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Supporting information

Aqueous singlet oxygen reaction kinetics of furfuryl alcohol: Effect of temperature, pH, and salt content.

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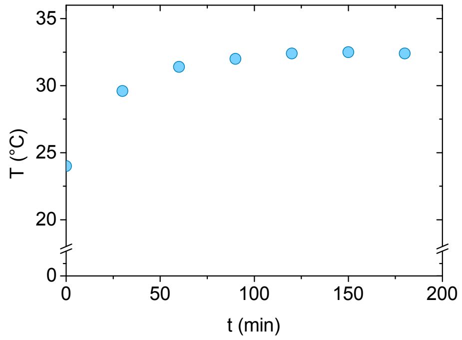

Figure S1 Temperature profile during a 3-hour photolysis experiment performed with 10 × 365 nm bulbs in a Rayonet reactor and a polymer heat filter cylinder between the bulbs and the sample tubes.

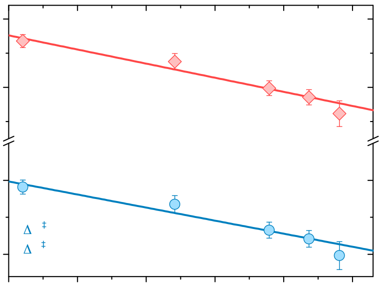

Figure S2 Arrhenius (orange) and Eyring (blue) plots obtained from steady-state experiments performed in the temperature range 6 – 47°C. The errors in $k_{rxn,FFA}$ are calculated assuming the error in k_d^{Δ} (eq.(4)) is equal to zero.

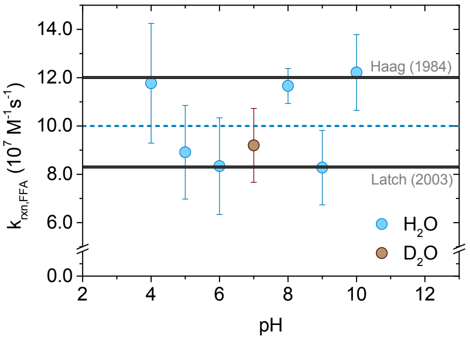

Figure S3 pH dependence on $k_{rxn,FFA}$ studied with the steady-state (β value) method determined at 26°C. The blue dotted line represents the average value measured in water (blue circles) of $(1.0 \pm 0.6) \times 10^8\ M^{-1}s^{-1}$. The errors in $k_{rxn,FFA}$ are calculated assuming the error in $k_{d\Delta}^{\Delta}$ (eq.(4)) is equal to zero.

k_d^Δ values measured in time-resolved experiments

As a double check, we report the measured k_d^Δ (singlet oxygen deactivation rate constant in water without added quenchers, the intercept of the Stern-Volmer plots) in the pH- and T-variation experiments.

k_d^Δ literature values in water range from $2.4 \times 10^5\ s^{-1}$ to $3.2 \times 10^5\ s^{-1}$ [1,2], and are known to have a weak T-dependence[3]. In the pH-variation experiments we measured a constant value of $(2.76 \pm 0.02) \times 10^5 s^{-1}$, in agreement with the available literature. Instead, in the T-variation experiments we observed k_d^Δ in the interval $2.69 - 3.00 \times 10^5\ s^{-1}$, with the lowest values observed at 10°C and the highest at 45°C.

T (°C)	**pH**	k_d^Δ ($10^5\ s^{-1}$)
19-20	3.07	2.78 ± 0.02
19-20	3.91	2.76 ± 0.02
19-20	5.11	2.79 ± 0.03
19-20	5.99	2.75 ± 0.02
19-20	6.97	2.76 ± 0.03
19-20	7.99	2.77 ± 0.02
19-20	9.1	2.76 ± 0.02
19-20	10.14	2.75 ± 0.04
19-20	10.93	2.78 ± 0.02
19-20	11.96	2.74 ± 0.03
5.1	6.8	2.71 ± 0.03
10	6.8	2.69 ± 0.03
25.1	6.8	2.78 ± 0.03
25.1	6.8	2.77 ± 0.05
30.1	6.8	2.90 ± 0.05
30.2	6.8	2.89 ± 0.04
35.1	6.8	2.85 ± 0.03
35.5	6.8	2.92 ± 0.05
40.2	6.8	2.96 ± 0.06
40.0	6.8	2.88 ± 0.08
45.1	6.8	2.88 ± 0.07
45.2	6.8	3.00 ± 0.04

Calculation of correction factors for old literature data

Singlet oxygen steady-state concentrations reported in previous studies that used $1.2 \times 10^8 M^{-1} s^{-1}$ for $k_{\mathrm{rxn,FFA}}$ are most likely underestimated by 10 – 20%, the actual value being dependent on the solution temperature and ionic strength, as well as the assumptions in the calculation of $[^1O_2]_{ss}$.

For instance, if FFA quenching is *not* taken into account (a reasonable approximation when $[FFA] < 110\ \mu M$[4]), $[^1O_2]_{ss}$ is determined as

$$[^1O_2]_{ss} = \frac{k_{obs,FFA}}{k_{rxn,FFA}} \tag{S1}$$

where $k_{obs,FFA}\,[s^{-1}]$ is the observed degradation rate constant for FFA. Thus, for a given $k_{obs,FFA}$ the following equation holds.

$$\frac{[^1O_2]_{ss}^{new}}{[^1O_2]_{ss}^{old}} = \frac{k_{rxn,FFA}^{old}}{k_{rxn,FFA}^{new}} \tag{S2}$$

where $[^1O_2]_{ss}^{old}$ is the singlet oxygen steady-state concentration calculated with $k_{rxn,FFA}^{old} = 1.2 \times 10^8 M^{-1} s^{-1}$ (Haag), and $[^1O_2]_{ss}^{new}$ is obtained with $k_{rxn,FFA}^{new}$, whose value depends on solution temperature and ionic strength (see eq.s (13) – (15) in the manuscript). The ratio $[^1O_2]_{ss}^{new}/[^1O_2]_{ss}^{old} = CF$ is the factor that can be used to convert old singlet oxygen concentration in new corrected values.

$$[^1O_2]_{ss}^{new} = CF \cdot [^1O_2]_{ss}^{old} \tag{S3}$$

Figure S4 reports CF values calculated in the temperature interval 20 – 40 ˚C for freshwaters (blue line) and seawaters (red line) using the equations of the main manuscript.

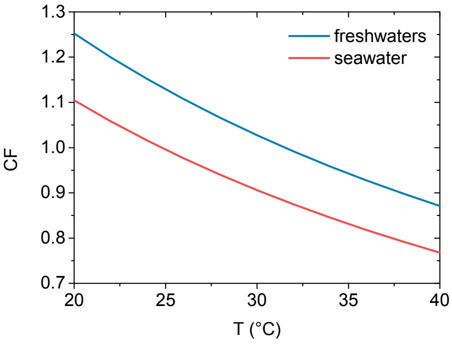

Figure S4 Correction factors (CF) in the temperature interval 20 – 40˚C for singlet oxygen concentrations in freshwater (blue line) and seawater (red line). A reference line (grey, dotted) is drawn at $CF = 1.0$.

References

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