

CHM 3400 – Problem Set 9

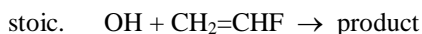
Due date: Monday, April 6th, via email, by midnight. NOTE: Exam 3 will be distributed at 5:00pm on Wednesday, April 8th, and will be due at 5:00pm on Thursday, April 9th. The exam covers material from Chapter 6 of Atkins. Do all of the following problems. Show your work.

“There is very little difference between one man and another; but what little there is very important.”

- William James

1) Baasandorj and coworkers (J.Phys.Chem.A 114 (2010) 4619-4633) recently examined the gas phase reaction of hydroxyl radical (OH) with CH₂=CHF. Surprisingly, they found a negative value for the activation energy for the reaction, suggesting there a multistep mechanism.

a) Consider the following mechanism for the reaction



where [M] is the concentration of gas solvent molecules. Find a general expression for the rate law predicted for the above mechanism.

b) Your general expression in b should have the following low pressure ([M] → 0) limiting behavior

$$d[\text{product}]/dt = (k_1 k_2 / k_{-1}) [\text{OH}] [\text{CH}_2=\text{CHF}] [\text{M}] \quad (1.3)$$

Assume that k₁, k₋₁, and k₂ each obey the Arrhenius equation. For what conditions, if any, will the observed rate law for the reaction have a negative activation energy?

2) For the following mechanisms predict the corresponding rate law

Decomposition of NO₂Cl



3) The general solution for second order heterogeneous kinetics for a reaction with stoichiometry and rate law



is, as shown in class

$$kt = \frac{1}{([B]_0 - [A]_0)} \ln \frac{[A]_0 [B]_t}{[B]_0 [A]_t} \quad [B]_0 \neq [A]_0 \quad (3.2)$$

Consider the specific case where [A]₀ = 0.0100 M, [B]₀ = 0.0200 M, and k = 0.0100 L/mol.s. How much time will it take for the concentration of A to decrease to a value [A] = 0.0050 M?

4) Gas phase recombination reactions play an important role in gas phase chemistry. One common mechanism for such reactions is the following



All reactants and products in the above mechanism are in the gas phase. AB^* represents an "energized" reaction intermediate, and M represents any gas phase molecule.

a) Based on the above mechanism find an expression for $d[AB]/dt$ and $d[AB^*]/dt$.

b) Using the steady state approximation the following expression can be obtained for the rate of the above reaction

$$\text{rate} = - \frac{d[A]}{dt} = \frac{k_1 k_2 [A][B][M]}{(k_{-1} + k_2 [M])} \quad (4.4)$$

What are the individual and overall reaction orders in the low pressure limit ($[M] \rightarrow 0$) and in the high pressure limit ($[M] \rightarrow \infty$)?

Solutions.

1) a) Based on the mechanism

$$d[\text{product}]/dt = k_2 [\text{OH-CH}_2\text{=CHF}][\text{M}]$$

If we make the steady state approximation for OH-CH₂=CHF, then

$$d[\text{OH-CH}_2\text{=CHF}]/dt \cong 0 = k_1[\text{OH}][\text{CH}_2\text{=CHF}] - k_{-1}[\text{OH-CH}_2\text{=CHF}] - k_2[\text{OH-CH}_2\text{=CHF}][\text{M}]$$

$$[\text{OH-CH}_2\text{=CHF}] = k_1[\text{OH}][\text{CH}_2\text{=CHF}]/(k_{-1} + k_2[\text{M}])$$

Substituting into our expression for rate gives

$$\frac{d[\text{product}]}{dt} = \frac{k_1 k_2 [\text{OH}][\text{CH}_2\text{=CHF}][\text{M}]}{(k_{-1} + k_2[\text{M}])}$$

b) In the low pressure limit ($[\text{M}] \rightarrow 0$) the second term in the denominator becomes negligible, and the rate law reduces to a low pressure limiting law

$$d[\text{product}]/dt = (k_1 k_2 / k_{-1}) [\text{OH}][\text{CH}_2\text{=CHF}][\text{M}] = k' [\text{OH}][\text{CH}_2\text{=CHF}][\text{M}]$$

Assume each individual rate constant fits an Arrhenius equation, so

$$k_1 = A \exp(-E_a/RT)$$

$$k_{-1} = B \exp(-E_b/RT)$$

$$k_2 = C \exp(-E_c/RT)$$

Then the apparent rate constant in the low pressure limit is

$$k' = \frac{[A \exp(-E_a/RT)][B \exp(-E_b/RT)]}{[C \exp(-E_c/RT)]} = (AB/C) \exp[-(E_a + E_b - E_c)/RT]$$

which has the same form as the Arrhenius equation, but with an apparent activation energy

$$E' = E_a + E_b - E_c$$

If $E_c > (E_a + E_b)$, then E' will be negative, as is observed in these experiments.

2) The overall rate is equal to the rate of the slow step, so

$$d[\text{Cl}_2]/dt = k_2 [\text{NO}_2\text{Cl}][\text{Cl}]$$

The intermediate is in pre-equilibrium, so

$$k_1 [\text{NO}_2\text{Cl}] = k_{-1} [\text{NO}_2][\text{Cl}] \quad [\text{Cl}] = (k_1/k_{-1}) [\text{NO}_2\text{Cl}]/[\text{NO}_2]$$

Substituting gives

$$\frac{d[\text{Cl}_2]}{dt} = \frac{(k_1 k_2 / k_{-1}) [\text{NO}_2\text{Cl}]^2}{[\text{NO}_2]}$$

predicting a reaction that is second order in NO₂Cl and - 1st order in NO₂.

3) We have

$$kt = \frac{1}{([B]_0 - [A]_0)} \ln \frac{[A]_0 [B]_t}{[B]_0 [A]_t}$$

and so

$$t = \frac{1}{k([B]_0 - [A]_0)} \ln \frac{[A]_0 [B]_t}{[B]_0 [A]_t}$$

We are given values for everything in the above equation except $[B]_t$. But based on the stoichiometry of the reaction

$$[B]_0 - [B]_t = [A]_0 - [A]_t$$

$$[B]_t = [B]_0 - ([A]_0 - [A]_t) = 0.0200 \text{ M} - (0.0100 \text{ M} - 0.0050 \text{ M}) = 0.0150 \text{ M}$$

and so

$$t = \frac{1}{(0.0100 \text{ L/mol}\cdot\text{s}) [(0.0200 \text{ M} - 0.0100 \text{ M})]} \ln \{ (0.0100) (0.0150) / (0.0050) (0.0200) \}$$

$$= 4055. \text{ s (or about 1.1 hour)}$$

4) a) $d[AB]/dt = k_2 [AB^*] [M]$

$$d[AB^*]/dt = k_1 [A] [B] - k_{-1} [AB^*] - k_2 [AB^*] [M]$$

b) $\text{rate} = - \frac{d[A]}{dt} = \frac{k_1 k_2 [A][B][M]}{(k_{-1} + k_2 [M])}$

In the low pressure limit ($[M] \rightarrow 0$) we have $k_1 \gg k_2 [M]$, and so

$$\text{rate} = - \frac{d[A]}{dt} \cong \frac{k_1 k_2 [A][B][M]}{(k_{-1})}$$

and so first order in A, B, and M, and so third order overall.

In the high pressure limit ($[M] \rightarrow \infty$) we have $k_1 \ll k_2 [M]$, and so

$$\text{rate} = - \frac{d[A]}{dt} \cong \frac{k_1 k_2 [A][B][M]}{(k_2 [M])} = k_1 [A] [B]$$

and so first order in A and B, and so second order overall.