Derivation of expression for the OH yield of the reaction CH₃CO + O₂

(ESI for the paper by Kovács et al.)

Γ₁b was determined by assuming a simple reaction scheme, consisting of reactions (1), (3) and the wall-loss of OH (wOH). To obtain Eq. (III), the following specific experimental conditions have to be taken into account: (i) in the experimental arrangement applied (see Fig. 1.) reactions (1) and (3) start at the same distance (i.e. reaction time) in our system (note, however, that CH₃CHO and O₂ were premixed before entering the reactor); (ii) acetaldehyde is added in a concentration consistent with a pseudo-first-order assumption for reaction (3); (iii) the O₂ concentration is increased until no further change in the OH concentration at any reaction times is observed.

The differential equation that describes OH loss in the absence of O₂ is the following:

\[
\frac{d[OH]}{dt} = -k'_1[OH] - k_{wOH}[OH], \quad [OH](t = 0) = [OH]_0
\]  

(A1)

where \( k'_1 = k_3[CH₃CHO] \) is the pseudo-first order rate constant of reaction (3), \( k_{wOH} \) is the first-order wall loss rate constant for OH, \( t \) is the reaction time and \([OH]_0\) is the initial OH concentration. The solution is a simple exponential function:

\[
[OH](t) = e^{-(k'_1+k_{wOH})t}[OH]_0
\]  

(A2)

In the presence of O₂, however, OH radical is also formed in reaction (1b), therefore, the coupled differential equations to be solved are the following:

\[
\frac{d[OH]^{O₂}}{dt} = -k'_1[OH]^{O₂} - k_{wOH}[OH]^{O₂} + k'_{1b}[CH₃CO], \quad [OH]^{O₂}(t = 0) = [OH]_0
\]  

(A3a)

\[
\frac{d[CH₃CO]}{dt} = k'_3[OH]^{O₂} - k'_1[CH₃CO], \quad [CH₃CO](t = 0) = 0
\]  

(A3b)

where \([OH]^{O₂}\) denotes the OH concentration in the presence of O₂. The solution of the above equations for OH is:

\[
[OH]^{O₂}(t) = e^{-(k'_1+k'_3+k_{wOH}+\Omega)^t/2}[OH]_0 \frac{(k'_1-k'_3+k_{wOH})(1-e^{\Omega t})+\Omega(1+e^{\Omega t})}{2\Omega}
\]  

(A4)
where

$$\Omega = \sqrt{(k'_3)^2 + (k'_3 - k'_{w\text{OH}})^2 + k'_3(-2k'_3 + 4\Gamma_{1b}k'_1 + 2k'_{w\text{OH}})}$$  \hspace{1cm} (A5)$$

The OH yield can be related to the relative change of the decay constant of OH in the absence ($\kappa_0$) and in the presence ($\kappa^*$) of O2:

$$\frac{\kappa_0 - \kappa^*}{\kappa_0} = \frac{d \ln [\text{OH}]^0}{dt} - \frac{d \ln [\text{OH}]/dt}{d \ln [\text{OH}]/dt}$$  \hspace{1cm} (A6)$$

Differentiation of the corresponding expressions yield:

$$\frac{\kappa_0 - \kappa^*}{\kappa_0} = \frac{2(-1 + e^{\Omega \tau})\Gamma_{1b}k'_3}{(k'_3 + k'_{w\text{OH}})(k'_3 - k'_1 + k'_{w\text{OH}})(1 - e^{\Omega \tau}) + \Omega (1 + e^{\Omega \tau})}$$  \hspace{1cm} (A7)$$

Under the conditions applied in the experiments, the following relationships were always satisfied:

(i) $k'_1 >> k'_3$, $k'_{w\text{OH}}$, therefore $\Omega \approx k'_1$

(ii) $k'_1 t >> 0$ on the timescale of interest (10-100 ms), therefore $1 << e^{\Omega \tau}$

Using both (i) and (ii), Eq. (A7) simplifies to:

$$\frac{\kappa_0 - \kappa^*}{\kappa_0} = \frac{\Gamma_{1b}k'_3}{k'_3 + k'_{w\text{OH}}} = \Gamma_{1b} \frac{\kappa_0 - k'_{w\text{OH}}}{\kappa_0}$$  \hspace{1cm} (A8)$$

which is equivalent to Eq. (III).