

Final author response to comments on the manuscript “Evidence of the water-cage effect on the photolysis of NO_3^- and FeOH^{2+} , and its implications for the photochemistry at the air-water interface of atmospheric droplets” by P. Nissenon et al.

Response to Dr. Romeo-Iulian Olariu

We thank Dr. Olariu very much for his observations. The reviewer discusses two issues. The first issue concerns the initial formation rate of nitrite and acetone at high 2-propanol concentrations. The reviewer notes that at high [2-propanol], the initial formation rate of acetone (R_{Acetone}) appears constant while the initial formation rate of nitrite (R_{Nitrite}) appears to decrease (Figure 2 of the manuscript). He suggests that there are additional reactions involving both acetone and nitrite and/or that some formation reactions are inhibited at high [2-propanol].

It is possible that the observed behavior of R_{Nitrite} is due to the concentration dependence of the formation processes. However, the experimental data and the associated errors do not allow the authors to determine this. Warneck and Wurzinger (1988) showed that the kinetics of acetone formation can be accounted for better than the formation of nitrite by the known processes of nitrate photolysis. This is probably due to the presence of unaccounted, additional processes that yield nitrite (Mark et al., 1996). Therefore, the initial formation rate of acetone is a better measure of the quantum yield of OH photoproduction, $\phi(\text{OH})$. The size of the error bars on R_{Acetone} at high [2 propanol] makes it difficult to determine the trend of R_{Acetone} in this region; R_{Acetone} may be decreasing in the same manner as nitrite, changing little, or increasing significantly. A more detailed discussion of the initial formation rate of nitrate and acetone at high [2-propanol] will be added to the manuscript.

The second issue raised by the reviewer concerns the relative concentrations of $\text{Fe}(\text{OH})_2^+$ and FeOH^{2+} at pH 2.5. At pH 2.5, the authors believe that the concentration of FeOH^{2+} is much greater than the concentration of $\text{Fe}(\text{OH})_2^+$ based on the following analysis:

The FeOH^{2+} and $\text{Fe}(\text{OH})_2^+$ equilibrium constants are,

$$K_1 = [\text{FeOH}^{2+}] [\text{OH}^-]^2 = 2 \times 10^{-26} \quad (1)$$

$$K_2 = [\text{Fe}(\text{OH})_2^+] [\text{OH}^-] = 4 \times 10^{-17} \quad (2)$$

(Note: $[\text{Fe}(\text{OH})_3]$ is not considered in this analysis because it is a solid)

At pH 2, $[\text{OH}^-] = 10^{-12}$ M, and Equation (1) yields $[\text{FeOH}^{2+}] = 2 \times 10^{-2}$ while Equation (2) yields $[\text{Fe}(\text{OH})_2^+] = 4 \times 10^{-5}$. At pH 3, $[\text{OH}^-] = 10^{-11}$ M, and Equation (1) yields $[\text{FeOH}^{2+}] = 2 \times 10^{-4}$ while Equation (2) yields $[\text{Fe}(\text{OH})_2^+] = 4 \times 10^{-6}$. For both pH values, $[\text{FeOH}^{2+}] \gg [\text{Fe}(\text{OH})_2^+]$. At intermediate pH values, such as pH 2.5, this relationship is true as well. The analysis above will be added to the manuscript.

References

- Mark, G., Korth, H.-G., Schuchmann, H.-P., and von Sonntag, C., 1996. The photochemistry of aqueous nitrate ion revisited, *Journal of Photochemistry and Photobiology A: Chemistry*, 101, 89–103.
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Response to Dr. Cecilia Arsene

We are grateful to Dr. Arsene for her comments. The reviewer requests more details about certain aspects of the manuscript. First, the reviewer asks why the droplet radii 1 μm , 2 μm , and 3 μm are chosen for the simulations. The authors calculate the fraction of benzene-OH reaction that could occur in the interfacial region (within 0.5 nm of the surface) of atmospherically relevant droplets. This fraction should be a function of the droplet size since the interfacial region makes up a smaller percentage of total droplet volume as the droplet radius increases. Therefore, three different radii are selected to examine how droplet size affects the importance of this reaction within the interfacial region. The droplet sizes selected for this study (radius = 1 μm , 2 μm , and 3 μm) are typical for droplets found in the troposphere. If different radii were chosen (e.g., 0.5 μm , 0.7 μm , and 0.9 μm), the authors expect that the same general trend would be observed – that is, the importance of reactions in the surface layer would be reduced in larger droplets and enhanced in smaller ones. The manuscript will be changed to make this point clearer.

Second, the reviewer asks why the authors selected benzene as a model aromatic substrate in order to assess its reaction rate with OH radicals. Benzene undergoes significant surface accumulation. There are different estimates for the possible extent of the surface accumulation of benzene compared to the bulk and in the study an accumulation factor of 75 is assumed, consistent with literature values (Vacha et al., 2006; Vione et al., 2007). Another reason for the choice of benzene is that this compound reacts very selectively with OH, and can be used as a probe of OH photoproduction in surface and atmospheric waters (Anastasio and McGregor, 2001; Takeda et al., 2004).

References

- Anastasio, C. and McGregor, K. G., 2001. Chemistry of fog waters in California's Central Valley: 1. In situ photoformation of hydroxyl radical and singlet molecular oxygen. *Atmospheric Environment* 35, 1079-1089.
- Takeda, K., Takedoi, H., Yamaji, S., Ohta, K. and Sakugawa, H., 2004. Determination of hydroxyl radical photoproduction rates in natural waters. *Analytical Sciences* 20, 153–158.
- Vácha, R., Jungwirth, P., Chenb, J., and Valsaraj, K., 2006. Adsorption of polycyclic aromatic hydrocarbons at the air-water interface: Molecular dynamics simulations and experimental atmospheric observations, *Physical Chemistry Chemical Physics*, 8, 4461–4467.
- Vione, D., Minero, C., Hamraoui, A., and Privat, M., 2007. Modelling photochemical reactions in atmospheric water droplets: An assessment of the importance of surface processes, *Atmospheric Environment*, 41, 3303–3314.

Response to anonymous reviewer #1

The authors thank the reviewer for taking time to comment on our work. The manuscript will benefit greatly from such feedback. The referee correctly states that the experiments do not measure quantum yields at the air-liquid interface. Rather, the experiments determine quantum yields with and without a solvent cage effect in the bulk liquid.

The authors will make this distinction clearer in the paper. The referee also has raised concerns about three assumptions made by the authors:

(1) The reviewer is concerned that loss of OH via recombination may occur outside the solvent cage since 2-propanol is not present in excess over much of its concentration range in the experiments. This would mean that the “solvent-cage free” quantum yields are not accurately estimated using the trapping method. The authors believe that the recombination of OH + NO₂, OH + Fe²⁺, and OH + OH outside the solvent cage at elevated [2-propanol] is unlikely. There is also evidence that some of these processes are unlikely at low [2-propanol] or without it. Detailed calculations for OH + NO₂ by Minero et al. (2007) showed that photogenerated nitrite traps practically all the OH, even in the absence of other scavengers, preventing recombination between OH and NO₂. This fact is valid *a fortiori* in the presence of 2-propanol as an OH scavenger.

2-propanol is the main OH scavenger above 10 μM, prevailing over Fe(II). At the highest adopted 2-propanol concentration (0.1 M), Fe(II) scavenges less than 0.01% of the photogenerated OH. In the case of H₂O₂, the recombination of OH + OH is inhibited by the presence of hydrogen peroxide, and *a fortiori* by 2-propanol in excess. The manuscript will be modified to make these points clearer.

(2) The reviewer asks if there is a reduced solvent-cage effect at the surface of water, which is assumed in the simulations.

Nissenson et al. (2006) found experimental evidence for a reduction in the solvent-cage effect at the air-liquid interface when Mo(CO)₆ in a 1-decene solvent was irradiated in aerosol form and as a bulk-liquid. The quantification of the solvent-cage effect in aqueous solution presents a number of experimental difficulties, which could explain why limited data are available on the topic. Winter and Benjamin (2004) conducted molecular dynamics simulations of ICN in water and found photolysis quantum yields are significantly higher near the surface compared to the bulk. Therefore, the authors believe it is reasonable to assume that the solvent-cage effect is reduced in the surface layer of water. The authors will include this discussion in the manuscript.

(3) In the simulations, the authors assume that the concentration of nitrate and FeOH²⁺ is uniform within the droplet, while the concentration of H₂O₂ is enhanced by a factor of two at the surface compared to the bulk. The reviewer is concerned that the authors are overestimating the surface concentration of nitrate and FeOH²⁺.

While initial calculations on the nitrate ion at infinite dilution (Salvador et al., 2003) suggested it has a propensity for the air-liquid interface, more recent studies at finite concentration (Dang et al., 2006) indicate that the ion tends to remain below the surface.

Molecular dynamics simulations (Thomas et al., 2007) of nitrate ions in a 1 M solution suggest that nitrate is less solvated close to the interface compared to the bulk. For example, on average there are about 8 water oxygen atoms within 4 Å of the nitrate N in the bulk, but only 6 water

oxygens in the case of nitrate near the interface (defined in that study as being within 8 Å of the surface). However, this still may be sufficiently close to the interface that a full solvent shell is not active and enhancement of surface photochemistry could occur.

Due to the uncertainty in the degree of surface segregation of nitrate in water droplets, the authors assume the concentration of nitrate is uniform throughout the droplets in the simulations. If this study overestimates the concentration of nitrate at the surface, the fraction of total benzene-OH reaction within the droplet that occurs at the surface would be reduced.

For FeOH^{2+} the authors note that even in the absence of any data, its surface concentration might be reduced compared to the bulk. However, doubly charged species likely are not completely repelled from the surface, especially in the presence of organic compounds or anions with some affinity for the surface (Sadiki et al., 2003). It is possible that the surface and bulk concentrations of FeOH^{2+} are equal in the presence of benzene and formate.

The concentration of H_2O_2 is enhanced by a factor of two at the air-liquid interface compared to the bulk (Vácha et al., 2004).

The authors will emphasize these caveats in the manuscript.

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Anastasio, C. and McGregor, K. G., 2001. Chemistry of fog waters in California's Central Valley: 1. In situ photoformation of hydroxyl radical and singlet molecular oxygen. *Atmospheric Environment* 35, 1079-1089.

Dang, L. X., Chang, T.-M., Roeselová, M., Garrett, B. C. and Tobias, D. J., 2006. On $\text{NO}_3\text{-H}_2\text{O}$ interactions in aqueous solutions and at interfaces. *Journal of Chemical Physics* 124, 066101-1 – 066101-3.

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Thomas, J. L., Roeselová, M., Dang, L. X. and Tobias, D. J., 2007. Molecular Dynamics Simulations of the Solution-Air Interface of Aqueous Sodium Nitrate. *Journal of Atmospheric Chemistry A* 111, 3091–3098.

Vácha, R., Slavíček, P., Mucha, M., Finlayson-Pitts, B. J. and Jungwirth, P., 2004. Adsorption of atmospherically relevant gases at the air/water interface: Free energy profiles of aqueous solvation of N₂, O₂, O₃, OH, H₂O, HO₂, and H₂O₂. *Journal of Physical Chemistry A* 108, 11573–11579.

Vácha, R., Jungwirth, P., Chenb, J., and Valsaraj, K., 2006. Adsorption of polycyclic aromatic hydrocarbons at the air-water interface: Molecular dynamics simulations and experimental atmospheric observations, *Physical Chemistry Chemical Physics*, 8, 4461–4467.

Vione, D., Minero, C., Hamraoui, A., and Privat, M., 2007. Modelling photochemical reactions in atmospheric water droplets: An assessment of the importance of surface processes, *Atmospheric Environment*, 41, 3303–3314.

Warneck, P., and Wurzinger, C., 1988. Product quantum yields for the 305-nm photodecomposition of NO₃⁻ in aqueous solution, *Journal of Physical Chemistry*, 92, 6278–6283.

Winter, N. and Benjamin, I., 2004. Photodissociation of ICN at the liquid/vapor interface of water, *Journal of Chemical Physics*, 121, 2253–2263.

Response to anonymous reviewer #2

The reviewer's comments are reported in bold style to allow an easier point-by-point reply.

The manuscript reports on quantum yields for OH production during the photodegradation of hydrogen peroxide, nitrate, and Fe(III) in the presence of variable concentrations of 2-propanol as an OH scavenger. The authors state that at high concentrations 2-propanol intercepts OH within the solvent cage, thus reducing recombination of OH with the other primary photofragment (e.g., NO₂) and increasing the effective quantum yield. They further believe that this condition mimics the reduced solvent cage effect that modeling has suggested is present in photoactive species at the air-water interface. Thus they use their bulk solution quantum yields determined at high 2-propanol concentrations to model photochemical production of OH at the interface. I see two main problems with the manuscript. The first (#1 below) is that the logic used to link their bulk solution results to interface photochemistry is not well supported and is very speculative. The second problem (#2 below) is that it appears the bulk solution results have been misinterpreted because of unexpected OH scavengers present in their solutions. In addition, there are three other areas that are problematic with the current manuscript.

The authors thank the reviewer for taking time to comment on our work. The manuscript will benefit greatly from his/her feedback. The authors hope that this response letter successfully addresses all of his/her concerns.

Major Comments:

1. Extrapolating from experimental results to surface conditions

The authors state that quantum yields determined from the bulk solution experiments at high 2-propanol concentrations are the same as values for the chromophores at an air-water interface, but they give no evidence of this. Furthermore, based on the competition kinetics data treatment described below, there is no good evidence that high chromophore concentrations reduce recombination of the intermediate reactive species. If the authors want to provide information about the efficiencies of photochemical processes at the air-water interface, it would be more convincing to perform experiments that examine interface processes, rather than speculate based on bulk solution data.

The referee correctly states that the experiments do not measure quantum yields at the air-liquid interface. Rather, the experiments determine quantum yields with and without a solvent-cage effect in the bulk-liquid. However, the difference between the two values may be the difference between quantum yields in the bulk and at the surface. The authors will make this distinction clearer in the paper.

2. An alternative explanation of the results

The authors implicitly assume that 2-propanol is the only OH sink in their solutions, with the exception of the H₂O₂ experiments, where H₂O₂ is also considered. Thus they attribute the observed increases in OH production with increasing 2-propanol concentration as evidence that 2-propanol is reducing the cage effect. However, there is an alternate, competition kinetics, interpretation of the results: there is a background level of contaminants in each solution that scavenges OH and adding 2-PrOH competes with these scavengers. The authors use this interpretation for the HOOH data but based on my analysis it applies nearly as well for the NO₃⁻ and Fe(III) data. Based on the experiences of my research group there are always OH scavengers in laboratory “purified” water. These can be reduced by treatment of the water (e.g., 254 nm irradiation for 24 hours), but never entirely removed.

In competition kinetics a plot of the inverse of the rate of product formation versus the inverse of the probe (e.g., 2-propanol) concentration yields a straight line. The slope and intercept of this line can be used to determine the first-order rate constant for OH consumption ($k'[\text{OH}]$) in the solution in the absence of 2-propanol (Zhou and Mopper, 1990), thus giving a measure of the background OH scavengers. If one does this for the authors' data, it first becomes apparent that the “background” production of acetone in each experiment (i.e., the rate of acetone formation at the lowest 2-propanol concentration for a given system) needs to be subtracted from each rate obtained at higher 2-propanol levels. After doing this the fits are reasonably good; there is some non-linearity in the Fe data, but the corresponding acetone production rates have large uncertainties.

The resulting experimental values for $k'[\text{OH}]$ (units of s⁻¹) are 6.3E5 (nitrate solutions), 6.0E4 (iron solutions), and 2.6E5 (hydrogen peroxide solutions); I have not calculated uncertainties, but relative standard errors are probably on the order of 20%. Are these reasonable values for $k'[\text{OH}]$? The calculated value for H₂O₂ is 2.7E5 s⁻¹ (i.e., 2.7E7 M⁻¹ s⁻¹ × 0.01 M), which matches the experimentally determined value from the competition kinetics plot. However, this good agreement does not mean that there are not other scavengers of OH in the solution, only that they are significantly smaller than 0.01 M H₂O₂. Indeed, the Fe(III) result of 6.0E4 s⁻¹ likely represents the contribution from other (non-H₂O₂) scavengers present in the lab water; this value is within the probable uncertainty of the $k'[\text{OH}]$ value for H₂O₂ and is consistent with the range of values we see in our laboratory purified water. The nitrate $k'[\text{OH}]$ value is the largest, possibly because of nitrite contamination in addition to the lab water contaminants: approximately 6E-5 M nitrite in the solutions would account for this OH sink, but this would represent a 0.6% mol/mol contaminant level in the nitrate salt, which is high.

The bottom line is that the authors' results for all three chromophores appear to be consistent with competition between OH-scavenging contaminants and 2-propanol for photoproduced OH. In this case there is no need to invoke a mechanism of 2-propanol intercepting primary photofragments before they can recombine. Following the logic of the manuscript, this also suggests there is no significant enhancement in the quantum yields for chromophores at the interface, although this logic is mostly speculative.

The reviewer raises the question whether 2-propanol is the main OH scavenger in all three solutions. This is an important question for interpreting the data. The reviewer hypothesizes that the experimental data reflect the competition between 2-propanol and other scavengers (impurities) in the purified laboratory water.

As noted by the reviewer, the first-order rate constant for OH consumption is $k'[\text{OH}] \approx 6.0\text{E}4 \text{ s}^{-1}$ for the iron solution experiments. In these experiments, OH may react with 2-propanol, Fe^{2+} , or impurities in the purified water. As discussed in the manuscript, the concentration of Fe^{2+} is too small to contribute significantly to OH consumption. For impurities in the purified laboratory water to account for the rest of the OH scavenging, the impurity concentration would have to be similar to that found in lake water (Vione et al., 2006), which is unusually high for purified laboratory water. Using $k'[\text{OH}] = 6.0\text{E}4 \text{ s}^{-1}$ and the literature values for the OH scavenging rate constant of dissolved organic carbon (DOC), the DOC concentration of the purified water would be 2 ppm, 1000 times higher than the result given by the DOC analyzer of the Milli-Q apparatus. Even if the value of 2 ppb DOC is too optimistic for the water used in the experiments, it is unlikely that DOC concentrations are a factor of 1000 greater than this value, especially considering 2 ppm DOC is significantly higher than the DOC concentration in the tap water (0.5 ppm) used as a source of the Milli-Q water (with an Elix purification system as intermediate step). If this were the case, it would imply that the purification system adds scavengers to the water instead of removing them. The same purified water adopted to make the solutions also is used for the background DOC analysis with a Shimadzu TOC 5000 analyzer. Background DOC values are in the range of 0.1-0.2 ppm, also accounting for accidental contamination. Accordingly, $k'[\text{OH}]$ in the laboratory purified water should be in the range of $\sim 1\text{E}3 \text{ s}^{-1}$, not $\sim 1\text{E}4 \text{ s}^{-1}$. This leaves 2-propanol as the major OH scavenger for the iron solution experiments.

The first-order rate constant for OH consumption is $k'[\text{OH}] \approx 6.3\text{E}5 \text{ s}^{-1}$ for the nitrate solution experiments. In these experiments, OH may react with 2-propanol, nitrite, or impurities in the purified water. It is difficult for organic-rich surface water to reach this value of $k'[\text{OH}]$, let alone purified laboratory water. Significant scavenging could be caused by elevated nitrite impurities, and the formation of nitrite from irradiated nitrate is measured to derive Figure 2 in the manuscript. However, it was found that the concentration of $6.3\text{E}-5 \text{ M NO}_2^-$ needed to account for $k'[\text{OH}] = 6.3\text{E}5 \text{ s}^{-1}$ could not be reached even at the longest adopted irradiation times – the initial nitrite concentration is orders of magnitude lower. This leaves 2-propanol as the major OH scavenger for the nitrate solution experiments.

The initial rate of acetone formation (R_{Acetone}) from reaction of OH with 2-propanol, in the presence of other scavengers (impurities), is calculated as a function of [2-propanol]. A constant OH production rate (R_{OH}) is calculated from absorbed photon fluxes and literature quantum yields. Upon application of the steady-state approximation to OH production, the authors derive an expression similar to Equation (12) in the manuscript,

$$R_{\text{Acetone}} = R_{\text{OH}} \cdot \frac{k \cdot [2\text{-propanol}]}{k \cdot [2\text{-propanol}] + k'[\text{DOC}]} \quad (1)$$

where k is the rate constant between OH and 2-propanol, and the value of $k'[\text{DOC}]$ is that proposed by the reviewer. The dotted lines in Figures 1 and 2 (in this document) show the trends in R_{Acetone} with changing $[\text{2-propanol}]$, which are significantly lower than the values in the experimental data. Also note that the above equation predicts that R_{Acetone} increases by a factor of ~ 300 from low ($1 \mu\text{M}$) to high (0.1 M) 2-propanol in the case of nitrate, and increases by a factor of ~ 30 times in the case of Fe(III). The corresponding experimental ratios are significantly smaller, 3.7 and 6.9 respectively.

Therefore, the authors believe that 2-propanol is the major OH scavenger in both the nitrate and Fe(III) systems. If dissolved impurities are the major OH scavengers, as hypothesized by the reviewer, the $k'[\text{OH}]$ values would be much higher than expected from purified laboratory water, the initial formation rate of acetone (R_{Acetone}) would be significantly lower than experimentally observed, and the ratio of R_{Acetone} at high $[\text{2-propanol}]$ compared to R_{Acetone} at low $[\text{2-propanol}]$ would be significantly higher than observed.

The discussion above will be included in Section 3.1 of the manuscript.

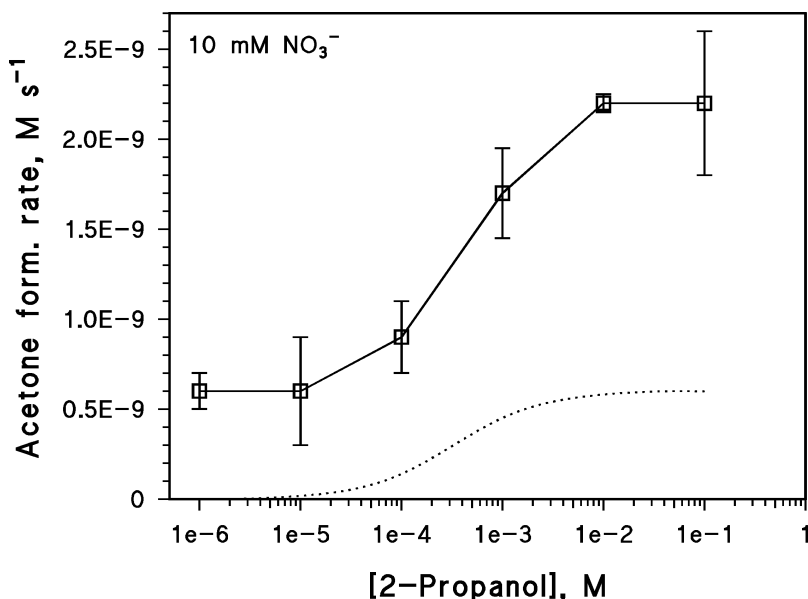


Figure 1: Initial formation rate of acetone as a function of the concentration of 2-propanol, upon UVB irradiation of 0.01 M NaNO_3 . The solid line is experimental observations while the dotted line is determined from Equation (1) of this document.

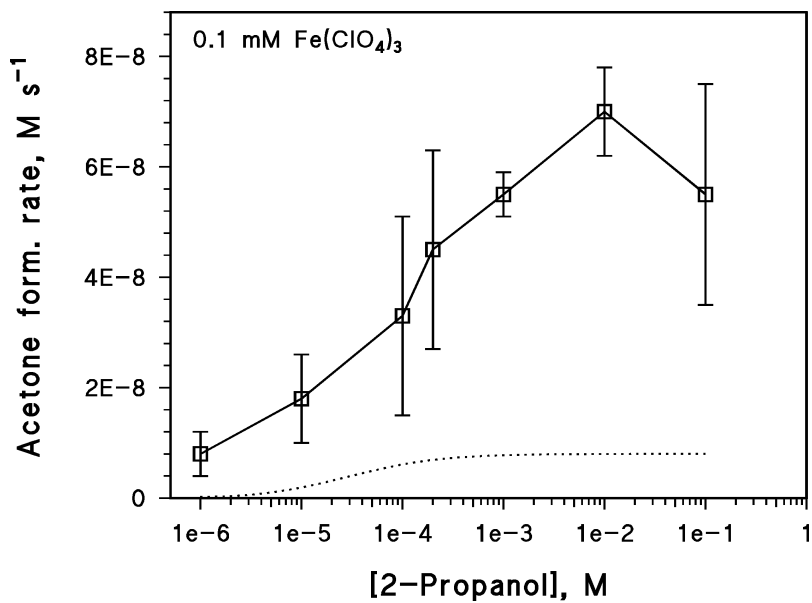


Figure 2: Initial formation rates of acetone as a function of the concentration of 2-propanol, upon irradiation (UVB) of 0.1 mM $\text{Fe}(\text{ClO}_4)_3$. The solid line is experimental observations while the dotted line is determined from Equation (1) of this document.

3. Comparison with other results

(a) One weakness of the current manuscript is that the quantum yield results are not critically compared with the available literature. Because of competition kinetics concerns, most past studies have used relatively high concentrations of scavengers in order to intercept essentially all of the photoformed OH. Thus these results should be directly comparable to the high 2-propanol concentration results in the current manuscript. The authors do a few comparisons for the nitrate and Fe(III) results, but this is rather cursory. A more thorough comparison shows that the nitrate result at high 2-propanol concentrations in the current manuscript (0.034) is a factor of 2-4 times higher than quantum yields determined by previous studies at room temperature at high concentrations of OH scavengers (0.009 - 0.017); (Zepp et al., 1987; Warneck and Wurzinger, 1988; Zellner et al., 1990; Chu and Anastasio, 2003; Goldstein and Rabani, 2007). This discrepancy suggests something is wrong with the value in the current manuscript.

The reviewer notes that the absolute values of the quantum yields observed in this study differ from previous studies at high [2-propanol]. However, some of the studies cited by the reviewer show similar trends in quantum yields with changing [2-propanol] or are not directly comparable to the current study.

Regarding nitrate, many of the studies cited above determine quantum yields using experimental conditions that are different than the authors' experiments. The most comparable study to the present work is that of Warneck and Wurzinger (1988). In that study, Warneck and Wurzinger determine the quantum yield of OH production from nitrate photolysis at varying concentrations of [2-propanol]. They find $\phi(\text{OH}) \approx 0.01$ at [2-propanol] = 0.0013 M (the lowest concentration examined), and observed a ~50% increase in $\phi(\text{OH})$ between the lowest and highest 2-propanol concentrations (0.0013 M to 0.13 M). They state that a decreased solvent-cage effect is a possible explanation of the phenomenon. Over the same concentration range, the authors find that $\phi(\text{OH})$ increases by a similar percentage, ~30%.

Mark et al. (1996) irradiated nitrate solutions at 254 nm in the presence of 2-propanol, varying the concentration of the alcohol over many orders of magnitude. They also find a considerable change in the formation rate of nitrite, which they attribute to a changing solvent-cage effect.

There is disagreement between the absolute value of the quantum yields found by Warneck and Wurzinger (1988) upon irradiation at 305 nm and the values reported in the current study. For example, the authors find that $\phi(\text{OH})$ approaches 0.01 at [2-propanol] $\leq 1\text{E-}5$ M. The error bars in the measurements in Warneck and Wurzinger (1988) and in the current study are too small to account for the differences in $\phi(\text{OH})$. Other possible explanations are: (1) A different operational temperature (30 vs. 22 °C), where the higher temperature adopted by this study might have an impact over the ability of 2-propanol to insert itself into the cage of the water molecules. Zellner et al. (1990) demonstrate the temperature dependence of quantum yields of nitrate, nitrite and hydrogen peroxide photolysis.; (2) Polychromatic versus monochromatic irradiation. The authors irradiate nitrate at longer wavelengths. Although the effect of polychromatic irradiation is accounted for in calculating the quantum yields, there might still be some difference because the

lamp used in the current study has an emission maximum at 313 nm. This may affect the calculated photolysis quantum yield if it is not constant with wavelength. However, the authors do not believe that the effect of (2) is sufficient to explain completely the difference in $\phi(\text{OH})$.

As shown in Warneck and Wurzinger (1988) and Mark et al. (1996), quantum yields vary with changing [2-propanol]. For assessing the relative importance of the reaction rates of OH with benzene at the surface compared to the bulk, the ratio of $\phi(\text{OH})$ is more important than the absolute value of $\phi(\text{OH})$. The authors calculate that 20% of the OH-benzene reaction would occur in the surface region for nitrate-water aerosols. That percentage would not change significantly if the adopted quantum yields in the calculations are multiplied by a constant value.

Other studies cited by the reviewer are less applicable to the present study than Warneck and Wurzinger (1988). For example, Goldstein and Rabani (2007) use 2-propanol as their scavenger but only examine the wavelength region 200–270 nm. The value of $\phi(\text{OH})$ determined in that study has limited applicability to the current study since the quantum yield is a strong function of wavelength. In addition, Goldstein and Rabani (2007) only investigated [2-propanol] = 0.02 M. Zepp et al. (1987) and Zellner et al. (1990) used different scavengers and found $\phi(\text{OH}) \sim 0.015\text{--}0.017$, which is a factor of 1.5–2 greater than the values reported in Warneck and Wurzinger (1988).

Regarding Fe(III), Benkelberg and Warneck (1995) examine OH production from Fe(III) photolysis at [2-propanol] = $2\text{E-}3$ M. They find $\phi(\text{OH}) \approx 0.18$ at 313 nm and $\phi(\text{OH}) \approx 0.08$ at 365 nm. The authors find similar values at [2-propanol] = $1\text{E-}5$ M, $\phi(\text{OH}) \approx 0.18$ at 313 nm and $\phi(\text{OH}) \approx 0.04$ at 365 nm. As with nitrate, different operational temperatures between Benkelberg and Warneck (1995) and the current study may play a role in 2-propanol's ability to react with OH in the solvent-cage. Also note that the authors in the present study adopted concentration values of 2-propanol up to 0.1 M, that is 50 times higher than Benkelberg and Warneck (1995).

This detailed comparison of the authors' results to results from previous studies will be included in the manuscript.

(b) What is the calculated quantum yield for OH formation from H_2O_2 photolysis? This is never stated, but it would be useful to compare this result with those from recent studies.

The quantum yield of OH formation from H_2O_2 photolysis is ≈ 1 (that is, approximately one OH molecule is produced for each H_2O_2 molecule that absorbs a photon). This value is consistent with Zellner et al. (1990) who found $\phi(\text{OH}) \approx 0.96\text{--}0.98$ over 308–351 nm.

The initial rate of acetone formation (R_{Acetone}) upon irradiation of the H_2O_2 solution increases with [2-propanol]. This trend likely is not related to a solvent-cage effect because hydrogen peroxide competes with 2-propanol in scavenging OH. At low [2-propanol], OH is scavenged primarily by H_2O_2 . As [2-propanol] increases, the alcohol becomes the main OH scavenger and the initial formation rate of acetone increases. The competition for OH between H_2O_2 and 2-propanol is accounted for in Equation (12) in the manuscript, which reproduces the experimental data well. Therefore, the trend of R_{Acetone} as a function of [2-propanol] may be explained by

assuming H_2O_2 and 2-propanol compete for OH without the need to assume that the photolysis quantum yield of OH production from H_2O_2 photolysis changes. The fact that the quantum yield does not vary significantly with 2-propanol means either (1) the geminate recombination of OH in the solvent cage is negligible or (2) the adopted experimental system is not suitable to examine the phenomenon.

All three systems examined in this study (nitrate, Fe(III), and H_2O_2) contain species that compete with 2-propanol for OH scavenging. For the nitrate and Fe(III) systems, the concentration of contaminants present in the purified laboratory water is too low to explain the experimental results. However, H_2O_2 is present in sufficiently high concentrations to explain the experimental results for the H_2O_2 system.

The discussion above will be included in the manuscript.

4. Experimental Methods

(a) Lack of blanks. There are two types of controls that need to be run to for each set of experimental conditions: (i) illumination of blank solutions containing 2-propanol (especially at the highest concentrations of propanol employed) and all other solution components (e.g., pH adjustment) but not chromophore, and (ii) dark blanks containing the illumination solution kept in the dark during the course of an experiment. The rates of acetone production in these blanks should be subtracted from the rate of production in the corresponding illumination solution.

(b) Measurements of photon flux. The authors use a power meter to determine photon fluxes, but this is not accurate enough for quantum yield determinations because it only measures the irradiance incident upon the sample and not the average flux experienced by the solution. These two quantities will be different because of internal reflection within the cells. Using a chemical actinometer under low-absorbing (i.e., dilute) conditions is much more accurate.

(c) Temperature. The authors do not report whether temperatures in their cell were controlled or measured. This is important information since the quantum yields are temperature dependent.

The reviewer is concerned that important measurements were not conducted during the experiments. In fact, the authors did conduct these measurements but did not report the results of the measurements in the original manuscript. The revised manuscript will include this information.

Blank experiments were conducted by the authors under both illuminated and dark conditions and the formation of acetone was observed. In the illuminated blank experiments, the authors find that the formation of acetone is negligible upon irradiation of 2-propanol alone. Similarly, in the dark blank experiments, negligible acetone is detected for the 2-propanol/nitrate, 2-propanol/Fe(III), and 2-propanol/ H_2O_2 solutions.

The authors measure both the photon flux from the lamp (with a power meter) and the average flux experienced by the solution (using a ferrioxalate actinometer). The power meter is used to observe the variability of the photon flux from the lamp between experiments, which is ~10%.

The reviewer is correct that quantum yields are temperature dependent. For example, Zellner et al. (1990) demonstrate the temperature dependence of OH production quantum yields from nitrate and H₂O₂ photolysis. For the experiments in the current study, the temperature of the irradiated solutions is kept at approximately 30°C.

5. Atmospheric significance

Even if there turns out to be significant enhancement of OH photoproduction at interfaces relative to the bulk, there need to be more convincing arguments that this effect matters. For example:

(a) The authors compare the relative importance of surface OH with that produced in the bulk volume and find it is minor but significant for OH-oxidation of benzene. But they do not compare the rate of formation of surface OH with the mass transport of OH from the gas phase to the surface. I have not performed the calculation, but for typical gas-phase OH concentrations, it seems very likely that the mass transport mechanism is much, much faster than OH formation from chromophores at the interface. If true, this would indicate the interface production is relatively insignificant.

The hydroxyl radicals that react with benzene within the surface layer of aerosols come from either mass transfer from the gas-phase or photolysis of nitrate, Fe(III), or H₂O₂. The reviewer raises the question whether mass transfer of OH from the gas-phase into aerosols would be the dominant source of hydroxyl radicals in the atmosphere.

The rate of mass transfer from the gas-phase to the aqueous phase is given by Schwartz (1986),

$$\frac{d[\text{OH}_{(\text{aq})}]}{dt} = k_{\text{mt}} \left([\text{OH}_{(\text{g})}] - \frac{[\text{OH}_{(\text{surf})}]}{\text{HRT}} \right) \quad (2)$$

where [OH_(surf)] is the concentration of OH in the surface layer, [OH_(g)] is the concentration of OH in the gas-phase, H is the Henry's law constant of OH, R is the universal gas constant, and T is temperature. The first order mass transfer coefficient (k_{mt}) is,

$$k_{\text{mt}} = \left(\frac{4a}{3v\alpha} + \frac{a^2}{3D_{\text{g}}} \right)^{-1} \quad (3)$$

where a is the droplet radius, v is the mean molecular velocity, α is the mass accommodation coefficient, and D_{g} is the gas-phase diffusion constant. For an aerosol of radius $a = 1\text{E-}6$ m surrounded by air at 298 K, $D_{\text{g}} \approx 2.5\text{E-}5$ m² s⁻¹ (Liu et al., 2009) and v is $(3RT/M)^{1/2} = 661$ m s⁻¹, where M is the molecular weight of OH. Hanson et al. (1992) report a lower limit for the mass accommodation coefficient of OH, $\alpha > 3.5\text{E-}3$.

In the extreme case where the aqueous phase concentration is zero and the mass accommodation coefficient is at its highest value ($\alpha = 1$), k_{mt} is $6.5E7 \text{ s}^{-1}$. During the day, the peak value of $[\text{OH}_{(g)}]$ is $\sim 1E7 \text{ molecules cm}^{-3}$ (Finlayson-Pitts and Pitts, 2000). Therefore, the maximum uptake rate of OH into the aerosol is $\sim 6.5E14 \text{ molecules cm}^{-3} \text{ s}^{-1}$, or $\sim 1.1E-5 \text{ M s}^{-1}$. However, this is the upper limit of OH uptake into the aerosol. If $\alpha = 3.5E-3$ and the OH concentration is lower ($\sim 1E6 \text{ molecules cm}^{-3}$), the rate of OH uptake would be reduced to $2.8E-9 \text{ M s}^{-1}$.

As shown in Figure 5 of the manuscript, the photolysis rate constant for nitrate at the surface under actinic irradiation is $\sim 3E-6 \text{ s}^{-1}$. For a typical concentration of nitrate, $1E-4 \text{ M}$ (Warneck, 1999), the rate of OH production via nitrate photolysis is $3E-10 \text{ M s}^{-1}$ at the surface. For Fe(III), the photolysis rate constant at the surface is $1.4E-2 \text{ s}^{-1}$ (not reported in the manuscript). In the surface layer of an aerosol with a typical concentration of Fe(III), $1E-6 \text{ M}$ (Warneck, 1999), the rate of OH production via FeOH^{2+} photolysis is $1.4E-8 \text{ M s}^{-1}$. For H_2O_2 , the photolysis rate constant at the surface is $9.3E-8 \text{ s}^{-1}$. Using similar analysis for an aerosol with a typical H_2O_2 concentration of $2E-5 \text{ M}$ (Warneck, 1999), the rate of OH production via H_2O_2 photolysis is $1.9E-12 \text{ M s}^{-1}$.

Therefore, the rate of OH production via photolysis in the surface layer for the nitrate/water and Fe(III)/water droplets may be comparable with the mass transfer of OH from the gas-phase under atmospheric conditions. It appears that OH production via photolysis in the surface layer of H_2O_2 /water aerosols may be significantly less than the mass transfer of OH from the gas-phase. However, the analysis above assumes that the aqueous concentration of OH is zero, which certainly is not the case in the atmosphere. A non-zero concentration of OH in the aqueous solution would lower the rate of OH mass transfer from the gas-phase to the aqueous phase.

The discussion above will be included as a new section in the manuscript, "Section 3.4 Atmospheric Implications."

(b) If OH photochemically produced at the air-water interface is not constrained by a solvent cage, it would seem that a significant fraction would escape into the gas phase rather than go into the aqueous particle. This would decrease the effectiveness of the interface chromophores as sources of condensed-phase OH. In addition, while I have not done the calculations, it seems unlikely that this would be a significant source of gas-phase OH.

The reviewer is correct that some fraction of the photochemically produced OH at the air-water interface would escape to the gas-phase. This would reduce the effectiveness of nitrate, Fe(III), and H_2O_2 as sources of condensed-phase OH. A caveat will be added to the paper.

The authors agree that the dominant source of gaseous OH is due to ozone photolysis, not from aqueous aerosols. However, as shown in the response to comment 5a, photochemically produced OH within the surface layer may contribute significantly to the condensed-phase OH available for reaction with benzene.

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