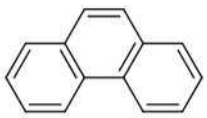
Example question: Photochemical reactions - solution

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/cm^2-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)


<phenanthrene>

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 $10^{2.4}$ $M^{-1}cm^{-1}$ and the reaction quantum yield is 0.01. The distribution function, $D(\lambda) = \alpha_D(\lambda)/\alpha(\lambda)$, is 1.02. (40 points)

Answer)

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

$$k_p^o = \frac{2.303\, W_0(\lambda)\alpha_D^0(\lambda)\epsilon_i(\lambda)\Phi_{ir}(\lambda)}{\alpha(\lambda)} = 2.303\, W_0(\lambda)D^0(\lambda)\epsilon_i(\lambda)\Phi_{ir}(\lambda)$$

$$= 2.303 \cdot 10^{-5}\, millieinistein/cm^2 - s \cdot 1.02 \cdot 10^{2.4}\, M^{-1}cm^{-1} \cdot 0.01$$

$$= 5.90 \times 10^{-5}\, s^{-1} = 0.21\, h^{-1}$$

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

65% of phenanthrene is lost

2. Following data are obtained for a clear midsummer day (averaged over 24 hours) and nitrobenzene. Using a reaction quantum yield of 2.9×10^{-3} for all wavelengths, determine the photolysis half-life of nitrobenzene in a well-mixed water body with negligible light absorption if clear days continue in the middle of summer.

wavelength range (nm)	center of wavelength (nm)	Z(24 h, λ) (millieinstein/cm^2-d)	molar absorption coeff. ($M^{-1}cm^{-1}$)
315-325	320	0.0073	800
325-335	330	0.0137	580
335-345	340	0.0187	560
345-355	350	0.0216	280

(45 points)

Answer)

For negligible light absorption with a wavelength-invariant Φ_{ir}, the near surface photolysis rate is obtained by:

$$k_p^0 = k_a^0\Phi_{ir} = 2.303\left[\sum_\lambda Z(\lambda)\cdot\epsilon_i(\lambda)\right]\Phi_{ir}$$

center of wavelength (nm)	$Z(24\ h,\ \lambda)$ (millieinstein/cm^2-d)	molar absorption coeff. ($M^{-1}cm^{-1}$)	$Z(24\ h,\ \lambda) \times \varepsilon_i\ (\lambda)$
320	0.0073	800	5.84
330	0.0137	580	7.95
340	0.0187	560	10.47
350	0.0216	280	6.05
		Sum	30.31

* unit for $Z(\lambda) \cdot \epsilon_i(\lambda)$:

$$millieinstein/cm^2 - d \times L/mole - cm \times 10^{-3}\ einstein/millieinstein \times 10^3\ cm^3/L$$

$$= einstein/mole - d$$

$$k_p^0 = 2.303 \times 30.31\ einstine/mole - d \times 2.9 \times 10^{-3}\ mole/einstein = 0.202\ d^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k_p^0} = \frac{\ln 2}{0.202\ d^{-1}} = 3.43\ d$$