**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "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. Nissenson et al.

Anonymous Referee #2

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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.

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.

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 propanol concentration as evidence that 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'OH) in the solution in the absence of 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'OH (units of 1/s) 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'OH? The calculated value for H2O2 is 2.7E5 1/s (i.e., 2.7E7 1/M 1/s * 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 result of 6.0E4 1/s likely represents the contribution from other (non-H2O2) scavengers present in the lab water; this value is within the probable uncertainty of the k'OH value for H2O2 and is consistent with the range of values we see in our laboratory purified water. The nitrate k'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.

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.

(b) What is the calculated quantum yield for OH formation from H2O2 photolysis? This is never stated, but it would be useful to compare this result with those from recent studies.

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.

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.

(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.

Recommendation

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I am sorry to say that I do not recommend publication. It is also not clear to me that the current data are novel enough that they would justify publication in ACP even after the necessary control experiments were performed. At that point the authors would have essentially simply repeated previously published experiments to determine OH quantum yields from H2O2, NO3- and Fe(III). It seems possible that the modeling component - with some assumptions about OH quantum yields at the interface - could be made into a short manuscript, but there are so many assumptions inherent in that exercise that it is all very speculative. The best outcome would be new experiments that examined photochemistry of these chromophores at the air-water interface, but of course this would entail a significant amount of new work.

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