

Eyring equation (T_c is the experimentally determined coalescence temperature):

$$k_{T_c} = \frac{k_B T_c}{h} e^{-\frac{\Delta G^\ddagger}{RT_c}}$$

Application of the logarithm on both sides and rearrangement enables us to calculate the free activation enthalpy:

$$\Delta G^\ddagger = RT_c \ln\left(\frac{k_B T_c}{h k_{T_c}}\right)$$

The exchange rate at the coalescence temperature can be calculated from the separation of the two signals that correspond to the two exchanging protons **A** and **B** in Hz by using

a) for non-coupling protons **A/B**:

$$k_{T_c} = \frac{\pi}{\sqrt{2}} |\nu_A - \nu_B| = 2.22 \Delta\nu$$

b) for *exchanging* protons **A/B** that couple with each other:

$$k_{T_c} = \frac{\pi}{\sqrt{2}} \sqrt{\Delta\nu^2 + 6J_{AB}^2} = 2.22 \sqrt{\Delta\nu^2 + 6J_{AB}^2}$$

Now, we can calculate the activation barrier for the racemization of 2,2'-diethyl-4,4'-bipyridine:

a) The 3J coupling is $^3J = 7.43$ Hz. As the two quartets in each signal overlap with twice that distance, we can conclude:

$$^2J_{AB} = 14.86 \text{ Hz}$$

This is important, because you need to use the coupling constant between the two exchanging protons at the methylene group, not that for the coupling with the neighboring methyl group.

b) The distance between the two signals is 0.12 ppm and the spectra were measured on a 500 MHz instrument. Consequently, we can calculate $\Delta\nu$ and k_{T_c} :

$$\Delta\nu = 0.12 \text{ ppm} * 500 \frac{\text{Hz}}{\text{ppm}} = 60 \text{ Hz}$$

Note: It is important to always provide the field strength of the instrument, when you provide calculated activation barriers from temperature-dependent NMR experiments. The distance in ppm is always the same. Consequently, the distance of the signals for **A** and **B** in Hz changes with the field strength. With it, the coalescence temperature also changes, so that the activation barrier is always the same independent of the instrument.

$$k_{T_c} = \frac{\pi}{\sqrt{2}} \sqrt{60^2 + 6(14.86)^2} = 155.8 \text{ Hz}$$

c) The coalescence temperature is the lowest temperature at which the two signals are melted together into one broad signal. In our case, we obtain from the spectra shown:

$$T_c = 363 \text{ K}$$

d) The constants needed in addition are:

Boltzmann constant: $k_b = 1,38065 * 10^{-23} \text{ J/K}$

Planck quantum: $h = 6.62607 * 10^{-23} \text{ J s}$

Universal gas constant: $R = 8.31446 \text{ J/K mol}$

e) When you input all these values into the equation for the free activation enthalpy, one obtains:

$$\Delta G^\ddagger = 8.31446 \frac{\text{J}}{\text{K mol}} * 363 \text{ K} * \ln \left(\frac{1.38065 * 10^{-23} \frac{\text{J}}{\text{K}} * 363 \text{ K}}{6.62607 * 10^{-34} \text{ J s} * 155.8 \text{ s}^{-1}} \right) = 74236 \frac{\text{J}}{\text{mol}} = 74.24 \frac{\text{kJ}}{\text{mol}}$$