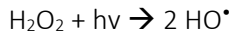
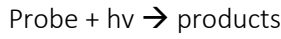


## Calculating hydroxyl radical scavenging term ST

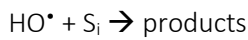
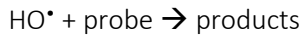
Bas Wols, Chengjin Wang, Olya Keen

During UV/H<sub>2</sub>O<sub>2</sub> treatment, the degradation of a probe compound in a water matrix with scavengers S<sub>i</sub> is described by the following simplified reaction scheme:

Photolysis reactions:



Second order reactions between OH. and probe or background components:



The rate equation for HO<sup>•</sup> (M s<sup>-1</sup>) is written as:

$$\frac{d[\text{HO}^\bullet]}{dt} = k_{\text{photo},\text{HO}}[\text{H}_2\text{O}_2] - \sum k_{\text{S}_i}[\text{HO}^\bullet][\text{S}_i] - k_{\text{HO},\text{probe}}[\text{HO}^\bullet][\text{probe}] \quad \text{Eq. 1}$$

where  $k_{\text{photo},\text{HO}}$  is the photogeneration rate constant of HO<sup>•</sup> from H<sub>2</sub>O<sub>2</sub> (s<sup>-1</sup>),  $k_{\text{S}_i}$  the second-order HO<sup>•</sup> reaction rate constant of a background scavenger (M<sup>-1</sup> s<sup>-1</sup>) and  $k_{\text{HO},\text{probe}}$  is the second-order HO<sup>•</sup> reaction rate constant of a probe (M<sup>-1</sup> s<sup>-1</sup>).

By introducing a total scavenging rate constant as  $ST = \sum k_{\text{S}_i}[\text{S}_i]$  (note that scavenging by H<sub>2</sub>O<sub>2</sub> is included in ST, but can be subtracted in the end to determine the innate ST that comes from background matrix alone), Eq. 1 becomes:

$$\frac{d[\text{HO}^\bullet]}{dt} = k_{\text{photo},\text{HO}}[\text{H}_2\text{O}_2] - ST[\text{HO}^\bullet] - k_{\text{HO},\text{probe}}[\text{HO}^\bullet][\text{probe}] \quad \text{Eq. 2}$$

The rate equation for the probe equals:

$$\frac{d[\text{probe}]}{dt} = -k_{\text{photo},\text{probe}}[\text{probe}] - k_{\text{HO},\text{probe}}[\text{HO}^\bullet][\text{probe}] \quad \text{Eq. 3}$$

where  $k_{\text{photo},\text{probe}}$  is the photolysis rate constant for the probe (s<sup>-1</sup>).

To simplify the mathematics, a few assumptions are made:

- Quasi-steady state HO<sup>•</sup> concentration,  $d\text{HO}^\bullet/dt=0$
- H<sub>2</sub>O<sub>2</sub> consumption is small, so that H<sub>2</sub>O<sub>2</sub> remains constant over time
- ST remains constant over time,  $dS/dt=0$
- The HO<sup>•</sup> scavenging by the probe is small compared to ST,  $k_{\text{HO},\text{probe}}[\text{probe}] \ll ST$
- The UV absorption remains constant over time

With these assumptions, the steady state HO<sup>•</sup> concentrations becomes (from Eq. 2):

$$[\text{HO}^\bullet]_{\text{ss}} = \frac{k_{\text{photo},\text{HO}}[\text{H}_2\text{O}_2]}{ST} \quad \text{Eq. 4}$$

The solution for the probe concentration over time becomes after integration of Eq. 3 over time  $t$ :

$$\ln\left(\frac{[\text{probe}]_t}{[\text{probe}]_0}\right) = -k_{\text{photo},\text{probe}}t - k_{\text{HO},\text{probe}}\frac{k_{\text{photo},\text{HO}}[\text{H}_2\text{O}_2]}{ST}t \quad \text{Eq. 5}$$

### Photogeneration rate constants

The photogeneration rate constant ( $k_{\text{photoHO}}$ ,  $\text{s}^{-1}$ ) either for  $\text{HO}^{\bullet}$  from  $\text{H}_2\text{O}_2$  can be calculated from the photogeneration rate ( $r_{\text{photoHO}} = k_{\text{photoHO}} \times [\text{H}_2\text{O}_2]$ ,  $\text{M s}^{-1}$ ). Let us consider a small volume of water. The Beer-Lambert law states that the radiation through a small volume with depth  $\Delta x$  diminishes logarithmically with the (decadic) absorption coefficient:

$$E'_p(x + \Delta x) = E'_p(x)10^{-a\Delta x} \quad \text{Eq. 6}$$

Where  $E'_p(x)$  is the photon fluence rate ( $\text{mEinstein cm}^{-2} \text{s}^{-1}$ ) at a depth  $x$  (cm), and  $a$  the total absorption ( $\text{cm}^{-1}$ ) of all compounds in the water ( $a = \sum \varepsilon_i [C_i]$ ).

The photogeneration rate in this small volume for  $\text{HO}^{\bullet}$  is obtained by considering the absorbed photons (first law of photochemistry states that only the absorbed photons could bring a chemical reaction) by  $\text{H}_2\text{O}_2$  in the small volume:

$$r_{\text{photoHO}}(x) = -\Phi_{\text{HO}} \left( \frac{\varepsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]}{a} \right) E'_p(x) \frac{(1 - 10^{-a\Delta x})}{\Delta x} \quad \text{Eq. 7}$$

Where  $a$  is the total absorption of all compounds (decadic based) in the water ( $a = \sum \varepsilon_i [C_i]$ ) ( $\text{cm}^{-1}$ ).

A similar expression is used by Beltran et al. (1995), Lopez et al. (2003).

The term  $\left( \frac{\varepsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]}{a} \right)$  represents the absorbed photons by  $\text{H}_2\text{O}_2$  over the total absorbed photons in the small volume,  $\varepsilon_{\text{H}_2\text{O}_2}$  represents the molar extinction coefficient of  $\text{H}_2\text{O}_2$  ( $\text{M}^{-1}\text{cm}^{-1}$ ) and  $\Phi_{\text{HO}}$  the quantum yield (mol/Einstein) of  $\text{HO}^{\bullet}$ .

If the product is  $a\Delta x$  small ( $<0.01$ ), the term  $1 - 10^{-a\Delta x}$  can be written as  $a\Delta x \ln(10)$ ,<sup>a</sup> so that Eq. 7 becomes:

$$r_{\text{photoHO}}(x) = -\ln(10) \Phi_{\text{HO}} \varepsilon_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2] E'_p(x) \quad \text{Eq. 8}$$

In a well-stirred system, e.g. a collimated beam, where the concentration of  $\text{H}_2\text{O}_2$  is constant over the depth, the photogeneration rate constant ( $k_{\text{photoHO}}$ ,  $\text{s}^{-1}$ ) can then be written as:

$$k_{\text{photoHO}}(x) = -\ln(10) \Phi_{\text{HO}} \varepsilon_{\text{H}_2\text{O}_2} E'_p(x) \quad \text{Eq. 9}$$

By integrating Eq. 9 over the depth ( $L$ , cm) of the sample, the volume averaged photogeneration rate constant becomes:

$$\begin{aligned} k_{\text{photoHO}} &= \frac{1}{L} \int_0^L k_{\text{photoHO}}(x) dx = -\ln(10) \Phi_{\text{HO}} \varepsilon_{\text{H}_2\text{O}_2} \frac{1}{L} \int_0^L E'_p(x) dx \\ &= -\ln(10) \Phi_{\text{HO}} \varepsilon_{\text{H}_2\text{O}_2} \frac{1}{L} \int_0^L E'_{p0} 10^{-ax} dx \\ &= -\Phi_{\text{HO}} \varepsilon_{\text{H}_2\text{O}_2} E'_{p0} \frac{1 - 10^{-aL}}{aL} \end{aligned} \quad \text{Eq. 10}$$

where  $E'_{p0}$  is the incident photon fluence rate ( $\text{mEinstein/cm}^2/\text{s}$ ) on the water surface.

Using the expression of the photogeneration rate constant, the degradation of the probe (Eq. 5) can be written as:

<sup>a</sup> Taylor series expansion:  $e^x = 1+x$ ,  $10^x = e^{(-\ln(10)x)} = 1 - \ln(10)x$ ,  $1 - 10^{ax} = \ln(10)ax$

$$\ln\left(\frac{[probe]_t}{[probe]_0}\right) = -E'_{p0} \frac{1 - 10^{-aL}}{aL} t \left( \Phi_{probe} \varepsilon_{probe} + \Phi_{HO} \varepsilon_{H2O2} \frac{k_{HO,probe}[H_2O_2]}{ST} \right) \quad Eq. 11$$

The average fluence rate (Bolton and Stefan, 2002) is defined as:

$$H' = \frac{tU_\lambda}{L} \int_0^L E'_p(x) = \frac{tU_\lambda}{L} \int_0^L E'_{p0} 10^{-ax} dx = \frac{tU_\lambda}{aL} E'_{p0} \frac{1 - 10^{-aL}}{\ln(10)} \quad Eq. 12$$

Where  $U_\lambda$  represents the energy of a photon (J Einstein<sup>-1</sup>). Applying the definition of the fluence rate, **Error! Reference source not found.** becomes:

$$\ln\left(\frac{[probe]_t}{[probe]_0}\right) = -\ln(10) \frac{H'}{U_\lambda} \left( \Phi_{probe} \varepsilon_{probe} + \Phi_{HO} \varepsilon_{H2O2} \frac{k_{HO,probe}[H_2O_2]}{ST} \right) \quad Eq. 13$$

If the direct photolysis of the probe is measured as the fluence-based rate constant ( $k_{UV}$ , cm<sup>2</sup>mJ<sup>-1</sup>), the degradation of the probe is equal to:

$$\ln\left(\frac{[probe]_t}{[probe]_0}\right) = -\left( k_{UV} + \ln(10) \frac{\Phi_{HO} \varepsilon_{H2O2} k_{HO,probe}[H_2O_2]}{U_\lambda ST} \right) H' \quad Eq. 14$$

From the measured probe degradation, and fluence rate of the collimated beam system (using a Bolton et al. (2015) spreadsheet), the scavenging rate constant can be calculated from Eq. 14:

$$ST = \frac{\ln(10) \frac{\Phi_{HO} \varepsilon_{H2O2}}{U_\lambda} k_{HO,probe}[H_2O_2] H'}{-\ln\left(\frac{[probe]_t}{[probe]_0}\right) - k_{UV} H'} \quad Eq. 15$$

Using  $k'_{HO} = -\frac{\ln\left(\frac{[probe]_t}{[probe]_0}\right)}{H'} - k_{UV}$  (cm<sup>2</sup>mJ<sup>-1</sup>), Eq. 15 becomes:

$$ST = \ln(10) \frac{\Phi_{HO} \varepsilon_{H2O2} k_{HO,probe}[H_2O_2]}{U_\lambda k'_{HO}} \quad Eq. 16$$

Because the contribution from H<sub>2</sub>O<sub>2</sub> to overall ST was not subtracted initially, it can be subtracted from ST determined by Eq. 16 to determine the ST that is based on the sample's background matrix alone.

## References

Lopez, A., Bozzi, A., Mascolo, G., and Kiwi, J. (2003). Kinetic investigation on UV and UV/H<sub>2</sub>O<sub>2</sub> degradations of pharmaceutical intermediates in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry*, 156(1-3):121{126.

Fernando J. Beltran, Gabriel Ovejero, Juan F. Garcia-Araya, and Javier Rivas, Oxidation of Polynuclear Aromatic Hydrocarbons in Water. 2. UV Radiation and Ozonation in the Presence of UV Radiation, *Industrial & Engineering Chemistry Research* 1995 34 (5), 1607-1615, DOI: 10.1021/ie00044a013.

Bolton, J.R., Stefan, M.I. Fundamental photochemical approach to the concepts of fluence (UV dose) and electrical energy efficiency in photochemical degradation reactions. *Research on Chemical Intermediates* 28, 857–870 (2002). <https://doi.org/10.1163/15685670260469474>

Bolton, J. R., Beck, S. E., & Linden, K. G. (2015). Protocol for the determination of fluence (UV dose) using a low-pressure or low-pressure high-output UV lamp in bench-scale collimated beam ultraviolet experiments. *IUVA News*, 17(1), 11-16.