Determining the Rate Law with Initial Rate

Problem 14-78

Hydroxide ion is involved in the mechanism of the following reaction but is not consumed in the overall reaction.

$$OCl^- + I^- \xrightarrow{OH^-} OI^- + Cl^-$$

(a) From the data given, determine the order of the reaction with respect to OCl^-, I^-, and OH^-.
(b) What is the overall reaction order?
(c) Write the rate equation, and determine the value of the rate constant, *k*.

$[OCl^-]$, M	$[I^-]$, M	$[OH^-]$, M	Rate Formation OI^-, M s^{-1}
0.0040	0.0020	1.00	4.8×10^{-4}
0.0020	0.0040	1.00	5.0×10^{-4}
0.0020	0.0020	1.00	2.4×10^{-4}
0.0020	0.0020	0.50	4.6×10^{-4}
0.0020	0.0020	0.25	9.4×10^{-4}

Solution:

This is just a rate law problem using initial rates. Even though the OH^- is not consumed, it still affects the rate and needs to be included in the rate law. As with other problems of this type, solve for each of the orders using pairs of reaction conditions.

(a)

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

$$\frac{4.8\times10^{-4}\ \frac{\text{M}}{\text{s}}}{2.4\times10^{-4}\ \frac{\text{M}}{\text{s}}} = \frac{k(0.0040\ \text{M})^a(0.0020\ \text{M})^b(1.00\ \text{M})^c}{k(0.0020\ \text{M})^a(0.0020\ \text{M})^b(1.00\ \text{M})^c}$$

$$2.0 = 2.0^a \qquad \boxed{a = 1}$$

$$\frac{5.0\times10^{-4}\ \frac{\text{M}}{\text{s}}}{2.4\times10^{-4}\ \frac{\text{M}}{\text{s}}} = \frac{k(0.0020\ \text{M})^a(0.0040\ \text{M})^b(1.00\ \text{M})^c}{k(0.0020\ \text{M})^a(0.0020\ \text{M})^b(1.00\ \text{M})^c}$$

$$2.08 = 2.0^b \qquad \boxed{b = 1.06 = 1}$$

$$\frac{2.4\times10^{-4}\ \frac{\text{M}}{\text{s}}}{4.6\times10^{-4}\ \frac{\text{M}}{\text{s}}} = \frac{k(0.0020\ \text{M})^a(0.0020\ \text{M})^b(1.00\ \text{M})^c}{k(0.0020\ \text{M})^a(0.0020\ \text{M})^b(0.50\ \text{M})^c}$$

$$0.522 = 2.0^c$$

$$\ln(0.522) = c\ln(2.0)$$

$$-0.6506 = c(0.693)$$

$$\boxed{c = -0.939 = -1}$$

(b) $\text{Rate} = k[\text{OCl}^-][\text{I}^-][\text{OH}^-]^{-1}$
so the overall reaction order is 1

(c)

$$4.8\times10^{-4}\text{M s}^{-1} = k(0.0040\ \text{M})(0.0020\ \text{M})(1.00)^{-1}$$

$$k = \frac{4.8\times10^{-4}\text{M s}^{-1}}{(0.0040\ \text{M})(0.0020\ \text{M})(1.00)^{-1}} = 60.0\ \text{s}^{-1}$$