

# Direct photolysis – natural water

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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 [ $A^-$ ]:

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

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

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

Then:

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

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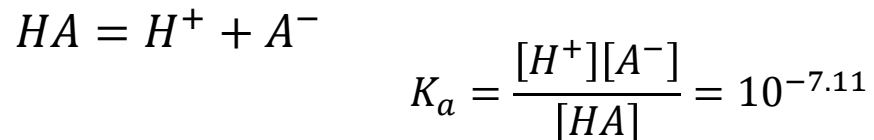
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From (1)-(3):

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

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

Now, recall from acid-base equilibrium:



Therefore,

$$\begin{aligned} \alpha_{ia} &= \frac{[HA]}{[HA]_{total}} = \frac{[HA]}{[HA] + [A^-]} = \frac{[HA]}{[HA] + K_a[HA]/[H^+]} = \frac{1}{1 + K_a/[H^+]} \\ &= \frac{1}{1 + 10^{-7.11}/10^{-7.5}} = 0.289 \end{aligned}$$

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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  $HA_{total}$ :

$$\begin{aligned} k_p^0(HA_{total}) &= \alpha_{ia} \times k_p^0(HA) + (1 - \alpha_{ia})k_p^0(A^-) \\ &= 0.289 \times 0.495 d^{-1} + (1 - 0.289) \times 0.259 d^{-1} = 0.327 d^{-1} \end{aligned}$$

Half-life is defined for a 1<sup>st</sup>-order reaction as:

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

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