Chemical Kinetics: Reaction Mechanisms (covering Topic 4a)

Chemistry 126

1. Provide the molecularity and rate law for each of the following elementary reaction steps.

   a.) $2NO_2\ (g) \rightarrow NO\ (g) + NO_3\ (g)$
   b.) $ICl\ (g) + H_2\ (g) \rightarrow HI\ (g) + HCl\ (g)$
   c.) $Cl_2\ (g) \rightarrow 2Cl\ (g)$

2. The reaction between 3-bromo-3-ethylpentane, $(CH_3CH_2)_3CBr$, and water can be used to produce the alcohol 3-ethyl-3-pentanol, $(CH_3CH_2)_3COH$ and hydrobromic acid (HBr). Consider the proposed mechanism below.

$$\text{Step 1:}\quad (CH_3CH_2)_3CBr\ (aq) \xrightarrow{k_1} (CH_3CH_2)_3C^+\ (aq) + Br^-\ (aq)$$

$$\text{Step 2:}\quad (CH_3CH_2)_3C^+\ (aq) + H_2O\ (l) \xrightarrow{k_2} (CH_3CH_2)_3COH_2^+\ (aq)$$

$$\text{Step 3:}\quad (CH_3CH_2)_3COH_2^+\ (aq) \xrightarrow{k_3} (CH_3CH_2)_3COH\ (aq) + H^+\ (aq)$$

   a.) What is the overall equation for this reaction?
   b.) Identify the intermediates.
   c.) Write the individual rate laws for each of the three elementary reaction steps. Argue that, for the mechanism as written,

$$(\textit{Reaction Rate})_1 = (\textit{Reaction Rate})_2 = (\textit{Reaction Rate})_3$$

   d.) What is the overall rate law for this reaction?

3. Ozone (O_3) is a major component of photochemical smog formed by the reaction of nitric oxide (NO_2), which is from car exhaust, and atmospheric oxygen. Consider the following mechanism.

$$\text{Step 1: } NO_2\ (g) \underset{h\nu}{\overset{k_1}{\longrightarrow}} NO\ (g) + O\ (g)$$

$$\text{Step 2: } O\ (g) + O_2\ (g) \xrightarrow{k_2} O_3\ (g)$$

   a.) What is the overall equation for this reaction?
   b.) Identify the intermediate in this mechanism.
   c.) Write the rate law for each elementary reaction step.
   d.) Provide the overall rate law for this reaction assuming a steady state.
   e.) Draw a graph depicting how the concentrations of NO_2, NO, O, O_2 and O_3 change with time. (No need to be quantitative here, just relatively correct. Hint: Consider the steady state.)

CHALLENGE PROBLEM:* Based on the mechanism given in Problem 3 and given $k_1 = 0.002\ s^{-1}$ and $k_2 = 30{,}000$ L/mol·s, consider the following problem: At 11:00 AM on a hot summer morning (85 ^oF) in Los Angeles after much commuter travel, $[NO_2] = 10$ ppm, and a state of smog emergency is called. Under these conditions, what must be the concentration of oxygen atoms, O(g), in the air in ppm, assuming a steady state? (Consider the O_2 pressure to be approximately 0.23 atm.) If all the cars were instantly turned off (as in the movie *The Day the Earth Stood Still*), at what time could the state of emergency be called off, if that required $[NO_2]$ to be less that 0.5 ppm?

***One bonus point; all or none; must be done ON YOUR OWN (or with a group)—not at the problem session with the teaching assistant!—must be turned in on a separate sheet of paper directly to your professor.**