Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

The Effect of Cations on NO_2 Production from the Photolysis of Thin Water Films Containing Nitrate

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Figure S1: Rate of OH formation as a function of added benzene concentration for solutions of either 5 mM $NaNO_3$ (orange) or $Mg(NO_3)_2$ (purple) at 298 K, pH 5.0 and using 313 nm illumination.

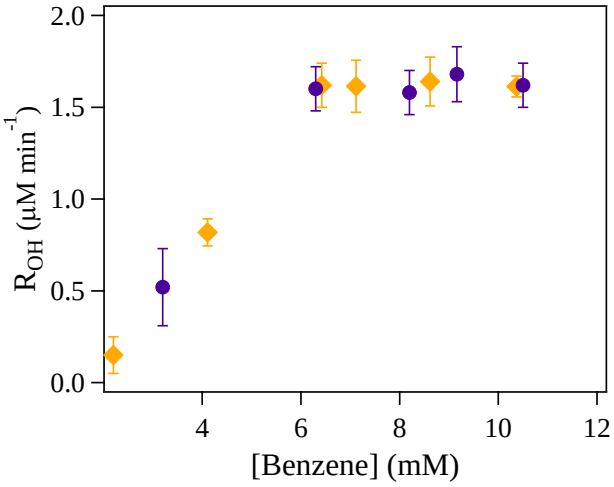
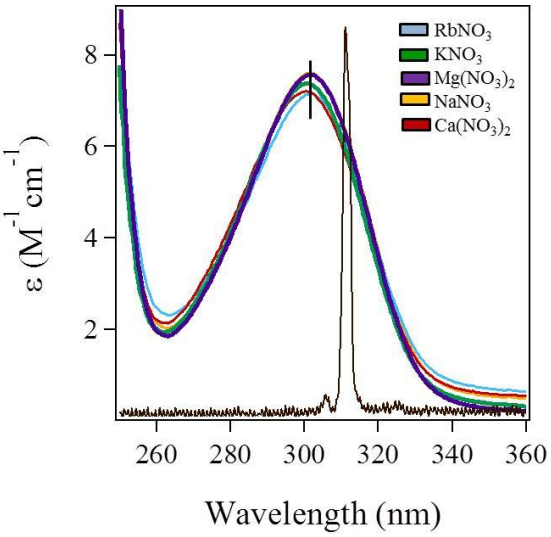


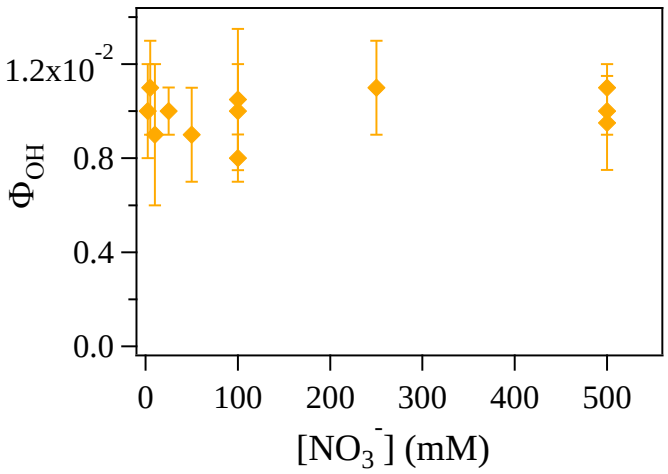
Figure S2: UV-vis spectra of $Ca(NO_3)_2$ (red), $NaNO_3$ (orange), $Mg(NO_3)_2$ (purple), KNO_3 (green) and $RbNO_3$ (blue) at 0.5 M concentrations of NO_3^-. The photolysis lamp spectrum is provided as the black line. The short black line is centered at 302 nm.



The molar absorptivities of $RbNO_3$, $Mg(NO_3)_2$ and $NaNO_3$ are centered around 302 nm (short black solid line), while KNO_3 and $Ca(NO_3)_2$ show a very small shift toward the blue (300 nm).

UV-vis spectra were also conducted at 2 M nitrate ion concentration and no substantial difference in the spectra was measured between the two concentrations.

Figure S3: Quantum yields of OH (298 K; pH 5.0; 313 nm illumination) as a function of $NaNO_3$ solution concentration. The sodium benzoate concentration was always two times the $NaNO_3$ concentration in order to sufficiently scavenge all of the OH generated.



Light Attenuation through Thin Films

To determine if there is significant light attenuation in our thin films we calculated the light absorbance using Beer's Law (equation S1),

$$A = \sigma\, l\, c \qquad \text{(eq. S1)}$$

where A is the absorbance, σ is the molar cross section of nitrate at 311 nm (5 M^{-1} cm^{-1}), *l* is the film thickness (approximately 800 nm), and c is the maximum concentration of nitrate in the film (10 M based on equilibrium saturation concentrations for $NaNO_3$). Based on these values, the upper bound of light absorbance in the films at 311 nm is 5×10^{-3}, which is negligible, indicating that there is negligible attenuation of the light in the films.

Expected Rate of NO_2 Formation

The expected R_{NO2} in our experiments (molecules cm^{-3} s^{-1}) is dependent on Eq. S2,

$$R_{NO2} = F_\lambda I_\lambda \phi \times (L \times W/V^{chamber}) \quad \text{(eq. S2)}$$

where I_λ is the photon flux (photons cm^{-2} s^{-1}), F_λ is the fraction of light absorbed, ϕ is the quantum yield of NO_2 formation from nitrate photolysis, L and W are the length and width of the thin film and $V^{chamber}$ is the volume of the Teflon chamber into which the NO_2 is emitted. For low light absorbing conditions F_λ can be approximated as

$$F_\lambda \approx 2.303\ \sigma_\lambda \frac{N_{NO3-}}{V^{film}}\ l \approx 2.303\ \sigma_\lambda \frac{N_{NO3-}}{L\,W} \quad \text{(eq. S3)}$$

where N_{NO3-} is the number of moles of nitrate added to the chamber, and l and V^{film} are the thickness and volume of the thin film and W and L are as defined above. Combining Eq.S2 and S3 yields S4.

$$R_{NO2} = I_\lambda \phi\ 2.303\ \frac{N_{NO3-}}{V^{chamber}} \sigma_\lambda \quad \text{(eq. S4)}$$

This shows that the R_{NO2} under our experimental conditions is not dependent on the aqueous-phase concentration of nitrate but rather the number of moles of nitrate added to the chamber.

Example of Interface Calculation

To calculate the interface quantum yield for KNO_3, we used the results of previous molecular dynamic simulations to estimate the increase of NO_3^- in the interface region in our thin

films compared to $NaNO_3$. The fraction of nitrate ions at the interface was determined (eq. S5, example for KNO_3) from the integrated density profile area of NO_3^- within ± 0.5 nm of the GDS, which for a 2 M KNO_3 solution[1] is 23%. From this we can calculate the ratio of interface to bulk NO_3^- for potassium solutions using eq. S5:

$$F_{KNO3} = \frac{N_K^{int}}{N_K^b} = \frac{0.23}{0.77} = 0.3 \qquad \text{(eq. S5)}$$

For $NaNO_3$, the integrated density profile area[2] of NO_3^- within ± 0.5 nm of the GDS is 3%, so $F_{NaNO3} = 0.03$. The relative enhancement in nitrate abundance in the interface region in going from $NaNO_3$ to KNO_3 is then $\frac{F_{KNO3}}{F_{NaNO3}} = \frac{0.3}{0.03} = 10$.

The MD simulations used to determine this relative enhancement were conducted using 1.5 nm thick slabs. The interface region of these simulations had a thickness of 1 nm (i.e., ± 0.5 nm with respect to the GDS), while the remaining thickness (for the bulk) is 0.5 nm. However, in our experiments the bulk thickness (799 nm, t_b) is significantly larger than the interface (1 nm, t_i). When calculating the interface quantum yield, we estimate the bulk-interface partitioning as the product of the initially assumed even "baseline" distribution of NO_3^- throughout the solutions (i.e., $\frac{N_{Na}^b}{N_K^{int}} = \frac{t_b}{t_{int}} = \frac{799}{1}$) divided by the MD-estimated factor of 10 enhancement for KNO_3 (eq. S6):

$$\phi_K^{int} = 0.73\,\frac{\phi_{Na}^b N_{Na}^b}{N_K^{int}} = 0.73\,\frac{\phi_{Na}^b\, t_b F_{NaNO3}}{t_i F_{KNO3}} = 0.73\,\frac{0.011 * 799\ \text{nm}}{1\ \text{nm} * 10} = 0.6 \qquad \text{(eq. S6)}$$

While we assume an "even" distribution of nitrate ions throughout the $NaNO_3$ film (i.e., an interface/bulk ratio of NO_3^- of 1/799), molecular dynamics modeling indicates that NO_3^- is suppressed at the interface and the interface/bulk ratio should be lower.[1, 2] If we use a lower ratio for $NaNO_3$ and propagate this to the KNO_3 case (still with the 10-fold enhancement in interfacial NO_3^- described in the text), the calculated interface quantum yield for NO_3^- will be higher than 0.6. While a value of 1 is an upper limit, an interface/bulk ratio consistent with the MD modeling [1, 2] would push the interfacial nitrate quantum yield to above 1, suggesting either that the absolute MD distributions for nitrate have significant error bars, or perhaps that other phenomena might also be enhancing NO_2 release.

Once the interface quantum yield was determined, the relative contribution of the interface was determined using eq. S7.

$$\frac{\phi_K^{int} N_K^{int}}{\phi_K^b N_K^b + \phi_K^{int} N_K^{int}} = \frac{1}{\frac{\phi_K^b N_K^b}{\phi_K^{int} N_K^{int}} + 1} \sim \frac{1}{\frac{\phi_K^b t_b F_{NaNO3}}{\phi_K^{int} t_i F_{KNO3}} + 1} = 0.4 \qquad \text{(eq. S7)}$$

References:

1 N. K. Richards, L. M. Wingen, K. M. Callahan, N. Nishino, M. T. Kleinman, D. J. Tobias and B. J. Finlayson-Pitts, *J. Phys. Chem. A*, 2011, **115** 5810-5821.

2 J. L. Thomas, M. Roeselová, L. X. Dang and D. J. Tobias, *J. Phys. Chem. A*, 2007, **111**, 3091-3098.