Chapter 15: Chemical Kinetics; Problems: 49, 51, 52, 53, 81, 84

Reaction Mechanisms:

49.   Rate = $k_3[Br^-][H_2BrO_3^+]$; We must substitute for the intermediate concentrations. Since steps 1 and 2 are fast equilibrium steps, then rate forward reaction = rate reverse reaction.

$k_2[HBrO_3][H^+] = k_{-2}[H_2BrO_3^+]$; $k_1[BrO_3^-][H^+] = k_{-1}[HBrO_3]$

$[HBrO_3] = \dfrac{k_1}{k_{-1}}[BrO_3^-][H^+]$; $[H_2BrO_3^+] = \dfrac{k_2}{k_{-2}}[HBrO_3][H^+] = \dfrac{k_2 k_1}{k_{-2}k_{-1}}[BrO_3^-][H^+]^2$

Rate = $\dfrac{k_3 k_2 k_1}{k_{-2}k_{-1}}[Br^-][BrO_3^-][H^+]^2 = k[Br^-][BrO_3^-][H^+]^2$

51.   a. $MoCl_5^-$

b. Rate = $\dfrac{d[NO_2^-]}{dt} = k_2[NO_3^-][MoCl_5^-]$ (Only the last step contains NO_2^-.)

We use the steady-state assumption to substitute for the intermediate concentration in the rate law. The steady-state approximation assumes that the concentration of an intermediate remains constant, i.e., d[intermediate]/dt = 0. To apply the steady-state assumption, we write rate laws for all steps where the intermediate is produced and equate the sum of these rate laws to the sum of the rate laws where the intermediate is consumed. Applying the steady-state approximation to $MoCl_5^-$:

$\dfrac{d[MoCl_5^-]}{dt} = 0$, so $k_1[MoCl_6^{2-}] = k_{-1}[MoCl_5^-][Cl^-] + k_2[NO_3^-][MoCl_5^-]$

$[MoCl_5^-] = \dfrac{k_1[MoCl_6^{2-}]}{k_{-1}[Cl^-] + k_2[NO_3^-]}$; Rate = $\dfrac{d[NO_2^-]}{dt} = \dfrac{k_1 k_2[NO_3^-][MoCl_6^{2-}]}{k_{-1}[Cl^-] + k_2[NO_3^-]}$

52.   Rate = $\dfrac{-d[O_3]}{dt} = k_1[M][O_3] + k_2[O][O_3] - k_{-1}[M][O_2][O]$; Apply steady-state approx. to O:

$\dfrac{d[O]}{dt} = 0$, so $k_1[M][O_3] = k_{-1}[M][O_2][O] + k_2[O][O_3]$, $k_1[M][O_3] - k_{-1}[M][O_2][O] = k_2[O][O_3]$

Substitute this expression into the rate law: Rate = $\dfrac{-d[O_3]}{dt} = 2\,k_2[O][O_3]$

Rearranging the steady-state approx. for [O]: $[O] = \dfrac{k_1[O_3][M]}{k_{-1}[M][O_2] + k_2[O_3]}$

Substituting into the rate law: Rate = $\dfrac{-d[O_3]}{dt} = \dfrac{2\,k_2 k_1[O_3]^2[M]}{k_{-1}[M][O_2] + k_2[O_3]}$

53.   a.   rate $= \dfrac{d[E]}{dt} = k_2[B^*]$; Assume $\dfrac{d[B^*]}{dt} = 0$, then $k_1[B]^2 = k_{-1}[B][B^*] + k_2[B^*]$

$[B^*] = \dfrac{k_1[B]^2}{k_{-1}[B] + k_2}$; The rate law is: Rate $= \dfrac{d[E]}{dt} = \dfrac{k_1k_2[B]^2}{k_{-1}[B] + k_2}$

   b.   When $k_2 \ll k_{-1}[B]$, then Rate $= \dfrac{d[E]}{dt} = \dfrac{k_1k_2[B]^2}{k_{-1}[B]} = \dfrac{k_1k_2}{k_{-1}}[B]$

Reaction is first order when the rate of the second step is very slow (when k_2 is very small).

   c.   Collisions between B molecules only transfer energy from one B to another. This occurs at a much faster rate than the decomposition of an energetic B molecule (B^*).

Additional Exercises:

81.   Rate $= k_2[I^-][HOCl]$; From the fast equilibrium first step:

$k_1[OCl^-] = k_{-1}[HOCl][OH^-]$, $[HOCl] = \dfrac{k_1[OCl^-]}{k_{-1}[OH^-]}$; Substituting into the rate equation:

Rate $= \dfrac{k_2k_1[I^-][OCl^-]}{k_{-1}[OH^-]} = \dfrac{k[I^-][OCl^-]}{[OH^-]}$

84.   a.   Let P_o = initial partial pressure of C_2H_5OH = 250. torr. If x torr of C_2H_5OH reacts, then at anytime:

$P_{C_2H_5OH} = 250. - x$, $P_{C_2H_4} = P_{H_2O} = x$; $P_{tot} = 250. - x + x + x = 250. + x$

Therefore, $P_{C_2H_5OH}$ at any time can be calculated from the data by determining x (= P_{tot} - 250.) and then subtracting from 250. torr. Using the $P_{C_2H_5OH}$ data, a plot of $P_{C_2H_5OH}$ vs. t is linear (plot not included). The reaction is zero order in $P_{C_2H_5OH}$. One could also use the P_{tot} vs. t data since P_{tot} increases at the same rate that $P_{C_2H_5OH}$ decreases. Note: The ln P vs. t plot is also linear. The reaction hasn't been followed for enough time for curvature to be seen. However, since $P_{C_2H_5OH}$ decreases at steady increments of 15 torr for every 10. s of reaction, then we can conclude that the reaction is zero order in C_2H_5OH.

From the data, the integrated rate equation involving P_{tot} is: $P_{tot} = \dfrac{15}{10.}t + 250.$

At t = 80. s, $P_{tot} = \dfrac{15}{10.}(80.) + 250. = 370$ torr

   b.   slope $= -k = -15$ torr/10. s $= 1.5$ torr/s (from $P_{C_2H_5OH}$ vs. t plot), k = 1.5 torr/s; The P_{tot} vs. t plot would give the same rate constant since P_{tot} increases at the same rate that $P_{C_2H_5OH}$ decreases.

   c.   zero order

   d. $P_{tot} = \dfrac{15}{10.}(300.) + 250. = 7.0 \times 10^2$ torr   This is an impossible answer!

Since only 250. torr of C_2H_5OH are present initially, the maximum pressure can only be 500. torr when all of the C_2H_5OH is consumed, i.e., $P_{tot} = P_{C_2H_4} + P_{H_2O} = 250. + 250. = 500.$ torr. Therefore, at 300. s, $P_{tot} = 500.$ torr.