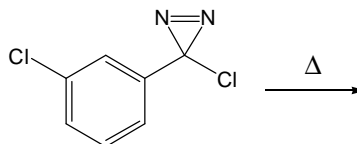


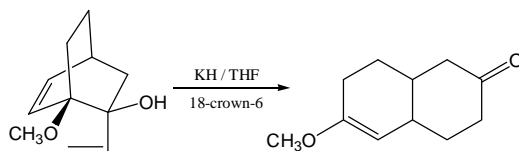
Practice Problem Set #1 (No credit, no due date)See answer key at <http://www.chem.umass.edu/~lahti/CHEM891>.

1. Make appropriate kinetic analysis plots on graph paper and calculate the activation parameters A , E_a , and ΔH^\ddagger , ΔS^\ddagger for the first-order thermal decomposition of 3-chloro-(3'-chlorophenyl)-diazirine, using the data given below. Note that the first rate constant for 60 °C is 0.00003 sec⁻¹. Give the Arrhenius A-value in exponential notation. Use units properly.

Temp / °C	k (0.0001 sec ⁻¹)
60.0	0.30
70.0	0.97
75.0	1.79
80.0	3.09
90.0	8.92
95.0	15.90



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 rearrangement activation energy is 30 kcal/mol, how long will a typical reaction half-life be at room temperature? Show your work. You may assume a typical A-value for a unimolecular reaction.
- (b) What is the activation energy of the oxy anionic Cope rearrangement, 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.



3. Using the Benson enthalpy group equivalents given below, estimate the relative percentages of C-C bond cleavage in *cis*-1,2-dimethylcyclobutane at 425 °C. Assume a typical Arrhenius pre-exponential A-factor of 10^{14} s^{-1} . Assume that only the two paths shown are available, and that activation enthalpy is equal to activation free energy. Please state any assumptions that you make in your analysis to convert the data given into an estimate of relative kinetics. (If you wish, you may try to compute the heats of formation of the two biradical intermediates shown below using any computational modeling program you wish, but be sure to describe your computations in a clear manner, including the methodology used.)

Why do you suppose that Path A is often called “wrong-bond cleavage”? Does your analysis support the use of this term to describe Path A?

Group	Enthalpy equivalent (ΔH°)
$\text{C}(\text{H})_3(\text{C})$	-10.20 kcal/mol
$\text{C}(\text{H})_2(\text{C})_2$	-4.93
$\text{C}(\text{C})_3(\text{H})$	-1.71
$\text{C}(\text{H})(\text{C})_2(\text{C}\cdot)$	-1.90
$\text{C}(\text{H})_3(\text{C}\cdot)$	-10.80
$\text{C}(\text{H})_2(\text{C})(\text{C}\cdot)$	-4.95
$\text{C}\cdot(\text{C})_2(\text{H})$	37.45
$\text{C}\cdot(\text{C})(\text{H})_2$	35.82
Cyclobutane strain	26.2

