Supplementary Material for

Concentrations of a Triplet Excited State are Enhanced in Illuminated Ice

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Accepted to Environmental Science: Processes and Impacts on December 8, 2016

Section S1. Kinetic Analysis of System

We first consider a relatively simple set of equations that describe the main sources and sinks for $^3DMB^*$ in our illuminated samples. $^3DMB^*$ is formed when ground-state DMB absorbs a photon (with rate constant $j_{hv,abs}$) to form an excited singlet state (via SR1), which can either decay back to the ground (singlet) state (SR2) or undergo intersystem crossing to reach the excited triplet state (SR3):

$$DMB + hv \rightarrow {}^1DMB^* \quad \text{(SR1)}$$

$$^1DMB^* \rightarrow DMB \quad \text{(SR2)}$$

$$^1DMB^* \rightarrow {}^3DMB^* \quad \text{(SR3)}$$

The quantum yield for intersystem crossing, Φ_{ISC}, describes the fraction of singlet excited states that form triplets via SR3. Thus, the product $j_{hv,abs}$[DMB] is the rate of light absorption by DMB in the sample and the product $j_{hv,abs}$ [DMB]Φ_{ISC} is the rate of triplet formation.

There are four main sinks for $^3DMB^*$ in our solution and LLR samples: reaction with dissolved oxygen (SR4, with rate constant $k_{O_2+\ ^3DMB^*}$), chemical reaction with phenol (SR5, with rate constant $k_{PhOH+\ ^3DMB^*}$), physical quenching by phenol (SR6, with an apparent rate constant k_Q), and unimolecular decay back to the ground state, e.g., via phosphorescence (SR7, with rate constant k'_{3DMB*}).

$$^3\text{DMB}^* + \text{O}_2 \rightarrow \text{DMB} + {}^1\text{O}_2^* \quad \text{(SR4)}$$

$$^3\text{DMB}^* + \text{PhOH} \rightarrow \text{products} \quad \text{(SR5)}$$

$$^3\text{DMB}^* + \text{PhOH} \rightarrow \text{DMB} + \text{PhOH} \quad \text{(SR6)}$$

$$^3\text{DMB}^* \rightarrow \text{DMB} \; (+ h\nu') \quad \text{(SR7)}$$

It is likely that SR6 is a net reaction that involves reaction SR5 to form a phenoxyl radical, followed by reduction of this radical back to PhOH.[1]

From the seven reactions above we can derive expressions for the steady-state concentration of ^{3}DMB*, [^{3}DMB*], and for the pseudo-first-order rate constant for loss of PhOH, k'_{PhOH}. The value of [^{3}DMB*] is determined by equating the formation and loss rates for the triplet

$$j_{h\nu,abs}[\text{DMB}]\Phi_{ISC} = \left(k_{\text{O}_2+\,{}^3\text{DMB}^*}[\text{O}_2] + \left(k_{\text{PhOH}+\,{}^3\text{DMB}^*} + k_{\text{Q}}\right)[\text{PhOH}] + k'_{3\text{DMB}*}\right)\left[{}^3\text{DMB}^*\right] \quad \text{(S1)}$$

and then re-arranging to

$$\left[{}^3\text{DMB}^*\right] = \frac{j_{\text{h}\nu,\text{abs}}[\text{DMB}]\Phi_{\text{ISC}}}{k_{\text{O}_2+\,{}^3\text{DMB}^*}[\text{O}_2] + \left(k_{\text{PhOH}+\,{}^3\text{DMB}^*} + k_{\text{Q}}\right)[\text{PhOH}] + k'_{3\text{DMB}*}} \quad \text{(S2)}$$

Rearranging Equation 3 in the main text we can express the background-corrected rate constant for phenol loss due to reaction with ^{3}DMB*, i.e., $k'_{\text{PhOH}} - j_{\text{PhOH}}$:

$$k'_{\text{PhOH}} - j_{\text{PhOH}} = k_{\text{PhOH}+\,{}^3\text{DMB}^*}\left[{}^3\text{DMB}^*\right] \quad \text{(S3)}$$

Substituting the DMB triplet steady-state concentration from S2 into S3 yields

$$k'_{\text{PhOH}} - j_{\text{PhOH}} = \frac{k_{\text{PhOH}+\,{}^3\text{DMB}^*}\, j_{\text{h}\nu,\text{abs}}[\text{DMB}]\Phi_{\text{ISC}}}{k_{\text{O}_2+\,{}^3\text{DMB}^*}[\text{O}_2] + (k_{\text{PhOH}+\,{}^3\text{DMB}^*} + k_{\text{Q}})[\text{PhOH}] + k'_{3\text{DMB}*}} \quad \text{(S4)}$$

There are two limiting cases for this background-corrected rate constant. The first is when dissolved oxygen is the dominant sink for ^{3}DMB*, i.e., at low phenol concentrations when $k_{O_2+\,^3DMB^*}[O_2] >> (k_{PhOH+\,^3DMB^*} + k_Q)[PhOH] + k'_{3DMB*}$. In this case Equation S4 simplifies to an expression that is independent of the phenol concentration:

$$k'_{PhOH} - j_{PhOH} \approx \frac{k_{PhOH+\,^3DMB^*} j_{h\nu,abs}[DMB]\Phi_{ISC}}{k_{O_2+\,^3DMB^*}[O_2]} \quad \text{(S5)}$$

The second limiting case is when phenol is the dominant sink for the triplet and S4 simplifies to

$$k'_{PhOH} - j_{PhOH} \approx \frac{k_{PhOH+\,^3DMB^*} j_{h\nu,abs}[DMB]\Phi_{ISC}}{(k_{PhOH+\,^3DMB^*} + k_Q)[PhOH]} \quad \text{(S6)}$$

In this case the steady-state concentration of ^{3}DMB* decreases with increasing phenol concentration (because PhOH is the major sink) and thus the rate constant for phenol loss is inversely proportional to [PhOH].

Section S2. Kinetic Explanation of the Slopes in Figure 1

Figure 1 shows the apparent rate constant for PhOH loss, k^*_{PhOH}, as a function of the DMB concentration for both ice and solution samples. Here we derive an equation to describe this relationship. We start with equation S4, rearranged slightly, in solution where O_2 is the dominant sink for the triplet state of DMB:

$$k'_{\mathrm{PhOH,LIQ}} = \left(\frac{k_{\mathrm{PhOH+3DMB*}} j_{\mathrm{h\nu,abs}} \Phi_{\mathrm{ISC}}}{k_{\mathrm{O_2 + {}^3DMB^*}} [\mathrm{O_2}]} \right)_{\mathrm{LIQ}} [\mathrm{DMB}]_{\mathrm{LIQ}} + j_{\mathrm{PhOH,LIQ}} \quad \text{(S7)}$$

To remove any influence of variations in photon fluxes between experiments we divide each term by $j_{2\mathrm{NB}}$ and make the substitutions from equations 4 and 5:

$$k^*_{\mathrm{PhOH,LIQ}} = \left(\frac{k_{\mathrm{PhOH+3DMB*}} j_{\mathrm{h\nu,abs}} \Phi_{\mathrm{ISC}}}{k_{\mathrm{O_2 + {}^3DMB^*}} [\mathrm{O_2}] j_{2\mathrm{NB}}} \right)_{\mathrm{LIQ}} [\mathrm{DMB}]_{\mathrm{LIQ}} + j^*_{\mathrm{PhOH,LIQ}} \quad \text{(S8)}$$

This is the general equation for the solution line in the plot of k^*_{PhOH} versus [DMB] in Figure 1, with a slope equal to the term in parentheses and a *y*-intercept equal to j^*_{PhOH}. Following a similar procedure, we can derive the analogous equation for the liquid-like regions of the ice samples:

$$k^*_{\mathrm{PhOH,LLR}} = \left(\frac{k_{\mathrm{PhOH+3DMB*}} j_{\mathrm{h\nu,abs}} \Phi_{\mathrm{ISC}}}{k_{\mathrm{O_2 + {}^3DMB^*}} [\mathrm{O_2}] j_{2\mathrm{NB}}} \right)_{\mathrm{LLR}} [\mathrm{DMB}]_{\mathrm{LLR}} + j^*_{\mathrm{PhOH,LLR}} \quad \text{(S9)}$$

Since the *x*-axis of Figure 1 is the concentration of DMB in the initial solution (prior to freezing), we make the substitution $[\mathrm{DMB}]_{\mathrm{LLR}} = F[\mathrm{DMB}]_{\mathrm{LIQ}}$ (where F is the freeze concentration factor) to yield

$$k^*_{\mathrm{PhOH,LLR}} = \left(\frac{k_{\mathrm{PhOH+3DMB*}} j_{\mathrm{h\nu,abs}} \Phi_{\mathrm{ISC}} F}{k_{\mathrm{O_2 + {}^3DMB^*}} [\mathrm{O_2}] j_{2\mathrm{NB}}} \right)_{\mathrm{LLR}} [\mathrm{DMB}]_{\mathrm{LIQ}} + j^*_{\mathrm{PhOH,LLR}} \quad \text{(S10)}$$

This allows us to consider the ice rate constant for PhOH loss in terms of the initial solution concentration of DMB, as in Figure 1.

Using the slope terms from Equations S8 and S10 we can compare the ratio of the ice and liquid slopes in Figure 1:

$$\frac{m_{\mathrm{LLR}}}{m_{LIQ}} = \frac{\left(\frac{k_{\mathrm{PhOH+3DMB*}} j_{\mathrm{h\nu,abs}} \Phi_{\mathrm{ISC}} F}{k_{\mathrm{O_2+\,^3DMB^*}}\,[\mathrm{O_2}]\, j_{\mathrm{2NB}}}\right)_{\mathrm{LLR}}}{\left(\frac{k_{\mathrm{PhOH+3DMB*}} j_{\mathrm{h\nu,abs}} \Phi_{\mathrm{ISC}}}{k_{\mathrm{O_2+\,^3DMB^*}}\,[\mathrm{O_2}]\, j_{\mathrm{2NB}}}\right)_{\mathrm{LIQ}}} \tag{S11}$$

There are likely two main variables that determine the difference in the LLR and LIQ values for the parameters in Equation S11: ionic strength (which is much higher in the LLRs compared to solution) and temperature (which is 15 °C lower in the LLRs compared to solution). Since the ^{3}DMB* reactions in our system involve only neutral species (i.e,. ^{3}DMB*, PhOH, and O_2), the impact of ionic strength is likely to be small. As for temperature, we do not know the temperature dependencies for the numerator and denominator in Equation S11, but here we examine the likely dependencies for individual terms. First, as discussed for Equation 10 in the main text, the second-order rate constant $k_{\mathrm{PhOH+3DMB*}}$ appears to have no significant temperature dependence based on solution kinetics of PhOH + ^{3}DMB* between 20 and 5 °C (Smith ref). Second, while we are unable to find data on the temperature dependence of the O_2 + ^{3}DMB* reaction, activation energies (E_a) for the reaction of O_2 with four other triplet states in toluene[2] are all small, near 10 kJ mol^{-1}. If E_a for $k_{\mathrm{O2+3DMB*}}$ is similar, this rate constant at -10°C would be only 30% smaller than the value at 5 °C. Based on these values, the ratio of these rate constants in Equation S11 is approximately unity, i.e.,

$$\frac{\left(\frac{k_{\mathrm{PhOH+3DMB*}}}{k_{\mathrm{O_2+\,^3DMB^*}}}\right)_{\mathrm{LLR}}}{\left(\frac{k_{\mathrm{PhOH+3DMB*}}}{k_{\mathrm{O_2+\,^3DMB^*}}}\right)_{\mathrm{LIQ}}} \approx 1 \tag{S12}$$

Similarly, j_{2NB} is independent of both temperature and phase:[3]

$$\frac{\left(\frac{1}{j_{2NB}}\right)_{LLR}}{\left(\frac{1}{j_{2NB}}\right)_{LIQ}} = 1 \quad \text{(S13)}$$

We expect that the rate constant for light absorption by DMB, $j_{hv,abs}$, is similarly independent of temperature, i.e.,

$$\frac{\left(j_{hv,abs}\right)_{LLR}}{\left(j_{hv,abs}\right)_{LIQ}} \approx 1 \quad \text{(S14)}$$

This is because the two components of $j_{hv,abs}$, the photon flux and DMB molar absorptivities, are essentially independent of T in our narrow range.

Making the three substitutions above into Equation S11 yields a ratio of slopes in Figure 1 of

$$\frac{m_{LLR}}{m_{LIQ}} = \frac{\left(\frac{\Phi_{ISC}F}{[O_2]}\right)_{LLR}}{\left(\frac{\Phi_{ISC}}{[O_2]}\right)_{LIQ}} = F\frac{\left(\frac{\Phi_{ISC}}{[O_2]}\right)_{LLR}}{\left(\frac{\Phi_{ISC}}{[O_2]}\right)_{LIQ}} \quad \text{(S15)}$$

Thus the ratio of the ice to liquid slopes is equal to the freeze-concentration factor modified by any change between liquid-like regions and solution in the quantum yield for intersystem crossing and the O_2 concentration. We do not know if either Φ_{ISC} or $[O_2]$ are significantly different between LLRs and solution, so the importance of these factors is unclear. For the latter term, if a liquid-like region at – 10 °C is in contact with air then its dissolved O_2 concentration is 30% higher than in an air-saturated solution at 5 °C (Section S3 below). However, micro-CT imaging shows that LLRs in our ice samples tend to be wrapped around internal gas bubbles whose composition is unknown.[4] If the partial pressure of O_2 in these bubbles is not equal to the atmospheric value then the LLR concentration of dissolved O_2, and the ratio of the slopes in equation S15, will vary accordingly.

Table S1. Summary table of measured values of k^*_{PhOH} and j^*_{PhOH}, and the corresponding calculated value of F_{EXP}. All error values are 1 standard error (SE), propagated from values of j_{2NB} and from k^*_{PhOH} and j^*_{PhOH} for ice and liquid samples (see text for more details). The standard condition for each experiment is 100 nM PhOH, 100 nM DMB, 2 mM total solute concentration, pH 4, and a temperature of -10 °C for ice and 5 °C for solution. In each set of tests, the test variable is changed while the remaining variables are kept at standard condition.

Phenol (nM)	k^*_{PhOH} (s^{-1}/s^{-1})	SE k^*_{PhOH}	j^*_{PhOH} (s^{-1}/s^{-1})	SE j^*_{PhOH}	F_{EXP}	SE F_{EXP}
-10 °C Phenol Dependence Test						
10	5.9E-02	1.2E-02	1.3E-02	3.3E-03	57	30
50	1.3E-01	1.8E-02	6.4E-03	8.1E-04	97	19
100	1.1E-01	1.2E-02	7.2E-03	2.3E-03	85	17
500	8.4E-02	1.3E-02	1.6E-03	1.5E-04	120	41
5 °C Phenol Dependence Test						
10	1.1E-03	3.9E-04	2.7E-04	4.7E-05	N/A	N/A
50	1.3E-03	1.6E-04	8.8E-05	9.7E-06	N/A	N/A
100	1.4E-03	2.0E-04	1.9E-04	2.6E-05	N/A	N/A
500	1.1E-03	1.7E-04	4.4E-04	9.5E-05	N/A	N/A
DMB (nM)	k^*_{PhOH} (s^{-1}/s^{-1})	SE k^*_{PhOH}	j^*_{PhOH} (s^{-1}/s^{-1})	SE j^*_{PhOH}	F_{EXP}	SE F_{EXP}
-10 °C DMB Dependence Test						
0	1.3E-02	3.3E-03	1.4E-02	2.5E-03	N/A	N/A
5	1.1E-02	1.5E-03	1.4E-02	2.5E-03	N/A	N/A
10	2.7E-02	1.2E-02	1.4E-02	2.5E-03	170	170
15	1.8E-02	5.0E-03	1.4E-02	2.5E-03	43	54
20	2.8E-02	2.9E-03	1.4E-02	2.5E-03	92	52
50	3.8E-02	8.7E-03	1.4E-02	2.5E-03	6	38
100	5.9E-02	1.2E-02	1.4E-02	2.5E-03	57	32
5 °C DMB Dependence Test						
0	2.7E-04	4.7E-05	2.7E-04	4.7E-05	N/A	N/A
50	1.1E-03	1.6E-04	2.7E-04	4.7E-05	N/A	N/A
100	1.1E-03	3.9E-04	2.7E-04	4.7E-05	N/A	N/A
150	2.1E-03	3.1E-04	2.7E-04	4.7E-05	N/A	N/A
200	2.4E-03	3.9E-04	2.7E-04	4.7E-05	N/A	N/A

Table S1, continued

TS (mM)	k^*_{PhOH} (s^{-1}/s^{-1})	SE k^*_{PhOH}	j^*_{PhOH} (s^{-1}/s^{-1})	SE j^*_{PhOH}	F_{EXP}	SE F_{EXP}
-10 °C Total Solute Concentration Dependence Test						
0.1	1.1E-01	2.0E-02	7.1E-03	1.3E-03	110	25
2.0	1.1E-01	1.2E-02	7.2E-03	2.3E-03	85	17
20.0	1.1E-01	1.6E-02	3.9E-03	1.1E-03	214	46
5 °C Total Solute Concentration Dependence Test						
0.1	1.2E-03	7.7E-05	3.2E-04	2.4E-05	N/A	N/A
2.0	1.1E-03	3.9E-04	2.7E-04	4.7E-05	N/A	N/A
20.0	9.2E-04	7.1E-05	4.3E-04	1.9E-05	N/A	N/A
5400	4.4E-03	2.4E-04	2.1E-03	4.8E-04	N/A	N/A
Temp (°C)	k^*_{PhOH} (s^{-1}/s^{-1})	SE k^*_{PhOH}	j^*_{PhOH} (s^{-1}/s^{-1})	SE j^*_{PhOH}	F_{EXP}	SE F_{EXP}
Temperature Dependence Test						
5	1.08E-03	3.92E-04	2.69E-04	4.73E-05	N/A	N/A
-5	8.39E-02	1.29E-02	2.66E-03	3.10E-04	67	15
-10	1.10E-01	1.17E-02	7.21E-03	2.26E-03	85	17
-15	8.39E-02	1.29E-02	1.99E-03	1.07E-04	68	15
-20	1.10E-01	1.17E-02	2.41E-03	1.47E-04	89	18
pH	k^*_{phenol} (s^{-1}/s^{-1})	se k^*_{phenol}	j^*_{phenol} (s^{-1}/s^{-1})	se j^*_{phenol}	F_{EXP}	se F_{EXP}
-10 °C pH Dependence Test						
3	1.60E-01	3.36E-02	1.06E-02	1.93E-03	86	24
4	1.10E-01	1.17E-02	7.21E-03	2.26E-03	85	17
5	6.32E-03	1.15E-03	6.17E-04	5.42E-05	190	370
5 °C pH Dependence Test						
3	1.92E-03	2.68E-04	1.88E-04	1.29E-05	N/A	N/A
4	1.08E-03	3.92E-04	2.69E-04	4.73E-05	N/A	N/A
5	2.48E-04	2.87E-05	2.17E-04	5.31E-05	N/A	N/A

Average (± 1 σ) F_{EXP} for all experiments = 95 ± 50

Section S3. Calculation of $^3DMB^*$ sinks in ice

As shown in Equation S2, the expression for the triplet concentration has a denominator that represents the total rate constant for loss of $^3DMB^*$. Under our conditions oxygen is the main sink for $^3DMB^*$,[1, 5] with an approximate rate constant in solution at room temperature of 2×10^9 M^{-1} s^{-1}.[1, 6-8]

We estimate the dissolved oxygen concentration within ice LLRs using Henry's Law:

$$[O_2] = p_{O2} K_H \quad \text{(S16)}$$

where p_{O2} represents the partial pressure of O_2 above the LLRs (which we assume is 0.21 atm, the atmospheric value) and K_H represents the Henry's Law constant, which is a function of temperature:[9]

$$K_H(T) = K_H^{\Theta} \times \exp\left(\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^{\Theta}}\right)\right) \quad \text{(S17)}$$

In this equation $K_H(T)$ is the Henry's Law constant at temperature T; K_H^{Θ} is the Henry's Law constant (1.3×10^{-3} M atm^{-1})[10] at reference temperature T^{Θ} (298.15 K); $\Delta_{sol}H$ is the enthalpy of dissolution (12.06 ± 0.04 kJ mol^{-1})[11]; and R is the ideal gas constant (8.314 J K^{-1} mol^{-1}).[12] Calculated values of $K_H(T)$ at 5 °C (solution) and –10 °C (ice) are 1.8×10^{-3} M atm^{-1} and 2.4×10^{-3} M atm^{-1}, respectively. These values result in O_2 concentrations in air-saturated water of 390 and 520 μM at 5 °C and –10 °C, respectively, corresponding to $k_{O2+3DMB*}[O_2]$ values of 7.8×10^5 s^{-1} (i.e., a triplet lifetime of 1.3 μs) and 1.0×10^6 s^{-1} (i.e., a triplet lifetime of 1.0 μs), respectively.

PhOH is a secondary sink for the DMB triplet in our system. Its concentration in ice LLRs can be estimated by multiplying its solution concentration by the freeze concentration factor at a given ice temperature and solution total solute concentration. Under our standard condition (2.0 mM TS, pH 4, -10 °C, 100 nM PhOH), the calculated F_{FPD} is 2.8×10^3 (see Equation 7 in the main text), while the average measured F_{EXP} is 77 ± 11. These freeze-

concentration factors give PhOH concentrations in the ice LLRs of 280 μM and 7.7 μM, respectively, corresponding to first-order rate constants of $^3DMB^*$ loss via PhOH of 1.8×10^5 s^{-1} and 4.8×10^3 s^{-1}, respectively. Assuming that O_2 and phenol are the only sinks for the DMB triplet in our LLRs, phenol would account for 18% of the triplet loss if F_{FPD} is the correct factor, but only 0.48% of triplet loss if F_{EXP} is the correct value. Our results showing that k^*_{PhOH} is independent of [PhOH] (Figure 2) indicate that PhOH is a minor sink for $^3DMB^*$, consistent with the calculation above using the measured value of F_{EXP}.

Section S4. Relationship between $^1O_2^*$ and $^3DMB^*$

The primary sink for $^3DMB^*$ in solution is reaction with O_2 to form $^1O_2^*$, which is the source of $^1O_2^*$ in our samples. In turn, the major sink for $^1O_2^*$ in solution is deactivation with water, resulting in a steady-state equation for solution $^1O_2^*$ of

$$\left[{}^1O_2^*\right]_{LIQ} = \frac{k_{O_2+\,{}^3DMB^*}\left[{}^3DMB^*\right]_{LIQ}[O_2]_{LIQ}}{k_{H_2O+\,{}^1O_2^*}\,[H_2O]} = \frac{k_{O_2+\,{}^3DMB^*}\left[{}^3DMB^*\right]_{LIQ}[O_2]_{LIQ}}{k'_{H_2O}} \quad \text{(S18)}$$

where $k_{H_2O+\,{}^1O_2^*}$ and $k_{O_2+\,{}^3DMB^*}$ are second-order rate constants and k'_{H2O} is the pseudo-first-order rate constant for $^1O_2^*$ loss due to water.

Substituting $[^3DMB^*]_{LIQ}$ calculated by Equation S2 into Equation S18 yields

$$\left[{}^1O_2^*\right]_{LIQ} \quad \text{(S19)}$$

$$= \frac{k_{O_2+\,{}^3DMB^*} j_{h\nu,abs}\Phi_{ISC}[DMB]_{LIQ}[O_2]_{LIQ}}{k'_{H_2O}\left(k_{O_2+\,{}^3DMB^*}\,[O_2]_{LIQ} + \left(k_{PhOH+\,{}^3DMB^*} + k_Q\right)[PhOH] + k'_{3DMB*}\right)}$$

Since O_2 is the dominant sink for $^3DMB^*$ in our samples, Equation S19 simplifies to

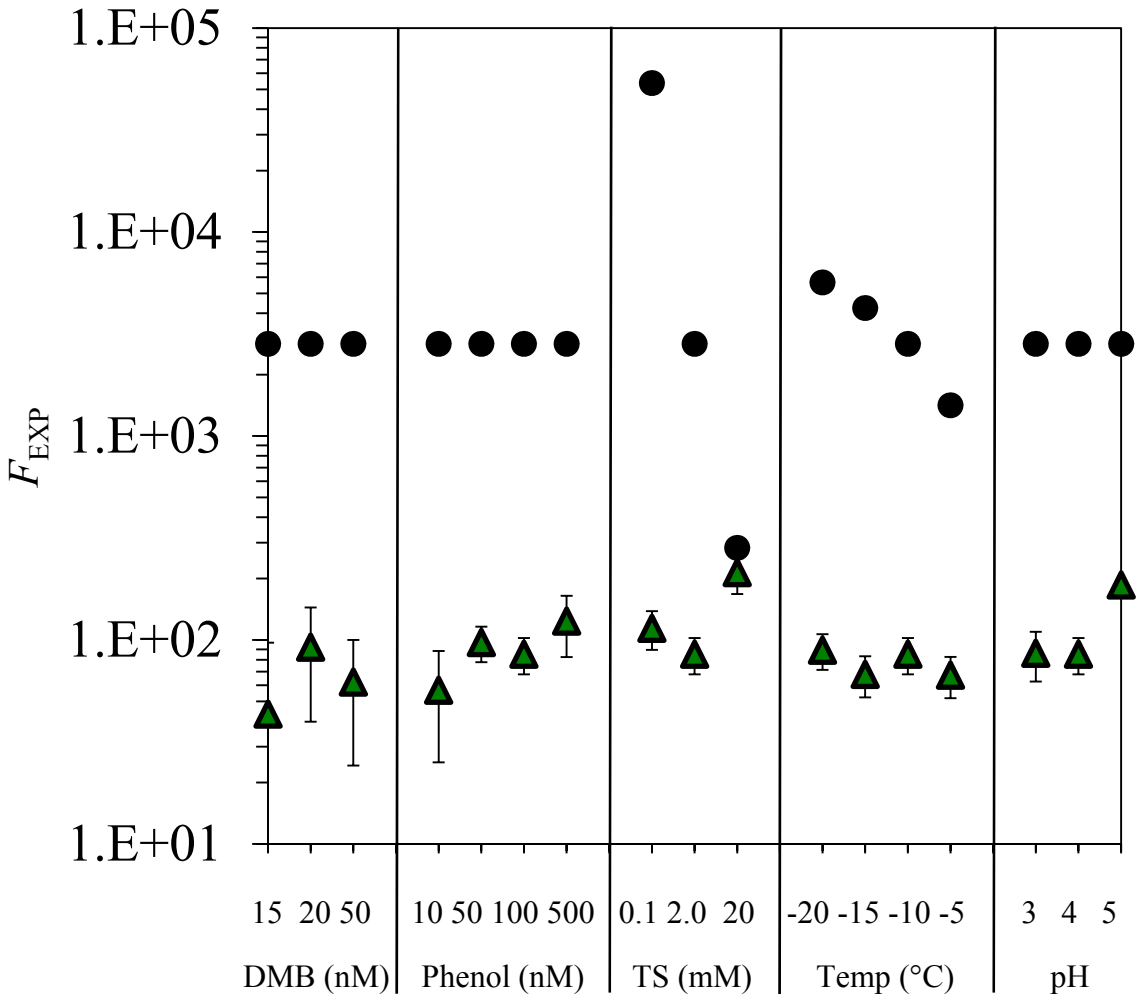
$$\left[{}^1O_2^*\right]_{LIQ} = \frac{k_{O_2+\,{}^3DMB^*} j_{h\nu,abs}\Phi_{ISC}[DMB]_{LIQ}[O_2]_{LIQ}}{k'_{H_2O}\,k_{O_2+\,{}^3DMB^*}\,[O_2]_{LIQ}} = \frac{j_{h\nu,abs}\Phi_{ISC}[DMB]_{LIQ}}{k'_{H_2O}} \quad \text{(S20)}$$

where the numerator on the right-hand side of this equation is the rate of DMB triplet formation. We can derive an analogous equation for the concentration in LLRs

$$\left[{}^1O_2^*\right]_{LLR} = \left(\frac{j_{h\nu,abs}\Phi_{ISC}}{k'_{H_2O}}\right)_{LLR} \times [DMB]_{LLR} \quad \text{(S21)}$$

These equations indicate that singlet oxygen in solution or LLRs should be independent of the dissolved O_2 concentration as long as oxygen is the major sink for the DMB triplet. Thus, under conditions where O_2 is the dominant sink of $^3DMB^*$, the steady-state concentration of triplet will decrease as the dissolved O_2 concentration increases (Equation S2). However, the steady-state concentration of $^1O_2^*$ is independent of the dissolved O_2 concentration as long as O_2

remains the dominant sink (Equation S20). Thus, when O_2 is the major sink for a triplet, changes in dissolved oxygen levels in LLRs (and other ice reservoirs) will affect the concentration of triplet excited state but not alter the singlet molecular oxygen level.



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148 **Figure S1.** Compilation of freeze-concentration factors (*F* values) for the five different types of

149 experiments performed. Solid black circles are calculated values of F_{FPD} from freezing point

150 depression while the green triangles are F_{EXP} values determined from experiments.

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