

## Summary

This manuscript focuses on an important photosensitized process that can potentially occur at the air-ocean surface and at the surfaces of sea-salt aerosols. The authors investigated excitation and quenching dynamics of the first excited triplet state of benzophenone (BP) in the presence of halogen ions. They reported new measurements of the quenching rate constants for halide ions. Their measurements suggest that free dihalogens such as BrCl can be produced by electron transfer from Br<sup>-</sup> to <sup>3</sup>BP, which is followed by well established chemistry of Br atoms in Cl-containing aqueous solutions. The conclusions would have been stronger if it were possible to more quantitatively model the evolution of the gas phase species (BrCl) from irradiated solutions of BP/Br<sup>-</sup>/Cl<sup>-</sup>. But even without this kinetic modeling, the manuscript is interesting. I support the publication of this article once these corrections have been made.

In general the writing is well structured, but some sentences are not (see suggestions below). There are a number of typos in the text; the authors should have taken some pity on the reviewers and checked their manuscript more carefully before submitting it. I spent quite a bit of time identifying these typos and listing them below. Fixing them will greatly improve the clarity and readability of the manuscript.

Please see the attached supplement for the detailed comments.

## Significant comments

P7686. Eq. (2) is incorrect. The “log” should be “ln” in such an equation to emphasize that it is a natural logarithm, not base-10 one. In addition, one should take ln of absorbance, not of I<sub>0</sub>/I as illustrated below (subscript “e” implies that base-e absorbance and extinction coefficients are used):

$$A_e = \ln\left(\frac{I_0}{I}\right) = \varepsilon_e l [\text{}^3\text{BP}]_0 e^{-k_1 t}$$
$$\ln(A_e) = \text{const} - k_1 t$$

I think this is a typo because authors do it correctly in Fig. 1.

P 7686, 23. It is not clear to me why such acidic conditions (pH=1) were used. The authors should justify their somewhat unexpected choice of pH in this experiment. Some HCl may be weakly evolving from the solution at such low pH, and potentially contributing to the Cl<sup>-</sup> signal captured by the NaOH scrubbing solution.

P7687. I would include the BP ground state spectrum and the previously reported <sup>3</sup>BP spectrum in Figure 2. This will make it clear that it is the <sup>3</sup>BP transient that is detected.

P7688, Eq. (3). It is not clear why the constant term is called “cte” instead of “const”. This equation uses k<sub>q</sub>, whereas Eq.(1) uses k<sub>2</sub>. The use of k<sub>q</sub> throughout the paper is preferred.

P7688. Hurley used benzophenone carboxylate. The authors should comment on whether this would affect the values. pH was different in their experiment as well.

P7688, 18, “rate diffusion constant” should be “diffusion-limited rate constant”

P7689. The formulae for the radical complexes do not add much to the explanation. Consider using a reaction diagram here.

P7692. Was short (6 s ) irradiation time chosen in order to prevent X2 photolysis?

P7692, bottom paragraph, and Figure 6. Does X<sup>-</sup> refer to the sum of Cl<sup>-</sup> and Br<sup>-</sup> concentrations? I would prefer to see the individual results for Cl<sup>-</sup> and Br<sup>-</sup>.

P7693, 7. Does the concentration of BP decrease without irradiation as well? If volatility is the issue, 6s of irradiation should have nothing to do with the observed BP reduction.

Table 1 caption needs a comment on the effects of pH since without this it is difficult to compare the measured rate constants. Is it possibly to reorganize this table so that the pH effect is more apparent (e.g., separate columns for slightly acidic / slightly basic measurements).

Figure 4. Was there a time-shift applied to one or both of the signals for clarity (the signal does not go up at t = 0)? Explain what the top and bottom axis refer to.

All figures: font size used in axis labels, tick labels, etc. is too small.

### **Minor typos & suggestions**

P7682, 8-9, consider “... quenches the triplet state; the resulting product has a transient ...”

P7682, 15, remove “This complexity ... fact that”; it is unnecessary

P7682, 16, remove “various and quite complex”

P7682, 18, replace “showing the presence of” with “including”

P7683, 3, replace “in this latter study” with “previously”

P7683, 6, “salty” -> “sea”

P7683, 9, remove “being the least abundant” (or, at least, correct misspelling of “abundant”)

P7683, 10, remove “the”

P7683, 13, remove “basically”

P7683, 16, replace “Independently ...” with “Regardless of their sources, once formed the halogen atoms ...”

P7683, 18, remove “Clearly,”

P7683, 19, suggest “now well recognized”

P7683, 29, suggest “the validity of such a complex proxy is questionable since chlorophyll is highly unstable in salt solutions.”

P7684, 4, remove comma

P7684, 5, “ketone” should be “ketones”

P7684, 8 suggest “singlet oxygen .... and ketyl radical, which ...”

P7684, 16 This is especially relevant for the fate...

P7684, 18 remove “do”

P7685, 7 remove “ensuring a clean liquid flow”

P7685, 12, “analyzing light” -> “light source”  
P7685, 27, add “the” before “triplet” and “presence”  
P7686, 3, suggest “from the slope of a logarithmic plot of the transient signals.”  
P7686, 4, remove “In”  
P7686, 11, remove “obtained from”  
P7687, 21, remove “do”  
P7688, 1, use “decreases substantially” rather than “is disappeared”  
P7688, 11, “reasonable” -> “reasonably”  
P7688, 13, remove “slight”  
P7688, 17, “close to” should be “close to the”  
P7688, 19, “oceanic”, not “oceanographic”  
P7688, 19, small, not smaller  
***P7688, and elsewhere, watch verb tenses, i.e., past interchanged with present***  
P7688, 27, “seek for” -> “investigated the possibility of”  
P7689, 6, vague ... specify which of the two mechanisms you are talking about  
P7689, 14, coulombic is misspelled  
P7689, 17, “the” unnecessary  
P7689, 18, replace “i.e.,” with “as”  
P7690, 2, remove repeated “in”  
P7690, 11, “on the other side” -> “in addition”  
P7690, 11, remove “media”  
P7690, 15, it was not stated explicitly that benzophenone was present in iodine-acetonitrile solution; please clarify this.  
P7690, 17, which wavelength? Two values were specified in the previous sentence. Was the absorption measured at 725 nm?  
P7690, 25, “is” -> “are”  
P7691, 2, “not clear what “with a corresponding to” refers to; needs to be corrected  
P7691, 4, “at short wavelengths”  
P7691, 5, “life time” -> “lifetime”  
P7691, 6, “may correspond” (remove “s”)  
P7691, 15, replace “may” with “will”  
P7692, 6, replace “may be via the sequence below” with “may occur via”  
P7692, 10, the “present” what? A word is missing here.  
P7692, 13, replace “(X being another halide)” with “(X,Y are halogen atoms)”  
P7693, 1, “observed” or “explained”? If this is an explanation, it needs some citations to go along.  
P7693, 11, “may” is used frequently, suggest “can” for more emphatic conclusion (where justified)  
P7693, 17, “somehow” -> “somewhat”  
P7693, 27 “participate” -> “cause”  
Table 1 caption, “study” -> “studies”  
Table 1 caption, remove “Table curve program”  
Figure 1 caption, “in presence of” -> “containing”  
Figure 1 caption, use “32 laser pulses averaged per data point”  
Figure 2 caption, “at the end of pulse” is uncertain. I would be more specific here.  
Figure 2 caption, should be “... concentration was 0.1 mM; laser energy was 25 mJ/pulse.”

Figure 3 caption, “Error bars are calculated as three times the standard deviation”  
Figure 4 caption, Use “after irradiating with 355 nm laser pulse”.