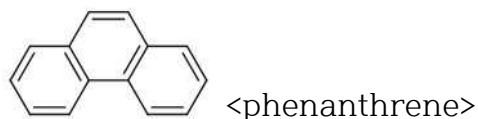


Example question: Photochemical reactions

You made a phenanthrene solution in distilled water in a transparent bottle and placed the bottle under an ultraviolet light with an intensity of 1×10^{-5} millieinstein/cm²-s and a (single) wavelength of 320 nm for 5 hours until use. Your lab-mate, who took this class a year ago, discovered the bottle. He/she told you should not have done so and had to make a new phenanthrene solution.

- i) Briefly describe the reason why your lab-mate told you so. Consider the chemical structure of phenanthrene shown below. (15 points)



Answer)

Phenanthrene may be susceptible to UV light because its resonance structure may act as a good chromophore.

- ii) Calculate how much fraction of phenanthrene would have lost due to direct photolysis. Assume that the UV light absorption by phenanthrene is negligible compared to the UV light absorption by water. Also assume that only very little change of UV light intensity occurs when the light passes the bottle containing the phenanthrene-dissolved water. The molar extinction coefficient for phenanthrene at 320 nm wavelength is $10^{2.4}$ M⁻¹cm⁻¹ and the reaction quantum yield is 0.01. The distribution function, $D(\lambda) = \alpha_D(\lambda)/\alpha(\lambda)$, is 1.02. (35 points)

Answer)

By the two assumptions, this situation satisfies the “negligible light absorption” case we discussed in the lecture:

$$k_p^o = \frac{2.303 W_0(\lambda) \alpha_D^0(\lambda) \epsilon_i(\lambda) \Phi_{ir}(\lambda)}{\alpha(\lambda)} = 2.303 W_0(\lambda) D^0(\lambda) \epsilon_i(\lambda) \Phi_{ir}(\lambda)$$
$$= 2.303 \cdot 10^{-5} \text{ millieinstein/cm}^2 \cdot \text{s} \cdot 1.02 \cdot 10^{2.4} \text{ M}^{-1} \text{cm}^{-1} \cdot 0.01$$
$$= 5.90 \times 10^{-5} \text{ s}^{-1} = 0.21 \text{ h}^{-1}$$

$$\frac{C}{C_0} = e^{-kt} = \exp(-0.21 \text{ h}^{-1} \cdot 5 \text{ h}) = 0.35$$

65% of phenanthrene is lost