EGEE 510 Kinetics in Solution Fall 2005

Another example of the importance of <u>mass transport</u> ... and of <u>RDS</u> ...

<u>Summary</u>:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [AB] \xrightarrow{k_2} \text{products}$$

"activation"

"Cage" (encounter pair) ... in contrast to gas-phase rxns, the encounter frequency is lower, but the time spent together is longer!

diffusion process

$k_1 \equiv k_d$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[AB]}{dt} = \frac{k_1 k_2}{k_{-1}+k_2}[A][B] \Rightarrow \text{RDS?}$$

* diffusion control : $k_2 >> k_{-1} \Rightarrow \underline{\text{Rate} = k_d [A][B]}$
* "activation" control : $k_2 << k_{-1} \Rightarrow \text{Rate} = k_2 K [A][B]$ $\quad K = \frac{k_1}{k_{-1}}$

<u>Estimation of k_d</u> ?

– mass transport rate $= 4\pi r^2 D_B \frac{dC_B}{dr}$, etc. $\Rightarrow$ Rate of rxn $= 4\pi(D_A+D_B) d_{AB}[A][B]$

$\therefore k_d = 4\pi R^* (D_A + D_B)$ $\quad R^* \cong R_A + R_B$ .. critical distance (of approach)

.. for $R_A \approx R_B \Rightarrow \boxed{k_d = \frac{8RT}{3\eta}}$

(and Stokes-Einstein eq. D vs. η)

indeed, of the order of $10^9 \frac{L}{mol \cdot s}$

.. But, for $H^+ + OH^- = H_2O(l)$, $k_d \cong 1.4\times10^{11} \frac{L}{mol\cdot s}$ Why? ⇒ 1st neglect intermolecular/interion forces (OK?)

$$R_{H_3O^+} + R_{OH^-} = \frac{\left(1.4\times10^{11}\frac{L}{mol\cdot s}\right)\left(\frac{1\,m^3}{10^3 L}\right)}{(4\pi)\left(6.022\times10^{23}\frac{1}{mol}\right)\left(9.31\times10^{-9}+5.3\times10^{-9}\frac{m^2}{s}\right)} \cong \underline{1.3\ nm}$$

Too large!?

$$k_d = 4\pi(D_A+D_B)d_{AB}\left[\frac{\frac{z_A z_B e^2}{4\pi\epsilon_0\epsilon d_{AB} RT}}{\exp\left(\frac{z_A z_B e^2}{4\pi\epsilon_0\epsilon d_{AB} RT}\right)-1}\right]$$

electrostatic factor

$\log k = \log k^0 + 2 z_A z_B A I^{0.5}$

$I\uparrow, k\downarrow$ (shielding!)

Check!!

$z_A z_B$	f
0	1
-1	3,65
-2	7.08
1	0.106
2	0.006