

## 27 Molecular reaction dynamics

### Solutions to exercises

#### Discussion questions

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- E27.1(b)** A reaction in solution can be regarded as the outcome of two stages: one is the encounter of two reactant species, which is followed by their reaction, the second stage, if they acquire their activation energy. If the rate-determining step is the former, then the reaction is said to be diffusion-controlled. If the rate-determining step is the latter, then the reaction is activation controlled. For a reaction of the form  $A + B \rightarrow P$  that obeys the second-order rate law  $v = k_2[A][B]$ , in the diffusion-controlled regime,

$$k_2 = 4\pi R^* D N_A$$

where  $D$  is the sum of the diffusion coefficients of the two reactant species and  $R^*$  is the distance at which reaction occurs. A further approximation is that each molecule obeys the Stokes–Einstein relation and Stokes' law, and then

$$k_2 \approx \frac{8RT}{3\eta}$$

where  $\eta$  is the viscosity of the medium. The result suggests that  $k_2$  is independent of the radii of the reactants.

- E27.2(b)** In the kinetic salt effect, the rate of a reaction in solution is changed by modification of the ionic strength of the medium. If the reactant ions have the same sign of charge (as in cation/cation or anion/anion reactions), then an increase in ionic strength increases the rate constant. If the reactant ions have opposite signs (as in cation/anion reactions), then an increase in ionic strength decreases the rate constant. In the former case, the effect can be traced to the denser ionic atmosphere (see the Debye–Huckel theory) that forms round the newly formed and highly charged ion that constitutes the activated complex and the stronger interaction of that ion with the atmosphere. In the latter case, the ion corresponding to the activated complex has a lower charge than the reactants and hence it has a more diffuse ionic atmosphere and interacts with it more weakly. In the limit of low ionic strength the rate constant can be expected to follow the relation

$$\log k = \log k^\circ + 2A z_A z_B I^{1/2}$$

- E27.3(b)** Refer to Figs 27.21 and 27.22 of the text. The first of these figures shows an attractive potential energy surface, the second, a repulsive surface.

- (a) Consider Fig. 27.21. If the original molecule is vibrationally excited, then a collision with an incoming molecule takes the system along the floor of the potential energy valley (trajectory C). This path is bottled up in the region of the reactants, and does not take the system to the saddle point. If, however, the same amount of energy is present solely as translational kinetic energy, then the system moves along a successful encounter trajectory  $C^*$  and travels smoothly over the saddle point into products. We can therefore conclude that reactions with attractive potential energy surfaces proceed more efficiently if the energy is in relative translational motion. Moreover, the potential surface shows that once past the saddle point the trajectory runs up the steep wall of the product valley, and then rolls from side to side as it falls to the foot of the valley as the products separate. In other words, the products emerge in a vibrationally excited state.

- (b) Now consider the repulsive surface (Fig. 27.22). On trajectory C the collisional energy is largely in translation. As the reactants approach, the potential energy rises. Their path takes them up the opposing face of the valley, and they are reflected back into the reactant region. This path corresponds to an unsuccessful encounter, even though the energy is sufficient for reaction. On a successful trajectory C\*, some of the energy is in the vibration of the reactant molecule and the motion causes the trajectory to weave from side to side up the valley as it approaches the saddle point. This motion may be sufficient to tip the system round the corner to the saddle point and then on to products. In this case, the product molecule is expected to be in an unexcited vibrational state. Reactions with repulsive potential surfaces can therefore be expected to proceed more efficiently if the excess is present as vibrations.

### Numerical exercises

**E27.4(b)** The collision frequency is

$$z = \frac{2^{1/2}\sigma\langle v \rangle p}{kT} \quad \text{where } \sigma = \pi d^2 = 4\pi r^2 \text{ and } \langle v \rangle = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\text{so } z = \frac{2^{1/2}p(4\pi r^2)\left(\frac{8RT}{\pi M}\right)^{1/2}}{kT} = \frac{16pN_A r^2 \pi^{1/2}}{(RTM)^{1/2}}$$

$$= \frac{16 \times (100 \times 10^3 \text{ Pa}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times (180 \times 10^{-12} \text{ m})^2 \times (\pi)^{1/2}}{[(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (28.01 \times 10^{-3} \text{ kg mol}^{-1})]^{1/2}}$$

$$= \boxed{6.64 \times 10^9 \text{ s}^{-1}}$$

The collision density is

$$Z_{AA} = \frac{1}{2}zN/V = \frac{zp}{2kT} = \frac{(6.64 \times 10^9 \text{ s}^{-1}) \times (100 \times 10^3 \text{ Pa})}{2(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} = \boxed{8.07 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}}$$

Raising the temperature at constant volume means raising the pressure in proportion to the temperature

$$Z_{AA} \propto \sqrt{T}$$

so the per cent increase in  $z$  and  $Z_{AA}$  due to a 10 K increase in temperature is  $\boxed{1.6 \text{ per cent}}$ , same as Exercise 27.4(a).

**E27.5(b)** The appropriate fraction is given by

$$f = \exp\left(\frac{-E_a}{RT}\right)$$

The values in question are

$$\text{(a) (i) } f = \exp\left(\frac{-15 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}\right) = \boxed{2.4 \times 10^{-3}}$$

$$\text{(ii) } f = \exp\left(\frac{-15 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) = \boxed{0.10}$$

$$\text{(b) (i) } f = \exp\left(\frac{-150 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}\right) = \boxed{7.7 \times 10^{-27}}$$

$$\text{(ii) } f = \exp\left(\frac{-150 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) = \boxed{1.6 \times 10^{-10}}$$

**E27.6(b)** A straightforward approach would be to compute  $f = \exp\left(\frac{-E_a}{RT}\right)$  at the new temperature and compare it to that at the old temperature. An approximate approach would be to note that  $f$  changes from  $f_0 = \exp\left(\frac{-E_a}{RT}\right)$  to  $f = \exp\left(\frac{-E_a}{RT(1+x)}\right)$ , where  $x$  is the fractional increase in the temperature. If  $x$  is small, the exponent changes from  $\frac{-E_a}{RT}$  to approximately  $\frac{-E_a}{RT}(1-x)$  and  $f$  changes from  $\exp\left(\frac{-E_a}{RT}\right)$  to  $\exp\left(\frac{-E_a(1-x)}{RT}\right) = \exp\left(\frac{-E_a}{RT}\right) \left[\exp\left(\frac{-E_a}{RT}\right)\right]^{-x} = f_0 f_0^{-x}$ . Thus the new Boltzmann factor is the old one times a factor of  $f_0^{-x}$ . The factor of increase is

- (a) (i)  $f_0^{-x} = (2.4 \times 10^{-3})^{-10/300} = \boxed{1.2}$   
 (ii)  $f_0^{-x} = (0.10)^{-10/800} = \boxed{1.03}$   
 (b) (i)  $f_0^{-x} = (7.7 \times 10^{-27})^{-10/300} = \boxed{7.4}$   
 (ii)  $f_0^{-x} = (1.6 \times 10^{-10})^{-10/800} = \boxed{1.3}$

**E27.7(b)** The reaction rate is given by

$$v = P\sigma \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} N_A \exp(-E_a/RT) [D_2][Br_2]$$

so, in the absence of any estimate of the reaction probability  $P$ , the rate constant is

$$\begin{aligned} k &= \sigma \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} N_A \exp(-E_a/RT) \\ &= [0.30 \times (10^{-9} \text{ m})^2] \times \left(\frac{8(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (450 \text{ K})}{\pi(3.930 \text{ u}) \times (1.66 \times 10^{-27} \text{ kg u}^{-1})}\right)^{1/2} \\ &\quad \times (6.022 \times 10^{23} \text{ mol}^{-1}) \exp\left(\frac{-200 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})}\right) \\ &= 1.71 \times 10^{-15} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = \boxed{1.7 \times 10^{-12} \text{ L mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

**E27.8(b)** The rate constant is

$$k_d = 4\pi R^* D N_A$$

where  $D$  is the sum of two diffusion constants. So

$$\begin{aligned} k_d &= 4\pi(0.50 \times 10^{-9} \text{ m}) \times (2 \times 4.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \\ &= \boxed{3.2 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}} \end{aligned}$$

In more common units, this is

$$k_d = \boxed{3.2 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}}$$

**E27.9(b)** (a) A diffusion-controlled rate constant in decylbenzene is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (3.36 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{1.97 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

(b) In concentrated sulfuric acid

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (27 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

**E27.10(b)** The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{3 \times (0.601 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = \boxed{1.10 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$

In more common units,  $k_d = \boxed{1.10 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}}$

The recombination reaction has a rate of

$$v = k_d[A][B] \quad \text{with } [A] = [B]$$

so the half-life is given by

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(1.10 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}) \times (1.8 \times 10^{-3} \text{ mol L}^{-1})} = \boxed{5.05 \times 10^{-8} \text{ s}}$$

**E27.11(b)** The reactive cross-section  $\sigma^*$  is related to the collision cross-section  $\sigma$  by

$$\sigma^* = P\sigma \quad \text{so} \quad P = \sigma^*/\sigma.$$

The collision cross-section  $\sigma$  is related to effective molecular diameters by

$$\sigma = \pi d^2 \quad \text{so} \quad d = (\sigma/\pi)^{1/2}$$

$$\text{Now } \sigma_{AB} = \pi d_{AB}^2 = \pi \left[ \frac{1}{2}(d_A + d_B) \right]^2 = \frac{1}{4} (\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2})^2$$

$$\begin{aligned} \text{so } P &= \frac{\sigma^*}{\frac{1}{4} (\sigma_{AA}^{1/2} + \sigma_{BB}^{1/2})^2} \\ &= \frac{8.7 \times 10^{-22} \text{ m}^2}{\frac{1}{4} [(0.88)^{1/2} + (0.40)^{1/2}]^2 \times 10^{-9} \text{ m}^2} = \boxed{2.22 \times 10^{-3}} \end{aligned}$$

**E27.12(b)** The diffusion-controlled rate constant is

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (293 \text{ K})}{3 \times (1.27 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})} = 5.12 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

In more common units,  $k_d = 5.12 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$

The recombination reaction has a rate of

$$\begin{aligned} v &= k_d[A][B] = (5.12 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}) \times (0.200 \text{ mol L}^{-1}) \times (0.150 \text{ mol L}^{-1}) \\ &= \boxed{1.54 \times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}} \end{aligned}$$

**E27.13(b)** The enthalpy of activation for a reaction in solution is

$$\begin{aligned}\Delta^\ddagger H &= E_a - RT = (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (6134 \text{ K}) - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &= 4.852 \times 10^4 \text{ J mol}^{-1} = \boxed{48.52 \text{ kJ mol}^{-1}}\end{aligned}$$

The entropy of activation is

$$\begin{aligned}\Delta^\ddagger S &= R \left( \ln \frac{A}{B} - 1 \right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus} \\ B &= \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})^2}{(6.626 \times 10^{-34} \text{ J s}) \times (1.00 \times 10^5 \text{ Pa})} \\ &= 1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}\end{aligned}$$

$$\begin{aligned}\text{so } \Delta^\ddagger S &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left( \ln \frac{8.72 \times 10^{12} \text{ L mol}^{-1} \text{ s}^{-1}}{(1000 \text{ L m}^{-3}) \times (1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1})} - 1 \right) \\ &= \boxed{-32.2 \text{ J K}^{-1} \text{ mol}^{-1}}\end{aligned}$$

**Comment.** In this connection, the enthalpy of activation is often referred to as 'energy' of activation.

**E27.14(b)** The Gibbs energy of activation is related to the rate constant by

$$\begin{aligned}k_2 &= B \exp\left(\frac{-\Delta^\ddagger G}{RT}\right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus} \quad \text{so } \Delta^\ddagger G = -RT \ln \frac{k_2}{B} \\ k_2 &= (6.45 \times 10^{13} \text{ L mol}^{-1} \text{ s}^{-1}) e^{-\{(5375 \text{ K})/(298 \text{ K})\}} = 9.47 \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1} \\ &= 947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}\end{aligned}$$

Using the value of  $B$  computed in Exercise 27.13(b), we obtain

$$\begin{aligned}\Delta^\ddagger G &= -(8.3145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left( \frac{947 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right) \\ &= \boxed{46.8 \text{ kJ mol}^{-1}}\end{aligned}$$

**E27.15(b)** The entropy of activation for a bimolecular reaction in the gas phase is

$$\begin{aligned}\Delta^\ddagger S &= R \left( \ln \frac{A}{B} - 2 \right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus} \\ B &= \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [(55 + 273) \text{ K}]^2}{(6.626 \times 10^{-34} \text{ J s}) \times (1.00 \times 10^5 \text{ Pa})} \\ &= 1.86 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}\end{aligned}$$

The rate constant is

$$\begin{aligned}k_2 &= A \exp\left(\frac{-E_a}{RT}\right) \quad \text{so } A = k_2 \exp\left(\frac{E_a}{RT}\right) \\ A &= (0.23 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times \exp\left(\frac{49.6 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (328 \text{ K})}\right) \\ &= 1.8 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}\end{aligned}$$

$$\begin{aligned} \text{and } \Delta^\ddagger S &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left( \ln \left( \frac{1.8 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{1.86 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right) - 2 \right) \\ &= \boxed{-93 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

**E27.16(b)** The entropy of activation for a bimolecular reaction in the gas phase is

$$\Delta^\ddagger S = R \left( \ln \frac{A}{B} - 2 \right) \quad \text{where } B = \frac{kRT^2}{hp^\ominus}$$

For the collision of structureless particles, the rate constant is

$$k_2 = N_A \left( \frac{8kT}{\pi\mu} \right)^{1/2} \sigma \exp \left( \frac{-\Delta E_0}{RT} \right)$$

so the prefactor is

$$A = N_A \left( \frac{8kT}{\pi\mu} \right)^{1/2} \sigma = 4N_A \left( \frac{RT}{\pi M} \right)^{1/2} \sigma$$

where we have used the fact that  $\mu = \frac{1}{2}m$  for identical particles and  $k/m = R/M$ . So

$$\begin{aligned} A &= 4 \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times \left( \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}{\pi \times (78 \times 10^{-3} \text{ kg mol}^{-1})} \right)^{1/2} \times (0.68 \times 10^{-18} \text{ m}^2) \\ &= 2.13 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ B &= \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})^2}{(6.626 \times 10^{-34} \text{ J s}) \times (1.00 \times 10^5 \text{ Pa})} \\ &= 4.33 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

$$\begin{aligned} \text{and } \Delta^\ddagger S &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left( \ln \left( \frac{2.13 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{4.33 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right) - 2 \right) \\ &= \boxed{-80.0 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

**E27.17(b)** (a) The entropy of activation for a unimolecular gas-phase reaction is

$$\Delta^\ddagger S = R \left( \ln \frac{A}{B} - 1 \right) \quad \text{where } B = 1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [See Exercise 27.17(a)]}$$

$$\begin{aligned} \text{so } \Delta^\ddagger S &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left( \ln \left( \frac{2.3 \times 10^{13} \text{ L mol}^{-1} \text{ s}^{-1}}{(1000 \text{ L m}^{-3}) \times (1.54 \times 10^{11} \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1})} \right) - 1 \right) \\ &= \boxed{-24.1 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

(b) The enthalpy of activation is

$$\begin{aligned} \Delta^\ddagger H &= E_a - RT = 30.0 \times 10^3 \text{ J mol}^{-1} - (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &= 27.5 \times 10^3 \text{ J mol}^{-1} = \boxed{27.5 \text{ kJ mol}^{-1}} \end{aligned}$$

(c) The Gibbs energy of activation is

$$\begin{aligned} \Delta^\ddagger G &= \Delta^\ddagger H - T\Delta^\ddagger S = 27.5 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (-24.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= \boxed{34.7 \text{ kJ mol}^{-1}} \end{aligned}$$

**E27.18(b)** The dependence of a rate constant on ionic strength is given by

$$\log k_2 = \log k_2^\circ + 2A z_A z_B I^{1/2}$$

At infinite dilution,  $I = 0$  and  $k_2 = k_2^\circ$ , so we must find

$$\begin{aligned} \log k_2^\circ &= \log k_2 - 2A z_A z_B I^{1/2} = \log(1.55) - 2 \times (0.509) \times (+1) \times (+1) \times (0.0241)^{1/2} \\ &= 0.323 \quad \text{and} \quad \boxed{k_2^\circ = 1.08 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}} \end{aligned}$$

## Solutions to problems

### Solutions to numerical problems

**P27.1**

$$\begin{aligned} A &= N_A \sigma^* \left( \frac{8kT}{\pi\mu} \right) \quad [\text{Section 27.1 and Exercise 27.16(a); } \mu = \frac{1}{2}m(\text{CH}_3)] \\ &= (\sigma^*) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \times \left( \frac{(8) \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(\pi) \times (1/2) \times (15.03 \text{ u}) \times (1.6605 \times 10^{-27} \text{ kg/u})} \right)^{1/2} \\ &= (5.52 \times 10^{26}) \times (\sigma^* \text{ mol}^{-1} \text{ m s}^{-1}) \end{aligned}$$

$$\text{(a)} \quad \sigma^* = \frac{2.4 \times 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}{5.52 \times 10^{26} \text{ mol}^{-1} \text{ m s}^{-1}} = \frac{2.4 \times 10^7 \text{ mol}^{-1} \text{ m}^3 \text{ s}^{-1}}{5.52 \times 10^{26} \text{ mol}^{-1} \text{ m s}^{-1}} = \boxed{4.4 \times 10^{-20} \text{ m}^2}$$

**(b)** Take  $\sigma \approx \pi d^2$  and estimate  $d$  as  $2 \times$  bond length; therefore

$$\sigma = (\pi) \times (154 \times 2 \times 10^{-12} \text{ m})^2 = 3.0 \times 10^{-19} \text{ m}^2$$

$$\text{Hence } P = \frac{\sigma^*}{\sigma} = \frac{4.35 \times 10^{-20}}{3.0 \times 10^{-19}} = \boxed{0.15}$$

**P27.3**

For radical recombination it has been found experimentally that  $E_a \approx 0$ . The maximum rate of recombination is obtained when  $P = 1$  (or more), and then

$$k_2 = A = \sigma^* N_A \left( \frac{8kT}{\pi\mu} \right)^{1/2} = 4\sigma^* N_A \left( \frac{kT}{\pi m} \right)^{1/2} \quad [\mu = \frac{1}{2}m]$$

$$\sigma^* \approx \pi d^2 = \pi \times (308 \times 10^{-12} \text{ m})^2 = 3.0 \times 10^{-19} \text{ m}^2$$

Hence

$$\begin{aligned} k_2 &= (4) \times (3.0 \times 10^{-19} \text{ m}^2) \times (6.022 \times 10^{23} \text{ mol}^{-1}) \\ &\quad \times \left( \frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})}{(\pi) \times (15.03 \text{ u}) \times (1.6605 \times 10^{-27} \text{ kg/u})} \right)^{1/2} \\ &= 1.7 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = \boxed{1.7 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}} \end{aligned}$$

The rate constant is for the rate law

$$v = k_2[\text{CH}_3]^2$$

$$\text{Therefore } \frac{d[\text{CH}_3]}{dt} = -2k_2[\text{CH}_3]^2$$

and its solution is  $\frac{1}{[\text{CH}_3]} - \frac{1}{[\text{CH}_3]_0} = 2k_2t$

For 90 per cent recombination,  $[\text{CH}_3] = 0.10 \times [\text{CH}_3]_0$ , which occurs when

$$2k_2t = \frac{9}{[\text{CH}_3]_0} \quad \text{or} \quad t = \frac{9}{2k_2[\text{CH}_3]_0}$$

The mole fractions of  $\text{CH}_3$  radicals in which 10 mol% of ethane is dissociated is

$$\frac{(2) \times (0.10)}{1 + 0.10} = 0.18$$

The initial partial pressure of  $\text{CH}_3$  radicals is thus

$$p_0 = 0.18 p = 1.8 \times 10^4 \text{ Pa}$$

$$\text{and } [\text{CH}_3]_0 = \frac{1.8 \times 10^4 \text{ Pa}}{RT}$$

$$\begin{aligned} \text{Therefore } t &= \frac{9RT}{(2k_2) \times (1.8 \times 10^4 \text{ Pa})} = \frac{(9) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(1.7 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}) \times (3.6 \times 10^4 \text{ Pa})} \\ &= \boxed{3.6 \text{ ns}} \end{aligned}$$

**P27.6** Figure 27.1 shows that  $\log k$  is proportional to the ionic strength for neutral molecules.

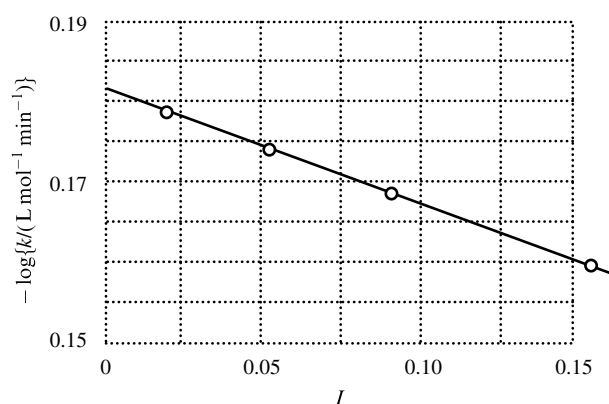


Figure 27.1

From the graph, the intercept at  $I = 0$  is  $-0.182$ , so

$$k^\circ = \boxed{0.658 \text{ L mol}^{-1} \text{ min}^{-1}}$$

**Comment.** In comparison to the effect of ionic strength on reactions in which two or more reactants are ions, the effect when only one is an ion is slight, in rough qualitative agreement with eqn 27.69.

**P27.7** 
$$\frac{\sigma^*}{\sigma} \approx \left( \frac{e^2}{4\pi\epsilon_0 d(I - E_{\text{ea}})} \right)^2 \quad [\text{Example 27.2}]$$

Taking  $\sigma = \pi d^2$  gives

$$\sigma^* \approx \pi \left( \frac{e^2}{4\pi\epsilon_0 [I(\text{M}) - E_{\text{ea}}(\text{X}_2)]} \right)^2 = \frac{6.5 \text{ nm}^2}{(I - E_{\text{ea}})/\text{eV}}$$



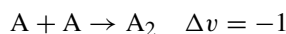
Thus,  $\sigma^*$  is predicted to increase as  $I - E_{\text{ea}}$  decreases. The data let us construct the following table

$\sigma^*/\text{nm}^2$	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub>
Na	0.45	0.42	0.56
K	0.72	0.68	0.97
Rb	0.77	0.72	1.05
Cs	0.97	0.90	1.34

All values of  $\sigma^*$  in the table are smaller than the experimental ones, but they do show the correct trends down the columns. The variation with  $E_{\text{ea}}$  across the table is not so good, possibly because the electron affinities used here are poor estimates.

**Question.** Can you find better values of electron affinities and do they improve the horizontal trends in the table?

**P27.10**



$$\begin{aligned} \Delta^\ddagger S &= R \left( \ln \left[ \frac{A}{\left(\frac{kT}{h}\right) \times \left(\frac{RT}{p^\ominus}\right)} \right] + 2 \right) \quad [27.63] \\ &= -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left[ \ln \left[ \frac{4.07 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} \left(\frac{\text{m}^3}{10^3 \text{ L}}\right)}{\frac{(1.381 \times 10^{-23} \text{ J K}^{-1}) \times (300 \text{ K})^2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})}{(6.626 \times 10^{-34} \text{ J s}) \times (1.013 \times 10^5 \text{ Pa})}} \right] + 2 \right] \\ &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times [\ln(2.631 \times 10^{-9}) + 2] \end{aligned}$$

$$\boxed{\Delta^\ddagger S = -148 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\begin{aligned} \Delta^\ddagger H &= E_{\text{a}} - 2RT = 65.43 \text{ kJ mol}^{-1} - 2 \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \\ &\quad \times \left( \frac{10^{-3} \text{ kJ}}{\text{J}} \right) \quad [27.60, 27.61] \end{aligned}$$

$$\boxed{\Delta^\ddagger H = 60.44 \text{ kJ mol}^{-1}}$$

$$\Delta^\ddagger H = \Delta^\ddagger U + \Delta^\ddagger(pV)$$

$$\Delta^\ddagger U = \Delta^\ddagger H - \Delta^\ddagger(pV) = \Delta^\ddagger H - \Delta v RT$$

$$= (60.44 \text{ kJ mol}^{-1}) - (-1) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times \left( \frac{10^{-3} \text{ kJ}}{\text{J}} \right)$$

$$\boxed{\Delta^\ddagger U = 62.9 \text{ kJ mol}^{-1}}$$

$$\Delta^\ddagger G = \Delta^\ddagger H - T \Delta^\ddagger S = 60.44 \text{ kJ mol}^{-1} - (300 \text{ K}) \times (-148 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left( \frac{10^{-3} \text{ kJ}}{\text{J}} \right)$$

$$\boxed{\Delta^\ddagger G = 104.8 \text{ kJ mol}^{-1}} \quad [27.59]$$

**P27.12** (a) The multilinear hypothesis is

$$E_a = c_1 \Delta G_b + c_2 I + c_3$$

where the constants  $c_1$ ,  $c_2$ , and  $c_3$  are independent of temperature. The substitutions  $E_a = -RT \ln(k/A)$  and  $\Delta G_b = -RT \ln(K_b)$  (eqns 25.25 and 9.19) give

$$-RT \ln\left(\frac{k}{A}\right) = -c_1 RT \ln(K_b) + c_2 I + c_3$$

$c_3$  may be eliminated by subtracting the analogous equation for the methylbenzene reference. Assuming that the pre-exponential  $A$  values for the reference and members of the series are comparable, the working equation becomes

$$-RT \ln\left(\frac{k}{k_{\text{toluene}}}\right) = -c_1 RT \ln\left(\frac{K_b}{K_{b,\text{toluene}}}\right) + c_2(I - I_{\text{toluene}})$$

substituting  $\Delta_p k = -\log\left(\frac{k}{k_{\text{toluene}}}\right)$ ,  $\Delta_p K_b = -\log\left(\frac{K_b}{K_{b,\text{toluene}}}\right)$ ,  $\Delta I = I - I_{\text{toluene}}$  gives

$$\Delta_p k = c_1 \Delta_p k_b + \frac{c_2 \Delta I}{RT \ln(10)} \quad (1)$$

The temperature dependence of  $\Delta_p k$  depends upon  $\Delta_p K_b$ .

$$RT \ln(10) \Delta_p K_b = \Delta G_b = \Delta H_b - T \Delta S_b$$

$$RT \ln(10) \Delta_p K_b = \Delta \Delta H_b - T \Delta \Delta S_b$$

$$= (cT - 1) \Delta \Delta H_b \quad (\text{assuming that } \Delta \Delta S_b = C \Delta \Delta H_b) \quad (2)$$

Evaluating the above equation at  $T = T_0 = 273.15 \text{ K}$  gives

$$\Delta \Delta H_b^0 = \frac{-RT_0 \ln(10) \Delta_p K_b^0}{cT_0 - 1} \quad (3)$$

where  $\Delta \Delta H_b(T_0) = \Delta \Delta H_b^0$  and  $\Delta_p K_b(T_0) = \Delta_p K_b^0$ . Assuming that  $\Delta H_b$  is approximately independent of temperature gives  $\Delta \Delta H_b = \Delta \Delta H_b^0$ . Substitute equation (3) into (2) and substitute the result into equation (1) to get

$$\Delta_p k = \frac{a T_0 (cT - 1) \Delta_p K_b^0}{T (cT_0 - 1)} + \frac{b \Delta I}{RT \ln(10)}$$

where the symbols  $c_1$  and  $c_2$  have been replaced with the symbols  $a$  and  $b$ .

(b) The activation parameters for the ring destruction of p-xylene are determined with a linear regression analysis of the experimental data plotted as  $\ln(k)$  versus  $1/T$  (eqn 25.25 and Example 25.5). The regression first gives:

$$\text{slope} = -8.875 \times 10^3 \text{ K}$$

$$\text{intercept} = 25.53$$

$$E_a = -R \times \text{slope} = 73.8 \text{ kJ mol}^{-1}$$

$$A = e^{\text{intercept}} \text{ L mol}^{-1} \text{ s}^{-1} = 1.223 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$$

$\Delta^\ddagger H$  and  $\Delta^\ddagger S$  values for solution reactions may be calculated with the following equation ( $k$  is the Boltzmann constant in these equations).

$$\Delta^\ddagger H = E_a - RT \quad \text{and} \quad \Delta^\ddagger S = R \ln \left( \frac{hA}{KekT} \right)$$

where the transmission coefficient  $K$  is assumed to equal 1. These equations may be deduced by modification of Sections 27.4 and 27.5 concepts to the solution phase. Eqn 27.42 becomes  $[C^\ddagger] = K^\ddagger[A][B]$ ; eqn 27.44 becomes  $k_2 = k^\ddagger K^\ddagger = k\nu K^\ddagger$  (eqn 27.45). Eqns 27.5 and 27.53 become  $k_2 = K\nu(kT\bar{K}^\ddagger/h\nu) = KkT\bar{K}^\ddagger/h$ .

Eqn 27.58 becomes  $k_2 = (KkT/h)e^{-\Delta^\ddagger G/RT}$  and eqn 27.60 becomes

$k_2 = (KkT/h)e^{\Delta^\ddagger S/R}e^{-\Delta^\ddagger H/RT}$ . According to the last equation,

$$\begin{aligned} \left( \frac{\partial \ln k_2}{\partial T} \right)_p &= \frac{1}{T} + \frac{1}{R} \left( \frac{\partial \Delta^\ddagger S}{\partial T} \right)_p + \frac{\Delta^\ddagger H}{RT^2} - \frac{1}{RT} \left( \frac{\partial \Delta^\ddagger H}{\partial T} \right)_p \\ &= \frac{1}{T} + \frac{1}{R} \left( \frac{\partial \Delta^\ddagger S}{\partial T} \right)_p + \frac{\Delta^\ddagger H}{RT^2} - \frac{1}{RT} \left[ T \left( \frac{\partial \Delta^\ddagger H}{\partial T} \right)_p \right] \quad (\text{eqn 4.16}) \\ &= \frac{1}{T} + \frac{\Delta^\ddagger H}{RT^2} \end{aligned}$$

Substitution into the formal definition of activation energy (eqn 25.26)  $E_a = RT^2(\partial \ln k_2/\partial T)_p$ , gives  $E_a = \Delta^\ddagger H + RT$  or  $\Delta^\ddagger H = E_a - RT$ . Substitution of this conclusion into the  $k_2$  equation gives

$$\begin{aligned} k_2 &= (KRT/h)e^{\Delta^\ddagger S/R}e^{-\Delta^\ddagger H/RT} = (KkT/h)e^{\Delta^\ddagger S/R}e^{-(E_a-RT)/RT} \\ &= (KekT/h)e^{\Delta^\ddagger S/R} \end{aligned}$$

Substituting of  $k_2 = Ae^{-E_a/RT}$  (eqn 25.25) and solving for  $\Delta^\ddagger S$  gives the final result.

$$\Delta^\ddagger S = R \ln \left( \frac{hA}{KekT} \right)$$

$T/K$	$k/10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$	$\Delta^\ddagger H/\text{kJ mol}^{-1}$	$\Delta^\ddagger S/\text{J K}^{-1} \text{ mol}^{-1}$
293.15	0.86	71.4	-40.8
303.15	2.5	71.3	-41.1
313.15	5.4	71.2	-41.4
323.15	13	71.1	-41.6
333.15	47	71.0	-41.9
343.15	59	70.9	-42.1

Entropy decreases upon formation of the transition state.

- (c) The 6 temperatures at which rate constants are measured may be indexed as  $i = 0, 1, 2, \dots, 5$ . The 7 arenes studied may be indexed as  $j = 0, 1, 2, \dots, 6$ .  $\Delta_p K$ ,  $\Delta_p K_b^0$ , and  $\Delta I$  values may be calculated for each arene at each temperature. Methybenzene (toluene is the reference arene). The values for  $\Delta_p k_{\text{exp}}(T)$  are calculated with the arrhenius parameters. The constants a, b, and c that appear in the equation deduced in part (a) are determined by systematically altering their values so that the sum of the squares of errors (SSE) between  $\Delta_p k_{\text{exp}}$  and the fitted equation  $\Delta_p k_{\text{fit}}$  is minimized.

$$\text{SSE}(a, b, c) = \sum_{j=0}^6 \left[ \sum_{i=0}^5 (\Delta_p k_{\text{exp}}(T_i) - \Delta_p k_{\text{fit}}(a, b, c, T_i))^2 \right]_j$$

Mathematical software like mathcad's given/minerr solve block easily perform the minimization. We find a best fit when

$$a = 0.413 \quad b = -0.192 \quad c = 1.39 \times 10^{-3} \text{ K}^{-1}$$

The goodness of the fit may be graphically evaluated by plotting the ratio  $\Delta_p k_{\text{fit}}/\Delta_p k_{\text{exp}}$  against  $\Delta_p K_{\text{exp}}$  for the 7 arenes at a temperature of choice. A good fit gives a ratio of 1 to within experimental error. The following plot gives the ratio at 293.15 K.

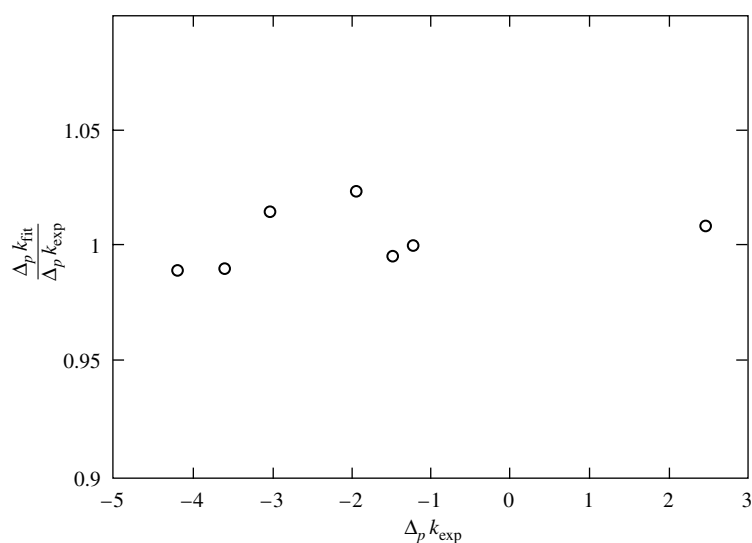


Figure 27.2

$\Delta_p k_{\text{fit}}$  volumes are within about  $\pm 3\%$  of the experimental values. This is a good fit, which confirms that the activation energy for arene distinction is multilinear in the basicity constant and the ionization energy. This is also evidence for the proposed arene ring oxidation mechanism.

### Solutions to theoretical problems

**P27.14** Programs for numerical integration using, for example, Simpson's rule are readily available for personal computers and hand-held calculators. Simplify the form of eqn 27.40 by writing

$$z^2 = \frac{kx^2}{4D}, \quad \tau = kt, \quad j = \left(\frac{A}{n_0}\right) \left(\frac{\pi D}{k}\right)^{1/2} [\text{J}]^*$$

Then evaluate

$$j = \int_0^\tau \left(\frac{1}{\tau}\right)^{1/2} e^{-z^2/\tau} e^{-\tau} d\tau + \left(\frac{1}{\tau}\right)^{1/2} e^{-z^2/\tau} e^{-\tau}$$

for various values of  $k$ .

$$\text{P27.16} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]\gamma_{\text{HA}}}\gamma_{\pm}^2 \approx \frac{[\text{H}^+][\text{A}^-]\gamma_{\pm}^2}{[\text{HA}]}$$

$$\text{Therefore, } [\text{H}^+] = \frac{[\text{HA}]K_a}{[\text{A}^-]\gamma_{\pm}^2}$$

$$\text{and } \log[\text{H}^+] = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]} - 2 \log \gamma_{\pm} = \log K_a + \log \frac{[\text{HA}]}{[\text{A}^-]} + 2AI^{1/2}$$

$$\text{Write } v = k_2[\text{H}^+][\text{B}]$$

$$\begin{aligned} \text{then } \log v &= \log(k_2[\text{B}]) + \log[\text{H}^+] \\ &= \log(k_2[\text{B}]) + \log \frac{[\text{HA}]}{[\text{A}^-]} + 2AI^{1/2} + \log K_a \\ &= \log v^\circ + 2AI^{1/2}, \quad v^\circ = k_2 \frac{[\text{B}][\text{HA}]K_a}{[\text{A}^-]} \end{aligned}$$

That is, the logarithm of the rate should depend linearly on the square root of the ionic strength,

$$\log v \propto I^{1/2}$$

$$\text{P27.18} \quad k_1 = \frac{kT}{h} \times \frac{q^\ddagger}{q} e^{-\beta\Delta E} \quad [\text{Problem 27.17}]$$

$$q^\ddagger = q_z^{\ddagger V} q_y^{\ddagger V} q_x^{\text{R}} \approx \left( \frac{kT}{hv^{\ddagger}} \right)^2 q^{\text{R}}$$

$$q^{\text{R}} \approx \frac{1.027}{\sigma} \times \frac{(T/\text{K})^{3/2}}{(B/\text{cm}^{-1})^{3/2}} \quad [\text{Table 20.4, } A = B = C] \approx 80$$

$$q = q_z^{\text{V}} q_y^{\text{V}} q_x^{\text{V}} \approx \left( \frac{kT}{hv} \right)^3$$

$$\text{Therefore, } k_1 \approx 80 \times \frac{v^3}{v^{\ddagger 2}} e^{-\beta\Delta E_0} \approx 80 \times 5.4 \times 10^4 \text{ s}^{-1} [\text{Problem 27.15}] = 4 \times 10^6 \text{ s}^{-1}$$

$$\text{Consequently, } D \approx (80) \times (2.7 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}) = \boxed{2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}} \text{ if } v^{\ddagger} = v \text{ and } \boxed{9 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}} \text{ if } v^{\ddagger} = \frac{1}{2}v.$$

**P27.20** It follows that, since  $\mathcal{N}_s$  and  $l$  are the same for the two experiments,

$$\frac{\sigma(\text{CH}_2\text{F}_2)}{\sigma(\text{Ar})} = \frac{\ln 0.6}{\ln 0.9} [\text{Problem 27.17}] = \boxed{5}$$

$\text{CH}_2\text{F}_2$  is a polar molecule; Ar is not.  $\text{CsCl}$  is a polar ion pair and is scattered more strongly by the polar  $\text{CH}_2\text{F}_2$ .

### Solutions to applications

**P27.22** Collision theory gives for a rate constant with no energy barrier

$$k = P\sigma \left( \frac{8kT}{\pi\mu} \right)^{1/2} N_A \quad \text{so} \quad P = \frac{k}{\sigma N_A} \left( \frac{\pi\mu}{8kT} \right)^{1/2}$$

$$\begin{aligned}
 P &= \frac{k/(\text{L mol}^{-1} \text{s}^{-1}) \times (10^{-3} \text{ m}^3 \text{ L}^{-1})}{(\sigma/\text{nm}^2) \times (10^{-9} \text{ m})^2 \times (6.022 \times 10^{23} \text{ mol}^{-1})} \\
 &\quad \times \left( \frac{\pi \times (\mu/\text{u}) \times (1.66 \times 10^{-27} \text{ kg})}{8 \times (1.381 \times 10^{-23} \text{ J K}^{-1}) \times (298 \text{ K})} \right)^{1/2} \\
 &= \frac{(6.61 \times 10^{-13})k/(\text{L mol}^{-1} \text{s}^{-1})}{(\sigma/\text{nm}^2) \times (\mu/\text{u})^{1/2}}
 \end{aligned}$$

The collision cross-section is

$$\sigma_{AB} = \pi d_{AB}^2 \quad \text{where } d_{AB} = \frac{1}{2}(d_A + d_B) = \frac{\sigma_A^{1/2} + \sigma_B^{1/2}}{2\pi^{1/2}} \quad \text{so } \sigma_{AB} = \frac{(\sigma_A^{1/2} + \sigma_B^{1/2})^2}{4}$$

The collision cross-section for  $\text{O}_2$  is listed in the *Data Section*. We would not be far wrong if we took that of the ethyl radical to equal that of ethene; similarly, we will take that of cyclohexyl to equal that of benzene. For  $\text{O}_2$  with ethyl

$$\begin{aligned}
 \sigma &= \frac{(0.40^{1/2} + 0.64^{1/2})^2}{4} \text{ nm}^2 = 0.51 \text{ nm}^2 \\
 \mu &= \frac{m_{\text{O}}m_{\text{e}}}{m_{\text{O}} + m_{\text{e}}} = \frac{(32.0 \text{ u}) \times (29.1 \text{ u})}{(32.0 + 29.1) \text{ u}} = 15.2 \text{ u}
 \end{aligned}$$

$$\text{so } P = \frac{(6.61 \times 10^{-13}) \times (4.7 \times 10^9)}{(0.51) \times (15.2)^{1/2}} = \boxed{1.6 \times 10^{-3}}$$

For  $\text{O}_2$  with cyclohexyl

$$\begin{aligned}
 \sigma &= \frac{(0.40^{1/2} + 0.88^{1/2})^2}{4} \text{ nm}^2 = 0.62 \text{ nm}^2 \\
 \mu &= \frac{m_{\text{O}}m_{\text{C}}}{m_{\text{O}} + m_{\text{C}}} = \frac{(32.0 \text{ u}) \times (77.1 \text{ u})}{(32.0 + 77.1) \text{ u}} = 22.6 \text{ u} \\
 \text{so } P &= \frac{(6.61 \times 10^{-13}) \times (8.4 \times 10^9)}{(0.62) \times (22.6)^{1/2}} = \boxed{1.8 \times 10^{-3}}
 \end{aligned}$$