Direct photolysis – natural water

Here 4NP exists in the water in either non-dissociated (HA) or dissociated (A^-) form, and the half-life is to be estimated for the sum of [HA] and [A^-]:

$$[HA]_{total} = [HA] + [A^-] \quad \textbf{(1)}$$

Denote ${k_p}^0(HA_{total})$ as the 1st order photolysis rate for the sum of HA and A^-:

$$-\frac{d[HA]_{total}}{dt} = {k_p}^0(HA_{total}) \times [HA]_{total} \quad \textbf{(2)}$$

Then:

$$-\frac{d[HA]_{total}}{dt} = -\left(\frac{d[HA]}{dt} + \frac{d[A^-]}{dt}\right) = -\left\{{k_p}^0(HA) \times [HA] + {k_p}^0(A^-) \times [A^-]\right\} \quad \textbf{(3)}$$

Direct photolysis – natural water

From (1)-(3):

$$k_p{}^0(HA_{total}) = \alpha_{ia} \times k_p{}^0(HA) + (1 - \alpha_{ia})k_p{}^0(A^-)$$

where $\alpha_{ia} = \dfrac{[HA]}{[HA]_{total}}$

Now, recall from acid-base equilibrium:

$$HA = H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = 10^{-7.11}$$

Therefore,

$$\alpha_{ia} = \frac{[HA]}{[HA]_{total}} = \frac{[HA]}{[HA] + [A^-]} = \frac{[HA]}{[HA] + K_a[HA]/[H^+]} = \frac{1}{1 + K_a/[H^+]}$$

$$= \frac{1}{1 + 10^{-7.11}/10^{-7.5}} = 0.289$$

Direct photolysis – natural water

Get photolysis rate constants for each species:

$$k_p{}^0(HA) = \Phi_{ir}(HA) \times k_a{}^0(HA) = (4.5 \times 10^3) \times (1.1 \times 10^{-4}) = 0.495\ d^{-1}$$

$$k_p{}^0(A^-) = \Phi_{ir}(A^-) \times k_a{}^0(A^-) = (3.2 \times 10^4) \times (8.1 \times 10^{-6}) = 0.259\ d^{-1}$$

Now we are ready to get the photolysis rate constant for HA_{total}:

$$k_p{}^0(HA_{total}) = \alpha_{ia} \times k_p{}^0(HA) + (1 - \alpha_{ia})k_p{}^0(A^-)$$

$$= 0.289 \times 0.495\ d^{-1} + (1 - 0.289) \times 0.259\ d^{-1} = 0.327\ d^{-1}$$

Half-life is defined for a 1^{st}-order reaction as:

$$t_{1/2} = \frac{ln2}{k} = \frac{ln2}{0.327\ d^{-1}} = 2.1\ days$$

We see half-life for 4NP should depend on pH.