Dynamics and Kinetics. Exercises 9: Solutions

Problem 1 (Beams of molecules)

We have colliding molecules and we define as A, the molecular beam, and as B, the target molecules. We want to compute the following ratio of the effective cross sections

$$\frac{\sigma_{\mathrm{CsCl/CH_2F_2}}}{\sigma_{\mathrm{CsCl/Ar}}} = ?$$

The flux of the beam is given by the expression

$$I(x) = I(0)\mathrm{e}^{-\sigma c_{\mathrm{B}} x},$$

where I is the final intensity, σ the cross section (not only reactive), c_{B} the concentration of molecules B and x the distance.

From the data of the problem we have that A = CsCl, while $\mathrm{B} = \begin{cases} \mathrm{CH_2F_2}, & \text{loss} = 40\%; \\ \mathrm{Ar}, & \text{loss} = 10\%. \end{cases}$

The cross section is

$$\sigma = -\frac{1}{c_{\mathrm{B}} l} \ln \frac{I(l)}{I(0)},$$

Therefore

$$\frac{\sigma_{\mathrm{CsCl/CH_2F_2}}}{\sigma_{\mathrm{CsCl/Ar}}} = \frac{\sigma_1}{\sigma_2} = \frac{\ln \frac{I_1(l)}{I_1(0)}}{\ln \frac{I_2(l)}{I_2(0)}} = \frac{\ln 0.60}{\ln 0.90} = 4.85.$$

The conclusion is that bigger molecules give rise to bigger cross sections.

Problem 2 (Steric factor)

We consider a bimolecular reaction

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{Prod}, \qquad \mathrm{Prod} = ?$$

The rate of reaction is

$$v = \frac{d[Prod]}{dt} = N_{\mathrm{Av}} \sigma_{\mathrm{exp}} \langle u \rangle [A][B] \mathrm{e}^{-\epsilon^0_{\mathrm{tr}}/k_{\mathrm{B}}T} = P N_{\mathrm{Av}} \sigma_{\mathrm{theor}} \langle u \rangle [A][B] \mathrm{e}^{-\epsilon^0_{\mathrm{tr}}/k_{\mathrm{B}}T},$$

and therefore $\sigma_{\mathrm{exp}} = P \times \sigma_{\mathrm{theor}}$, where $\langle u \rangle$ is the mean relative velocity, $\varepsilon^0_{tr} / k_{\mathrm{B}}T$ the fraction of reactive collisions and P the steric factor.

From the data of the problem we know that $\sigma_{AA} = 0.95\ \mathrm{nm}^2$, while $\sigma_{BB} = 0.65\ \mathrm{nm}^2$.

The theoretical cross-section for $A + B$ is

$$\sigma_{AB} = \pi d^2 = \pi (r_A + r_B)^2 = \pi \left(\frac{d_A + d_B}{2}\right)^2 = \pi \left(\frac{\sqrt{\frac{\sigma_{AA}}{\pi}} + \sqrt{\frac{\sigma_{BB}}{\pi}}}{2}\right)^2 = \left(\frac{\sqrt{\sigma_{AA}} + \sqrt{\sigma_{BB}}}{2}\right)^2.$$

In our case

$$\sigma_{AB} = \sigma_{\mathrm{theor}} = 0.793 \times 10^{-18} \mathrm{m}^2 \Rightarrow P = \frac{\sigma_{\mathrm{exp}}}{\sigma_{\mathrm{theor}}} = 1.16 \times 10^{-3}.$$

P is smaller than one, as expected, since the reaction, in order to occur, needs certain orientations.

Problem 3 (Steric factor larger than one: Harpoon mechanism)

The harpoon mechanism enables the following reaction

$$\mathrm{Na+Cl_2 \rightarrow NaCl+Cl},$$

creating a pair of ions $\mathrm{Na^+/Cl_2{}^-}$, as summarized schematically by the relation

$$\mathrm{Na^+ + Cl_2{}^- \rightarrow NaCl + Cl}.$$

From the energy balance we know that

$$\Delta E = E_{\mathrm{I}}\left(\mathrm{Na}\right) - E_{\mathrm{ea}}\left(\mathrm{Cl}_2\right) - \frac{e^2}{4\pi\epsilon_0 r},$$

Where E_I is the ionization potential, E_{ea} the electron affinity and $-\frac{e^2}{4\pi\epsilon_0 r}$ the electrostatic interaction. The electron transfers when eh energy balance is zero, therefore

$$\Delta E = 0 \Leftrightarrow r = \frac{e^2}{4\pi\epsilon_0\left(E_{\mathrm{I}} - E_{\mathrm{ea}}\right)} = \frac{\left(1.602\times10^{-19}\mathrm{C}\right)\times 1\cdot e}{4\pi\cdot 8.85\times10^{-12}\mathrm{F/m}\left(5.1-2.38\right)eV} = 5.3\times10^{-10}\mathrm{m}.$$

In the last step we have used a trick: usually we have quantities expressed in electron volt while, remembering that 1C = 1F · 1V, we managed to be only left with volt so that we got the answer just dividing the numbers.
Now we can compute the steric factor *P*

$$P = \frac{\sigma_{\mathrm{exp}}}{\sigma_{\mathrm{theor}}} = \frac{\pi r^2}{\pi d^2} = \left(\frac{5.3\mathrm{\AA}}{3.5\mathrm{\AA}}\right)^2 = 2.3,$$

where *d* is the minimum distance of Na + Cl neutral and *r* is the distance at which the electron transfers.
The conclusion is that the harpoon speeds up the reaction 2.3 times.