

22.1 Answers:

Assuming that the radius of methyl radical is the C-H bond length, $d = R + R = 308\text{pm}$, so the collision cross section is:

$$\sigma = \pi d^2 = 2.979 \times 10^{-19} \text{ m}^2$$

the reduced mass of the two methyl radicals in the dimerization reaction is:

$$\mu = \frac{1}{2} m_{\text{CH}_3} = 7.5 m_u = 1.245 \times 10^{-26} \text{ kg}$$

So the theoretical pre-exponential factor is:

$$A^* = \sigma \sqrt{\frac{8kT}{\pi\mu}} N_A = 1.646 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

then we can get the **P factor**:

$$P = \frac{A}{A^*} = 0.146$$

and then we can get the **reactive cross section**:

$$\sigma^* = P\sigma = 4.344 \times 10^{-20} \text{ m}^2$$

22.2 Answers:

According to the collision theory, we can get the pre-exponential factor A:

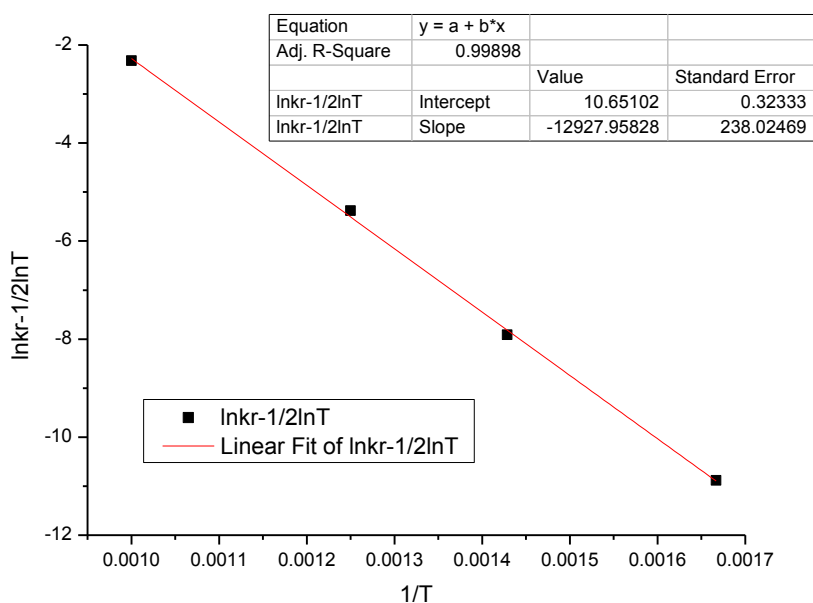
$$A = \sigma^* N_A \sqrt{\frac{8k}{\pi\mu}} \times T^{\frac{1}{2}}$$

then we can rewrite the Arrhenius equation as follows:

$$\begin{aligned} k_r &= A \exp\left(-\frac{E_a}{RT}\right) = \sigma^* N_A \sqrt{\frac{8k}{\pi\mu}} \times T^{\frac{1}{2}} \times \exp\left(-\frac{E_a}{RT}\right) \\ \Rightarrow \ln(k_r) - \frac{1}{2} \ln T &= \ln(\sigma^* N_A \sqrt{\frac{8k}{\pi\mu}}) - \frac{E_a}{R} \frac{1}{T} \end{aligned}$$

therefore, the left part of the equation above is proportional to T^{-1} . As a result, the following figure can be drawn using the data given in the question (considering the SI

units):



the relative coefficient is 0.999, and the intercept is 10.651, that is:

$$\ln(\sigma^* N_A \sqrt{\frac{8k}{\pi\mu}}) = 10.651$$

then we can get the **reactive cross section** is:

$$\sigma^* = 2.312 \times 10^{-21} m^2$$

and the **P factor** is:

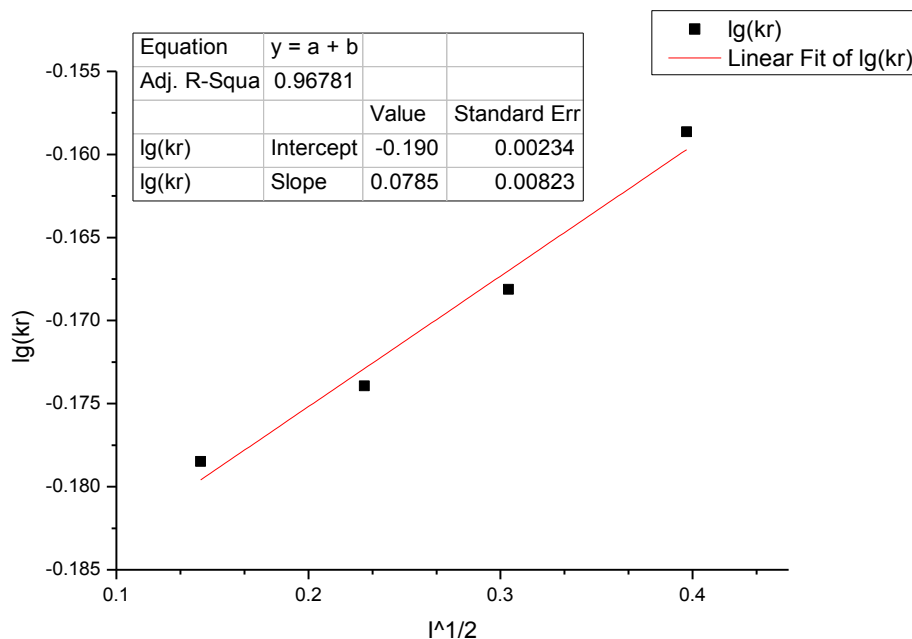
$$P = \frac{\sigma^*}{\sigma} = 3.853 \times 10^{-3}$$

22.6 Answers:

According to the data of reaction rate constant, we know that the reaction order is second. Therefore, we can hypothesize:

$$\lg k_r = a + bI^{1/2}$$

As a result, the following figure can be drawn:



the relative coefficient is 0.968, so the $\lg(k_r)$ changes linearly with the squared root of the ionic strength of the solution; and the intercept is -0.190, that is:

$$\lg k^\circ = -0.190$$

$$\Rightarrow k^\circ = 0.646 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$$

which means the limiting value of k_r at zero ionic strength.

According to the transmission theory, we can get:

$$\lg k_r = \lg k^\circ - \lg \frac{\gamma_{C^\#}}{\gamma_A} + \lg \gamma_B$$

$$\Rightarrow \lg \gamma_B = \lg k_r + \lg k^\circ$$

in which the $\gamma_A, \gamma_B, \gamma_{C^\#}$ stand for the activity coefficients of ion, neutral molecule and mediate complex respectively. Because the $\lg k_r$ changes linearly with the squared root of the ionic strength of the solution and $\lg k^\circ$ is a constant, we know that $\lg \gamma$ of a neutral molecule is dependent on the squared root of the ionic strength linearly also.