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

(ESI for the paper by Kovács et al.)

Γ_{1b} 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:

$$\frac{d[OH]}{dt} = -k_3'[OH] - k_{wOH}[OH], \qquad [OH](t=0) = [OH]_0 \qquad (A1)$$

where $k_3' = k_3[CH_3CHO]$ 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:

$$[OH](t) = e^{-(k_3' + k_{wOH})t}[OH]_0 \qquad (A2)$$

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:

$$\frac{d[OH]^{O_2}}{dt} = -k_3'[OH]^{O_2} - k_{wOH}[OH]^{O_2} + k_{1b}'[CH_3CO], \qquad [OH]^{O_2}(t=0) = [OH]_0 \qquad (A3a)$$

$$\frac{d[CH_3CO]}{dt} = k_3'[OH]^{O_2} - k_1'[CH_3CO], \qquad [CH_3CO](t=0) = 0 \qquad (A3b)$$

where $[OH]^{O_2}$ denotes the OH concentration in the presence of O₂. The solution of the above equations for OH is:

$$[OH]^{O_2}(t) = e^{-(k_1' + k_3' + k_{wOH} + \Omega)t/2}[OH]_0 \frac{(k_1' - k_3' + k_{wOH})(1 - e^{\Omega t}) + \Omega(1 + e^{\Omega t})}{2\Omega} \qquad (A4)$$

where

$$\Omega = \sqrt{(k_3')^2 + (k_1' - k_{wOH})^2 + k_3'(-2k_1' + 4\Gamma_{1b}k_1' + 2k_{wOH})} \tag{A5}$$

The OH yield can be related to the relative change of the decay constant of OH in the absence (κ_0) and in the presence (κ^*) of O_2:

$$\frac{\kappa_0 - \kappa^*}{\kappa_0} = \frac{d\ln[OH]^{O_2}/dt - d\ln[OH]/dt}{d\ln[OH]/dt} \tag{A6}$$

Differentiation of the corresponding expressions yield:

$$\frac{\kappa_0 - \kappa^*}{\kappa_0} = \frac{2(-1 + e^{\Omega t})\Gamma_{1b}k_1'k_3'}{(k_3' + k_{wOH})(k_3' - k_1' + k_{wOH})(1 - e^{\Omega t}) + \Omega(1 + e^{\Omega t})} \tag{A7}$$

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

(*i*) $k_1' \gg k_3'$, k_{wOH}, therefore $\Omega \approx k_1$

(*ii*) $k_1't \gg 0$ on the timescale of interest (10-100 ms), therefore $1 \ll e^{\Omega t}$

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

$$\frac{\kappa_0 - \kappa^*}{\kappa_0} = \Gamma_{1b}\frac{k_3'}{k_3' + k_{wOH}} = \Gamma_{1b}\frac{\kappa_0 - k_{wOH}}{\kappa_0}, \tag{A8}$$

which is equivalent to Eq. (III).