Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

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Supplemental information for:

Degradation of organic pollutants in/on snow and ice by singlet molecular oxygen ($^1O_2$*) and an organic triplet excited state

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Supplemental Discussion

Section S1. Calculating the fraction of $^1O_2$* that reacts with a given pollutant. In liquid samples, water (or D_2O) is the dominant sink for $^1O_2$*. The fraction of $^1O_2$* that reacts with a pollutant (p) in illuminated H_2O solution is given by:

$$f_{p+1O2*}^{\mathrm{LIQ}} = \frac{k_{p+1O2*}[p]}{k_{p+1O2*}[p] + k'_{\mathrm{H2O}}} \qquad \text{(S1)}$$

where k_{p+1O2*} is the second-order rate constant for reaction of p with $^1O_2$*, [p] is the concentration of p in the unfrozen solution, and k'_{H2O} is the first-order deactivation rate constant of $^1O_2$* with water. On ice, solutes are concentrated into liquid-like regions (LLRs) and thus the LLR concentration of the pollutant must be considered in the fraction calculation. Assuming that essentially all of the pollutant ends up in LLRs in the frozen sample, the LLR concentration of p is greater than the initial aqueous concentration by a factor of the freeze concentration factor, F_{LLR} (see equation 2 and the associated discussion in the main text). This increased pollutant concentration in LLRs must be taken into account when choosing the initial aqueous concentration of pollutant; here we choose aqueous pollutant concentrations so that the pollutant is a minor sink for $^1O_2$* on ice (i.e., $f < 30\%$). To accomplish this, we calculate the ice-phase fraction of $^1O_2$* that reacts with a pollutant as:

$$f_{p+1O2*}^{\mathrm{LLR}} = \frac{k_{p+1O2*}[p]F_{\mathrm{LLR}}}{k_{p+1O2*}[p]F_{\mathrm{LLR}} + k'_{\mathrm{H2O}}} \qquad \text{(S2)}$$

We estimate F_{LLR} by freezing-point depression as indicated in equation 2 of the main text. The fraction of $^1O_2$* that reacts with the pollutant under our various experimental conditions is given in Table S1.

Section S2. Regression information for plots in figure 1 of the main text. Absolute values of the slope (k'_{TRP}; s^{-1}), R^2, and j_{2NB} (s^{-1}) for each experiment are: 2.8E-05, 0.99, 0.049 (liquid, hν only); 1.2E-04, 0.98, 0.049 (liquid, RB + hν); 1.9E-04, 0.99, 0.028 (ice, hν only); and 2.4E-02, 0.96, 0.020 (ice, RB + hν) with 0.065 mM TS. With 6 mM TS these values are: 8.1E-05, 0.99, 0.043 (ice, hν only) and 4.9E-04, 0.94, 0.027 (ice, RB + hν).

Section S3. ^{3}RB* enhancement and pollutant loss in degassed samples. In our air-saturated samples containing Rose Bengal we expect that the two main losses for a pollutant are reaction with singlet oxygen, $^1O_2$*, and reaction with the Rose Bengal triplet, ^{3}RB*,

$$p + {}^1\mathrm{O_2}^* \rightarrow \text{products}$$
$$p + {}^3\mathrm{RB}^* \rightarrow \text{products}$$

with rate constants of k_{p+1O2*} and k_{p+3RB*}, respectively. We do not consider direct photodegradation as a sink here because it is slow and we have subtracted it from the measured values of k'_p in the air-saturated and degassed samples.

The 2NB-normalized, pseudo-first order rate constant for loss of p under these conditions is

$$k^*_p = k_{p+1O2*}[{}^1\mathrm{O_2}^*] + k_{p+3RB*}[{}^3\mathrm{RB}^*]$$

Considering the ratio of the pollutant loss rate constant in air-saturated and degassed conditions gives us

$$\frac{k_p^*}{k_{p,degassed}^*} = \frac{k_{p+1O2}[{}^1\mathrm{O}_2^*] + k_{p+3RB*}[{}^3\mathrm{RB}^*]}{k_{p+1O2}[{}^1\mathrm{O}_2^*]_{degassed} + k_{p+3RB*}[{}^3\mathrm{RB}^*]_{degassed}} \qquad \text{(S3)}$$

Because of the lack of dissolved oxygen in the degassed samples we expect $[{}^1\mathrm{O_2}^*]_{\mathrm{degassed}} \approx 0$. In addition, if we assume that the rate of formation of the RB triplet is unaffected by degassing, then the ratio

$[^3\mathrm{RB}^*]_{\mathrm{degassed}}/[^3\mathrm{RB}^*] = \tau_{\mathrm{3RB^*,degassed}}/\tau_{\mathrm{3RB^*}} \approx 130\ \mu\mathrm{s}/3\ \mu\mathrm{s}$.[1,2] Thus $[^3\mathrm{RB}^*]_{\mathrm{degassed}} \sim 40 \times [^3\mathrm{RB}^*]$; i.e., the steady-state concentration of RB triplet is increased by a factor of approximately 40 if O_2 is removed from a sample. Making these substitutions into equation S3 gives

$$\frac{k_p^*}{k_{p,\mathrm{degassed}}^*} \sim \frac{k_{p+1O2^*}[\,^1O_2^*] + k_{p+3RB^*}[\,^3\mathrm{RB}^*\,]}{40 k_{p+3RB^*}[\,^3\mathrm{RB}^*\,]} \qquad \text{(S4)}$$

This is equivalent to

$$\frac{k_p^*}{k_{p,\mathrm{degassed}}^*} \sim \frac{k_{p+1O2^*}[\,^1O_2^*]}{40 k_{p+3RB^*}[\,^3\mathrm{RB}^*\,]} + \frac{1}{40} \sim \frac{k_{p+1O2^*}[\,^1O_2^*]}{40 k_{p+3RB^*}[\,^3\mathrm{RB}^*\,]} \qquad \text{(S5)}$$

where the 1/40 term is neglected since it is much smaller than the other term for our values (Figure 4). Rearranging this equation yields

$$\frac{k_{p+3RB^*}[\,^3\mathrm{RB}^*\,]}{k_{p+1O2^*}[\,^1O_2^*]} \sim \frac{1}{40}\,\frac{k_{p,\mathrm{degassed}}^*}{k_p^*} \qquad \text{(S6)}$$

This indicates that, relative to $^1O_2^*$, the importance of the RB triplet state in the degradation of p in the air-saturated sample is approximately 1/40th of the ratio of the degassed to air-saturated rate constants for loss of p. We can manipulate this equation to estimate the fraction of total pollutant loss that is due to $^3\mathrm{RB}^*$ in the air-saturated sample:

$$f_{\mathrm{p+3RB^*}} = \frac{k_{p+3RB^*}[\,^3\mathrm{RB}^*\,]}{k_{p+3RB^*}[\,^3\mathrm{RB}^*\,] + k_{p+1O2^*}[\,^1O_2^*]} \sim \frac{1}{1+\frac{40\,k_p^*}{k_{p,\mathrm{degassed}}^*}} \qquad \text{(S7)}$$

Figure 4 (right-side y-axis) shows a plot of the estimated $^3\mathrm{RB}^*$ contribution to pollutant loss in the air-saturated samples based on applying equation S7 to the results of Figure 4 (left-side y-axis) in the main text.

Section S4. Kinetic solvent isotope effect on ice. To understand the impact of D_2O on pollutant loss in/on ice, we first consider the ratio:

$$\frac{k_{p,\mathrm{D2O}}^*}{k_{p,\mathrm{H2O}}^*} \qquad \text{(S8)}$$

where $k^*_{p,\mathrm{D2O}}$ and $k^*_{p,\mathrm{H2O}}$ are the photon-flux-normalized, pseudo-first-order rate constants for loss of pollutant in D_2O and H_2O, respectively. Since $k^*_p = k_{p+1O2}[^1O_2^*]$, and the steady-state concentration of $^1O_2^*$ can be described in terms of its rate of formation ($R_{f,1O2^*}$) and sum of sinks, Equation S8 in solution can be written as:

$$\frac{k_{p+1O2^*}[^1O_2^*]_{\mathrm{D2O}}}{k_{p+1O2^*}[^1O_2^*]_{\mathrm{H2O}}} = \frac{k_{p+1O2^*}R_{f,1O2^*}/(k_{p+1O2^*}[p]+k'_{\mathrm{D2O}})}{k_{p+1O2^*}R_{f,1O2^*}/(k_{p+1O2^*}[p]+k'_{\mathrm{H2O}})} = \frac{k_{p+1O2^*}[p]+k'_{\mathrm{H2O}}}{k_{p+1O2^*}[p]+k'_{\mathrm{D2O}}} \qquad \text{(S9)}$$

where all terms are expressed at the same photon flux (i.e., the same j_{2NB} value) and we assume that the rate of formation of $^1O_2^*$ in D_2O is the same as it is in H_2O and that the second-order rate constant for reaction of $^1O_2^*$ with p (i.e., k_{p+1O2^*}) is the same in D_2O and H_2O. Modifying this equation to ice conditions (i.e., in LLRs) yields:

$$\frac{k_{p+1O2^*}[p]F_{\mathrm{LLR}}+k'_{\mathrm{H2O}}}{k_{p+1O2^*}[p]F_{\mathrm{LLR}}+k'_{\mathrm{D2O}}} \qquad \text{(S10)}$$

Under conditions where H_2O is the dominant sink in H_2O-ice samples, while the pollutant is the dominant sink in D_2O-ice samples, Equation S10 resolves to:

$$\frac{k^*_{p,\mathrm{D2O}}}{k^*_{p,\mathrm{H2O}}} = \frac{k'_{\mathrm{H2O}}}{k_{p+1\mathrm{O2*}}[p]F_{\mathrm{LLR}}} \qquad \text{(S11)}$$

Given that k'_{H2O} is 2.2×10^5 s^{-1} at –10 °C, Equation S11 is applicable for our –10°C ice samples at 0.065 mM TS for all three pollutants. As shown in Table S2, values of the ratio $k^*_{p,\mathrm{D2O}}/k^*_{p,\mathrm{H2O}}$ as determined from equation S11 range from 0.7 to 2.6 for our three pollutants under these conditions. That is, values of $k^*_{p,\mathrm{D2O}}/k^*_{p,\mathrm{H2O}}$ are much lower than expected if D_2O is the main sink for $^1O_2$* in the D_2O ice samples.

Supplemental Tables:

Table S1: The calculated fraction of $^1O_2*$ that reacts with a given pollutant (f_p) under different experimental conditions. Values in square brackets are the typical concentrations of each pollutant (in nanomolar) for a given condition; concentrations for ice samples are in the pre-frozen, aqueous solution. The fraction of $^1O_2*$ that is deactivated by the solvent (H_2O or D_2O) is 1-f_p.

Solvent/Pollutant	f_p at 5˚C (LIQ) with 0.065 mM TS	f_p at –10˚C (ICE) with 0.065 mM TS	f_p at –10˚C (ICE) with 6.0 mM TS
H_2O			
FFA	0.00003 [50]	0.29 [30]	0.0074 [50]
TRP	0.00001 [50]	0.20 [30]	0.0047 [50]
BPA	0.00002 [50]	0.12 [10]	0.0078 [50]
D_2O			
FFA	0.0004 [50]	0.85 [30]	0.12 [50]
TRP	0.0002 [50]	0.79 [30]	0.082 [50]
BPA	0.0003 [50]	0.67 [10]	0.13 [50]

Table S2: The ratio of the pollutant loss rate constant in D_2O to that in H_2O in liquid-like regions in/on ice as determined by equation S11 (–10 °C, 0.065 mM total solutes, and pollutant concentrations as shown in Table S1). Due to differences in the $^1O_2*$ deactivation rate constant in D_2O and H_2O, the pollutant is a major sink for $^1O_2*$ in D_2O ice but is a minor sink in H_2O ice.

Pollutant	$\frac{k'_{\mathrm{H2O}}}{k_{p+1\mathrm{O2}*}[p]F_{\mathrm{LLR}}}$
FFA	0.7
TRP	1.5
BPA	2.6

Supplemental Figures:

Figure S1.

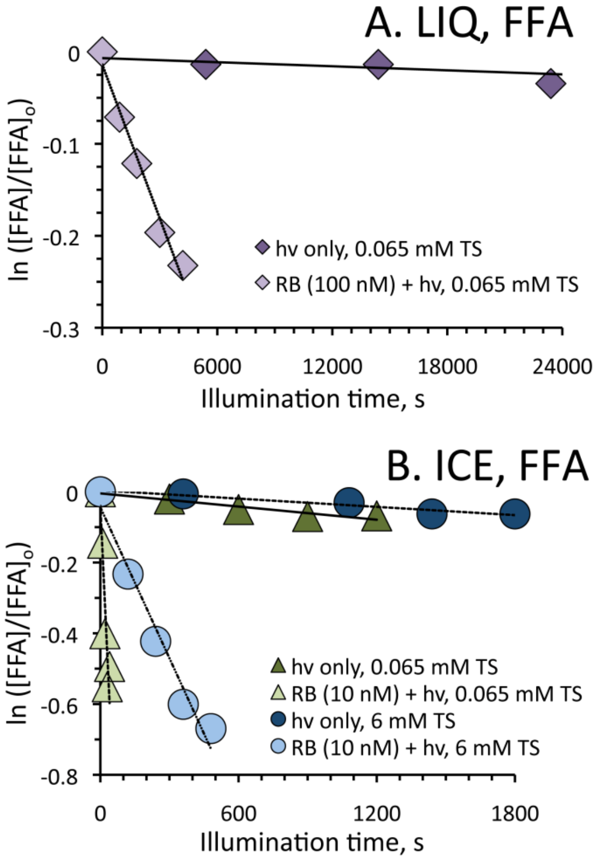

Figure S1. Loss of furfuryl alcohol (FFA) in liquid (A; 5˚C) and ice (B; –10˚C) samples both with an added sensitizer for $^1O_2$* (RB + h*ν*) and without (h*ν* only). All samples were illuminated with 549 nm light. Absolute values of the slope (k'_{FFA}; s^{-1}), R^2, and j_{2NB} (s^{-1}) for each experiment are: 7.4E-07, 0.92, 0.053 (liquid, h*ν* only); 5.6E-05, 0.98, 0.052 (liquid, RB + h*ν*); 6.2E-05, 0.92, 0.088 (ice, h*ν*-only); and 3.9E-05, 0.94, 0.043 (ice, RB + h*ν*) with 0.065 mM TS. With 6 mM TS these values are: 0.014, 0.87, 0.020 (ice, h*ν* only) and 1.4E-03, 0.97, 0.011 (ice, RB + h*ν*).

Figure S2.

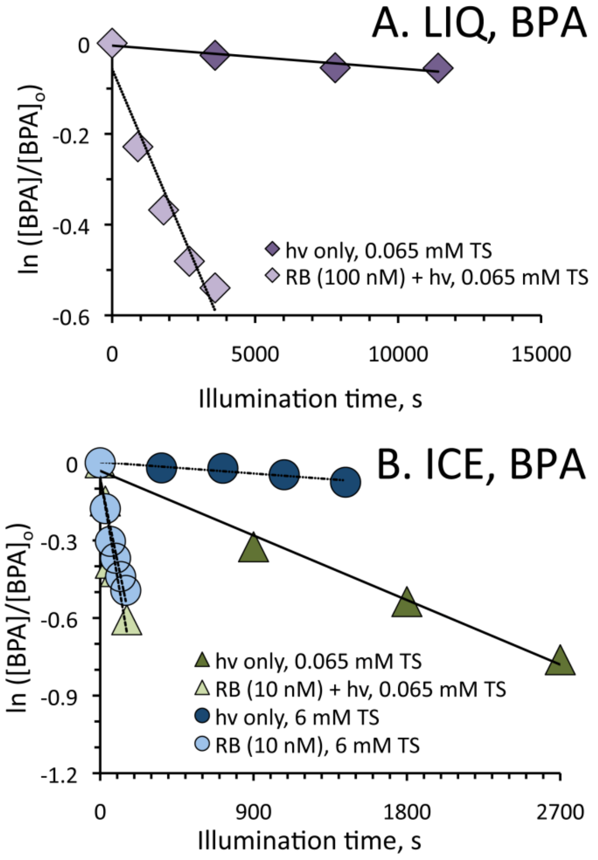

Figure S2. Loss of bisphenol A (BPA) in liquid (A; 5˚C) and ice (B; –10˚C) samples both with an added sensitizer for $^1O_2$* (RB + h*v*) and without (h*v* only). All samples were illuminated with 549 nm light. Absolute values of the slope (k'_{BPA}; s^{-1}), R^2, and j_{2NB} (s^{-1}) for each experiment are: 5.0E-06, 0.91, 0.059 (liquid, h*v*-only); 1.5E-04, 0.95, 0.059 (liquid, RB + h*v*); 2.8E-04, 0.99, 0.28 (ice, h*v*-only); and 3.8E-03, 0.93, 0.026 (ice, RB + h*v*) with 0.065 mM TS. With 6 mM TS these values are: 4.9E-05, 0.93, 0.043 (ice, h*v*-only) and 3.2E-03, 0.94, 0.026 (ice, RB + h*v*).

Figure S3.

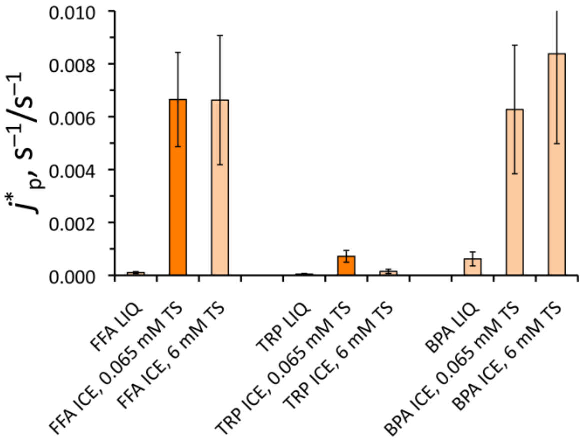

Figure S3. 2NB-normalized, direct photodegradation rate constants of pollutants in degassed solutions in glass vials illuminated with 549 nm light. Measured values are shown in dark orange and calculated values are shown in light orange. For FFA and TRP we measured direct photodegradation in a vial with degassed, 0.065 mM TS ice. We scaled these values by the corresponding ratio of direct photodegradation rate constants measured in Teflon ice pellet molds (IPM) to calculate the values for the degassed liquid and 6.0 mM TS degassed ice samples. For example, to calculate the direct photodegradation of FFA in/on ice with 6.0 mM TS from the 0.065 mM ice sample we use: $j^*_{\mathrm{FFA,6mM\text{-}TS,ICE,vial}} = j^*_{\mathrm{FFA,0.065mM\text{-}TS,ICE,vial}} \times (j^*_{\mathrm{FFA,6mM\text{-}TS,ICE,IPM}} / j^*_{\mathrm{FFA,0.065mM\text{-}TS,ICE,IPM}})$. Direct photodegradation of BPA under all conditions are scaled to FFA loss in/on ice with 0.065 mM TS in the same manner. For example, at 6 mM TS we calculate: $j^*_{\mathrm{BPA,6mM\text{-}TS,ICE,vial}} = j^*_{\mathrm{FFA,0.065mM\text{-}TS,ICE,vial}} \times (j^*_{\mathrm{BPA,6mM\text{-}TS,ICE,IPM}} / j^*_{\mathrm{FFA,0.065mM\text{-}TS,ICE,IPM}})$

References:

(1) Canonica, S.; Jans, U.; Stemmler, K.; Hoigne, J., *Environ. Sci. Technol.*, 1995, **29**, 1822-1831.
(2) Shimizu, O.; Watanabe, J.; Naito, S.; Shibata, Y., *J. Phys. Chem. A*, 2006, **110**, 1735-1739.