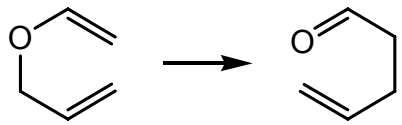
Chemistry 5011/8011 Friday, October 21

Problem Set 5
Due: *In class, Friday, October 28*

1. When heated, vinyl allyl ether undergoes a Claisen rearrangement to form 4-penten-1-al. Kinetic runs were performed in a pressurized cell with optical windows, and the progress of the reaction was monitored by measuring relative sample absorbance (A/A_∞) at λ = 313 nm over time; the increase in absorbance at this wavelength corresponded to appearance of the aldehyde.[1] Data from runs taken at different temperatures is posted on the course website.

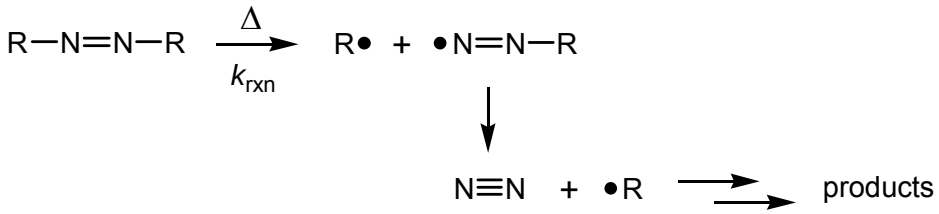


   a) From the posted data, determine the Arrhenius activation energy (E_a) and pre-exponential factor (A) for this reaction.

   b) Independently, determine the enthalpy and entropy of activation ($\Delta H^\ddagger$ and $\Delta S^\ddagger$) from the data. (In other words, do not just transform E_a and A into $\Delta H^\ddagger$ and $\Delta S^\ddagger$.)

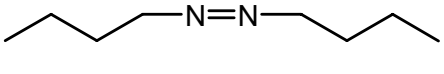
   c) Do these values relate in the way they should?

2. Pyrolysis of an azoalkane initially generates an intermediate pair of radicals, which then go on to yield molecular nitrogen and decomposition products in subsequent steps.

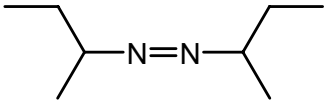


[1] Schuler, F. W.; Murphy, G. W. *J. Am. Chem. Soc.* **1950**, *72*, 3155.

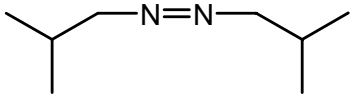
First-order rate constants for the pyrolysis of four different azoalkanes, measured at different temperatures,[2] are posted on the course website.



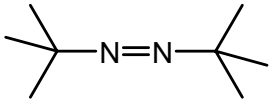
1,1'-azobutane



2,2'-azobutane



1,1'-azoisobutane



2,2'-azoisobutane

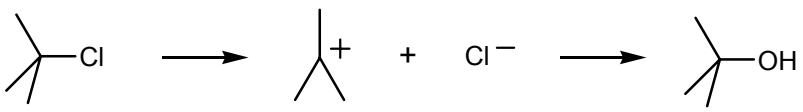
a) Data was measured for each azoalkane at two different reactant concentrations. Would you predict this to have any effect on the measured rate constants for that molecule? If so, what effect? If not, why not?

b) Based on this data, calculate enthalpies and entropies of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the pyrolysis of each molecule.

c) Are the magnitudes and signs (positive or negative) of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for all of the reactions consistent with the reaction mechanism?

d) The four different reactants gave four different sets of values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Explain these differences in terms of the structures and expected energies of the species involved in the reaction.

3. The hydrolysis of *tert*-butyl chloride in 80% EtOH/20% H_2O occurs through an S_N1 mechanism, for which the rate-determining step is dissociation of the starting material into a *tert*-butyl cation and a chloride anion.



[2] Blackham, A. U.; Eatough, N. L. **1962**, *84*, 2922.

Although one might imagine that the activation entropy for forming two species from one would be strongly positive, $\Delta S^{\ddagger}$ = -6.6 cal/mol·K.[3] Why could this be?

Problems to try on your own:

MPOC, Chapter 7: Problems 22, 24.
Kinetics, Chapter 4: Problem 7.

[3] Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.