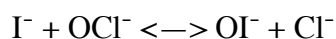


Problem Set 22: Reaction Mechanisms

Due Nov 18, 2008

1. What is the difference between a chemical mechanism (reaction mechanism) and a kinetic mechanism? What is an elementary step?
2. Is it possible to have more than one chemical mechanism which is consistent with an observed kinetic mechanism? If you are told that a reaction goes via a particular chemical mechanism, can you derive more than one kinetic mechanism which is consistent with this mechanism?
3. If it is possible to have more than one chemical mechanism which is consistent with an observed kinetic mechanism, draw a free energy profile (with G on the y coordinate and reaction progress on the x coordinate) illustrating why this is possible.

4. The kinetics of the reaction



have been studied in a basic solution. The initial rate of I^- disappearance ($d[\text{I}^-]/dt$) has been measured for several different starting concentrations of substrates:

<u>Initial Conc of I^- (M)</u>	<u>Initial Conc of OCl^- (M)</u>	<u>Initial Conc of OH^- (M)</u>	<u>$d[\text{I}^-]/dt$ (M/sec)</u>	
2×10^{-3}	1.5×10^{-3}	1.00	1.8×10^{-4}	(1)
4×10^{-3}	1.5×10^{-3}	1.00	3.6×10^{-4}	(2)
2×10^{-3}	3×10^{-3}	2.00	1.8×10^{-4}	(3)
4×10^{-3}	3×10^{-3}	1.00	7.2×10^{-4}	(4)

- (a) Hydroxide ion does not appear as either a reactant or a product, yet comparing experiments 3 and 4 shows that the concentration of hydroxide affects the rate of the reaction. What is an appropriate name for hydroxide in this reaction?
- (b) The rate law for this reaction can be written:

$$\frac{d[\text{I}^-]}{dt} = k[\text{I}^-]^a[\text{OCl}^-]^b[\text{OH}^-]^c$$

Examine the data carefully and determine the proper values for a, b, and c. The way to do this is to look at two experiments which differ in the concentration of only one component. If the concentration of that component doubles and the rate goes up by 4, then you know that the reaction is second order in that component. There is exactly enough information in the table to allow you to determine all three values.

- (c) Determine the value of k. Be sure to give the correct units.
- (d) Check your work. Make sure that the rate equation that you have written gives the correct value of $d[\text{I}^-]/dt$ for all four experiments.