(H)$_3$(C$\cdot$)	-10.80
C(H)(C)$_2$(C$\cdot$)	-1.90
C$\cdot$(C)(H)$_2$	35.82
	45.4 kcal/mol
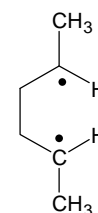
C(H)$_3$(C$\cdot$)	2 x -10.80 kcal/mol
C(H)$_2$(C)(C$\cdot$)	2 x -4.95
C$\cdot$(C)$_2$(H)	2 x 37.45
	43.40 kcal/mol

C(H)$_3$(C)	2 x -10.20 kcal/mol
C(H)$_2$(C)$_2$	2 x -4.93
C(C)$_3$(H)	2 x -1.71
strain	+26.2
	-7.5 kcal/mol

amounts of the cyclobutane ring opening are to use the Arrhenius expression, and to assume that the A-value is the same for the formation of both biradicals.

$$\frac{k_A}{k_B} = \frac{A_A}{A_B} e^{-(enthalpy\_differnce)/RT} \sim e^{-(43400-45400)/1.987\times(425+273.15)}$$

Note the conversion of the 425ºC to absolute temperature, and the use of R = 1.987 cal/mol-K. Solving the above equation, we get a ratio of k_A/k_B = 0.236. This means that 19% of the reaction goes via Path A, wrong bond cleavage at 425ºC.

45.4 kcal/mol

43.0 kcal/mol

B   A

-7.5 kcal/mol
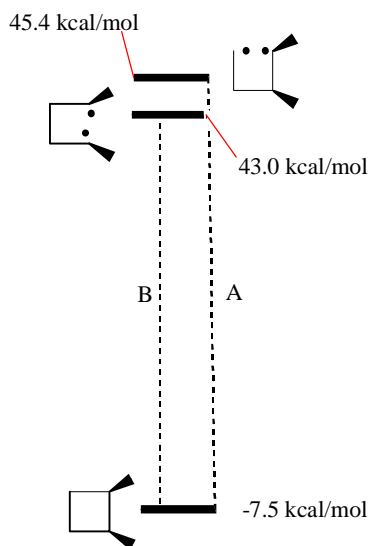
The same answer comes from figuring out the activation barriers from the cyclobutane to each biradical, applying same Arrhenius argument as used above. This analysis is shown below, to demonstrate that the shortcut used above works (it can be used whenever a molecule can undergo a reaction by passing through more than one transition state or intermediate).

We are applying the pseudothermodynamic model here, by *assuming* that the transition states which lead to biradical intermediates A and B are separated by the same amount of energy that separates the intermediates.

$$\frac{k_A}{k_B} = \frac{A_A}{A_B} \frac{e^{-(45400-(-7500))/1.987\times(425+273.15)}}{e^{-(43400-(-7500))/1.987\times(425+273.15)}}$$

Assuming as before that the A-values for conversion of the cyclobutane converting to the biradicals are the same, we get a ratio of k_A/k_B = 0.236. The activation barriers E_a for Path A and Path B are 52.9 and 50.9 kcal/mol, respectively.