Photooxidation of Halides by Chlorophyll at the Air−Salt Water Interface

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Glancing angle laser-induced fluorescence was used to follow the kinetics of chlorophyll loss at the air−salt water interface under the influence of visible radiation. Aqueous solutions of NaCl, NaBr, NaI, KNO_3, and $NaNO_2$ in a range of concentrations up to ~1 M were used as substrates. The first-order reaction rate depends linearly on salt concentration for the halide salts but does not vary with concentration for nitrate or nitrite salts. At the same salt concentration, the chlorophyll loss rate is greatest for the bromide-containing solutions, followed by those containing chloride and then iodide. The results are consistent with a mechanism in which photoproduced chlorophyll cations are reduced by halide anions and subsequently react with the halogen atoms thus produced. This mechanism gives a novel route for gas-phase halogenated species, and possibly nitrogen oxides, to be released to the marine boundary layer.

Introduction

The transfer of species between the marine boundary layer (MBL) and the ocean surface is of interest because the ocean acts as both a source and a sink for many atmospheric species.[1,2] The sea surface microlayer (SML) is an organic-enriched layer present at the air−sea interface and has been shown to have different physical and chemical properties than that of subsurface waters.[3] Because species transferred between the air and ocean must pass through the SML, the properties of this layer are important in understanding these transfer processes. The SML has been shown to contain an abundance of organic compounds which are enriched with respect to their subsurface concentrations;[4−8] for example, there is up to twice the concentration of chlorophyll-*a* in the SML as that in bulk seawater.[3,9] Recent experimental work has shown that the presence of surfactants such as those found in the SML can have a significant effect on gaseous uptake and reactions taking place at aqueous interfaces.[10−13] For example, the presence of a monolayer of sodium dodecyl sulfate suppresses the uptake coefficient of N_2O_5 onto NaCl aerosols by an order of magnitude.[14] The uptake of anthracene and pyrene from the gas phase to the air−aqueous interface is enhanced by a factor of 3 when the aqueous surface is coated by an octanol monolayer.[12] As well as serving as the initial surface encountered by gas-phase reagents, the SML is the part of the ocean most readily available to solar radiation. Given the abundance of organic matter in the SML, the concentration of photoactive organic species is likely greater there relative to bulk waters, and therefore, photochemistry occurring in the SML could be significant. Recent studies have indicated that photoactive organic compounds likely to be present at the SML could be a source for halogen species to the atmosphere due to photooxidation of aqueous halides.[15,16]

Photoactive halogen compounds are emitted from the ocean surface and may photodissociate to form reactive halogen atoms. Currently, the known sources for the release of gas-phase molecular iodine from the ocean surface are via the photolysis of iodine-containing organic molecules,[17,18] the oxidation of iodide by ozone,[17,18] and the oxidation of phytoplankton by ozone.[19] The main contribution to chlorophyll and other organic matter at the ocean surface is from phytoplankton.[2,7] Chlorophyll-*a* concentrations at the ocean surface have been thoroughly determined via satellite measurements because they are necessary for evaluating phytoplankton blooms.[20] The release of gas-phase bromine and chlorine species is believed to occur due to chemistry associated with sea salt aerosols,[1] with evidence of chloride[21] and bromide[22] activation at the air−aqueous interface by gas-phase oxidants. After its entry into the MBL, gas-phase iodine may remove NO_x species and ozone via reaction and also give rise to particle formation.[17,19] The lighter halogens enter into catalytic ozone removal cycles, affecting the oxidizing strength of the local environment.

We have recently investigated the reaction of chlorophyll with ozone at the salt water surface under both dark[23] and illuminated conditions.[15] The rate of the chlorophyll loss reaction is enhanced, and the reaction shows a change in the kinetic mechanism in the presence of actinic radiation. We proposed that this observation was due to the reaction of chlorophyll with reactive chlorine atoms (reaction 4), formed via the following mechanism:

$$\mathrm{Chl} + h\nu \leftrightarrows \mathrm{Chl}^* \rightarrow \mathrm{Chl}^+ + e^- \tag{1}$$

$$\mathrm{Chl}^+ + \mathrm{Cl}^- \rightarrow \mathrm{Chl} + \mathrm{Cl} \tag{2}$$

$$\mathrm{Cl} + \mathrm{Cl}^- \leftrightarrows \mathrm{Cl_2}^- \tag{3}$$

$$\mathrm{Chl} + \mathrm{Cl} \rightarrow \mathrm{Products} \tag{4}$$

$$\mathrm{Chl}^* + \mathrm{O_3} \rightarrow \mathrm{Chl}^+ + \mathrm{O_3}^- \tag{5a}$$

$$e^- + \mathrm{O_3} \rightarrow \mathrm{O_3}^- \tag{5b}$$

$$\mathrm{O_3}^- + \mathrm{H_2O} \rightarrow \mathrm{OH} + \mathrm{OH}^- + \mathrm{O_2} \tag{6}$$

$$\mathrm{OH} + \mathrm{Cl}^- \rightarrow \mathrm{OH}^- + \mathrm{Cl} \tag{7}$$

where Chl represents chlorophyll. This mechanism was confirmed by transient absorption measurements of electrons (reaction 1) in

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the absence of salt and of Cl_2^- (reaction 3) in the presence of chloride anions.[15] The molecular chlorine anion can only be formed by the addition of atomic chlorine to a chlorine anion (reaction 3), thus providing strong evidence for the production of chlorine atoms.

The purpose of the present work was to further explore this mechanism by investigating the kinetics of chlorophyll loss at the surface of various salt solutions in the presence of light but without the influence of ozone. Experiments were performed using several concentrations (up to ~1M) of NaCl, NaBr, NaI, KNO_3, and $NaNO_2$ in order to determine the influence of the nature of the anion and its concentration on the chlorophyll loss kinetics.

Experimental Section

The experimental method used is similar to that described in previous publications by our group.[15,23] Approximately 100 mL of pH-adjusted (pH ~ 8.3, pH of the ocean[24]) salt solution was placed in a 250 mL Pyrex three-necked round-bottom flask equipped with quartz side windows, and approximately three drops of chlorophyll extract were gently added to the aqueous surface using a Pasteur pipet. The solution was allowed to sit for at least 15 min to let the extract spread as evenly as possible over the aqueous substrate. In order to study photoreactions, a 20 W halogen desk lamp, whose output resembles that of a blackbody at ~3000 K,[25] was situated at about 10 cm from the flask, and its output was directed through the round-bottom flask onto the surface of the solution. The chlorophyll concentration at the water surface was monitored by the fluorescence intensity at 676 nm excited by the 355 nm output of a frequency-tripled Nd:YAG laser operating at 10 Hz with 1.6 mJ/pulse. The laser output entered the flask through a quartz side window and impinged upon the surface at an angle of >75° to the surface normal. The laser light excited the chlorophyll at the interface, and the resulting fluorescence was collected by a liquid light guide mounted approximately 0.5 cm above the water surface. The light was filtered through an optical long-pass filter (allowing $\lambda \geq 560$ nm), then passed through a 1/8 m monochromator set to 676 nm (maximum fluorescence for chlorophyll-*a*), and detected by a red-enhanced photomultiplier tube. The signal was averaged over 4−16 laser shots in a digital oscilloscope and then collected from the oscilloscope using a custom-made Labview program and saved for further analysis.

Chlorophyll was extracted using the following method: approximately 100 mL of loosely packed and destemmed spinach leaves was placed in a beaker, and the leaves were ground to a pulp either using a hand blender or a mortar and pestle. Spectrograde (>99.5%) acetone from Caledon, approximately 1 mL at a time, was slowly added to the pulp, and the mixture was thoroughly blended. This was repeated until a smooth consistency was achieved. The mixture was then filtered by gravity to remove any residue, and about 5 mL of deep emerald green filtrate, which fluoresced in the red when exposed to visible light, was collected and stored in amber glass vials for use in experiments.

All salt solutions used were made up using 18 MΩ deionized water. Sodium nitrite (≥99.0%) was purchased from Sigma−Aldrich, and all other salts (≥99.0%) used were from ACP; these include NaCl, NaBr, NaI, KNO_3, and $NaNO_2$. Just before use, a 100 mL sample of the desired concentration of salt solution was adjusted to a pH between 8.3 and 8.6 using 2.5×10^{-3} M sodium hydroxide or 1×10^{-4} M hydrochloric acid. Nitrate and nitrite solutions were not used until they had sat for several hours in order to reach room temperature after dissolution.

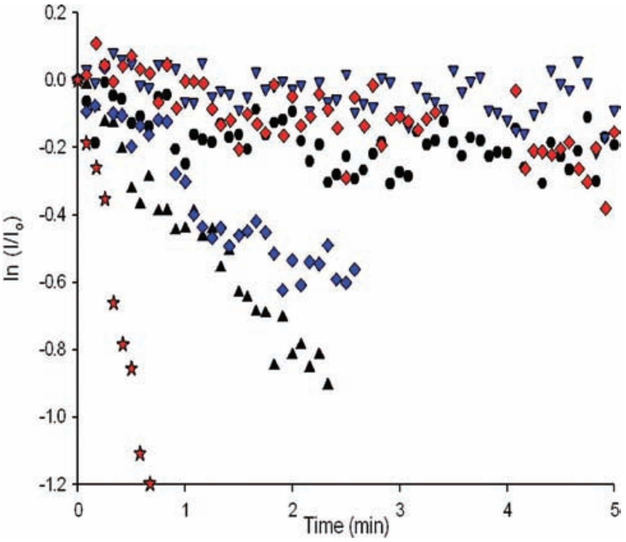

Figure 1. The loss of chlorophyll over time at various aqueous interfaces, in the dark, on pure water (black inverted triangles), pure water with pH adjusted to ~8 (blue circles) and salt water (red diamonds) solutions, on illuminated pure water (black triangles), illuminated pure water with pH adjusted to ~8 (blue diamonds), and illuminated salt water (red stars).

Results

Under illumination, the loss of chlorophyll at the surface on all substrates was significantly faster than that observed in the dark. In the dark, no dependence of the loss rate on the nature of the salts present was observed. However, the loss rate on illuminated salt water is greater than that on illuminated pure water. Under illumination from the halogen desk lamp, the loss rates increased by an order of magnitude for pure water and by a factor of 50 for the 1 M NaCl solution over that measured in the dark. Examples of the increased loss rate of chlorophyll in the presence of salts are shown in Figure 1; the slopes correspond to the observed rate of chlorophyll loss, k_{obs}. In this figure, the rate of chlorophyll decay in the dark on salt solutions, pure water, and pure water adjusted to a pH of 8 is the same ($k_{obs} \sim 0.04 \pm 0.02$ min^{-1}); this is shown by red diamonds, black circles, and blue inverted triangles, respectively. Under illumination, the decay of chlorophyll on pure water is enhanced for both pure and pH-adjusted (to pH ~ 8) water ($k_{obs} \sim 0.5 \pm 0.2$ min^{-1}), shown as black triangles and blue diamonds, respectively. The kinetics of chlorophyll loss on the 1 M NaCl solution also shows a large enhancement under illumination ($k_{obs} \sim 2.2 \pm 0.4$ min^{-1}); this result is displayed as stars.

These experiments were repeated for 1 M solutions of NaBr and NaI as well. Typical results of the loss of chlorophyll with respect to time on these various salt substrates are shown in Figure 2. The fastest loss rate of chlorophyll occurred on NaBr solutions, represented by blue squares in the figure, followed by loss of chlorophyll on NaCl solutions, shown as red stars. The slowest loss of chlorophyll at the air−aqueous interface was seen on NaI solutions, displayed as green diamonds.

The magnitude of the chlorophyll loss rate depends on both the concentration and the identity of the halide salt. The linear dependence of the loss rates on the concentrations of the various salts can be seen in Figure 3, where the results using NaBr, NaCl, and NaI are shown as blue squares, red stars, and green diamonds, respectively. The slopes for the chlorophyll photodegradation rate versus concentration on

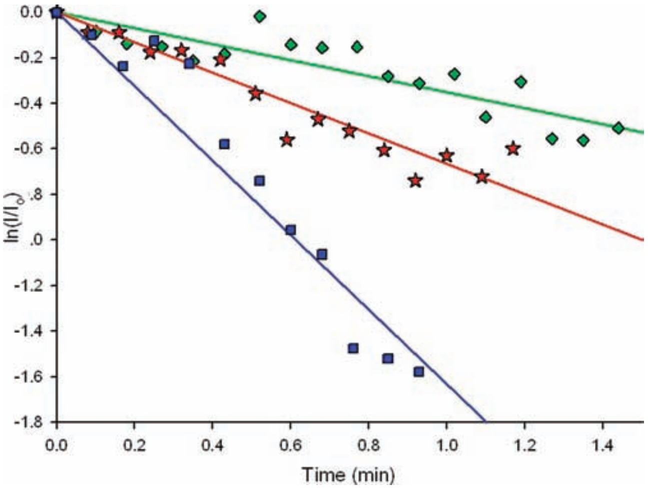

Figure 2. Examples of the pseudo-first-order loss kinetics of chlorophyll at the illuminated surface of 1 M solutions of NaI (green diamonds), NaCl (red stars), and NaBr (blue squares) with corresponding linear fits.

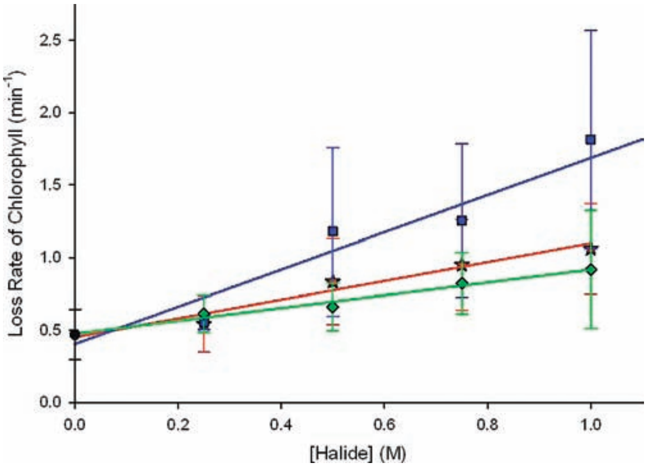

Figure 3. The dependence of chlorophyll loss on halide concentration for NaBr (blue squares), NaCl (red stars), and NaI (green diamonds). The corresponding lines are linear fits, with the errors bars showing the 1σ uncertainty levels based on the average of 5−10 separate experiments.

various NaBr, NaCl, and NaI solutions were 1.3 ± 0.4, 0.7 ± 0.3, and 0.4 ± 0.2 $\text{min}^{-1}\ \text{M}^{-1}$, respectively. The error bars shown in Figure 3 show the 1σ uncertainties due to the averaging of 5−10 separate runs.

Chlorophyll loss was not observed to be photoenhanced in the presence of either nitrite or nitrate over the concentration ranges explored here. The average rate of chlorophyll photodegradation was approximately the same as that on pure water, 0.5−0.7 min^{-1}. Figure 4 displays the results obtained as a function of the salt concentration for these salts.

Discussion

The increased loss rate of chlorophyll in the presence of actinic radiation implies that photodegradation of chlorophyll is taking place. The halogen desk lamp emission spectrum overlaps well with the chlorophyll-*a* absorption spectrum.[26] We propose that the slower photochemical loss on pure water surfaces is probably due to the sequence

$$\text{Chl} + h\nu \leftrightarrows \text{Chl*} \rightarrow \text{Chl}^{+} + \text{e}^{-} \qquad (1)$$

$$\text{Chl*} + \text{O}_2 \rightarrow \text{Chl}^{+} + \text{O}_2^{\,-} \qquad (8)$$

$$\text{e}^{-} + \text{O}_2 \rightarrow \text{O}_2^{\,-} \qquad (9)$$

$$\text{Chl}^{+} + \text{O}_2^{\,-} \rightarrow \text{Chl} + \text{O}_2 \qquad (10)$$

$$\text{O}_2^{\,-} + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{OH}^{-} \qquad (11)$$

$$\text{O}_2^{\,-} + \text{Chl} \rightarrow \text{Products} \qquad (12a)$$

$$\text{HO}_2 + \text{Chl} \rightarrow \text{Products} \qquad (12b)$$

where chlorophyll loss is enhanced in the presence of light due to photoredox reactions with oxygen. The photoexcitation of organic matter is the primary source of $\text{O}_2^{\,-}$ in the ocean.[27] Similar reactions have been known to occur in the ocean, such as the production of peroxy radicals, RO_2, produced by H-atom abstraction or photooxidation of organic matter.[4] Once HO_2 is produced, it can react rapidly with chlorophyll (reaction 12b) if such reactions in the aqueous phase occur similarly to gas-phase reactions with short-chain alkanes.[28,29]

In the presence of halide salts, the loss of chlorophyll increases drastically over that seen on pure water, indicating that salts (halides, in particular) have a strong influence on the reaction. This effect may be explained by a photosensitized mechanism due to reactions 1−4 applied to Br^{-}, Cl^{-}, or I^{-}.[15] The observation of hydrated electrons following the illumination of chlorophyll in aqueous solution and the further observation of $\text{Cl}_2^{\,-}$ in illuminated chlorophyll/NaCl solutions give strong support to this general mechanism.[15]

The greatest loss rate of chlorophyll at the air−aqueous interface occurs in the presence of Br^{-}, then Cl^{-}, followed by I^{-}; little to no loss was observed in the presence of $\text{NO}_2^{\,-}$ or $\text{NO}_3^{\,-}$. This trend observed for halides can be explained by reactions 2 and 4. Reaction 2 is expected to proceed rapidly in solution; on the basis of the aqueous-phase redox potentials as shown in Table 1,[30] we would speculate that I^{-} would be oxidized most rapidly, followed by Br^{-} and then Cl^{-}. This expectation corresponds well with recent results by Jammoul

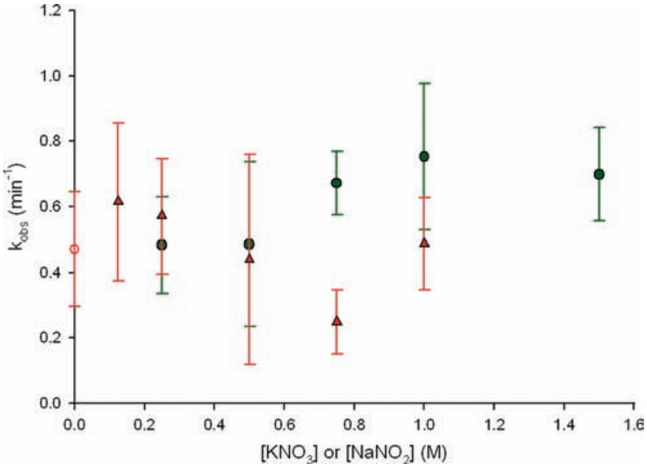

Figure 4. The observed rate of loss of chlorophyll versus nitrate (green circles) and nitrite (red triangles) concentrations. The errors bars display the 1σ uncertainty levels based on the average of 5−10 separate experiments.

TABLE 1: Reduction Potentials of Various One-Electron Couples Involving Free Radicals in Aqueous Media[30]

species	redox potential (mV)
Cl^-/Cl	2500
Br^-/Br	2000
I^-/I	1200
NO_3^-/NO_3	2300
NO_2^-/NO_2	970

et al., who observed the rapid oxidation of X^- due to the quenching of excited triplet-state benzophenone[16] with $I^- > Br^- > Cl^-$. However, in order for the reaction to proceed through reaction 4 and be measured by us via the loss of chlorophyll, the halogen atom formed in reaction 2 must react with the chlorophyll molecule. In both gas phase and solution,[31] iodine atoms are much less reactive toward organics than are atomic chlorine or bromine.[31,32] In solution, the kinetics of chlorine atom reactions with organics are generally close to diffusion-limited,[33] whereas those of bromine are somewhat slower.[34−36] This trend follows generally that displayed by the reactivities of halogen atoms toward organics in the gas phase.[32,37,38] On the basis of these observations, we expect reaction 4 to proceed most rapidly with Cl and slowest with I. Therefore, the observed loss rates of chlorophyll due to reaction 4 represent a convolution of the rate of oxidation of the halide anions (related to their redox potentials) and the kinetics of the reaction of the newly formed halogen atom with chlorophyll.

We observe no enhanced reaction in the presence of nitrate or nitrite anions. These species are known to produce OH radicals, with a small quantum yield, upon photolysis in solution.[39] Under the conditions of our experiments, this process is probably not contributing to the degradation of chlorophyll due to the low intensity of the halogen desk lamp filtered by the Pyrex flask and its poor spectral overlap with aqueous-phase nitrite and nitrate absorption spectra.[40] Given the redox potentials presented in Table 1, both nitrate and nitrite anions are expected to be oxidized by the chlorophyll cation, as indicated by reaction 2. However, the reaction kinetics of the nitrate radicals thus formed with organics in solution are generally slower than those of Cl or Br; for example, the reaction between propionaldehyde and a chlorine atom is about 1000 times faster than that with nitrate radicals.[41,42] Reactions of NO_2 with organic species are very slow in the gas phase[43−46] and therefore are not expected to be important in this case. Therefore, if the oxidation step does take place as expected but reaction with organics does not, reaction 2 presents a novel source for NO_x in the lower troposphere. We are currently undertaking further studies to determine the importance of this effect.

Photochemical loss of chlorophyll at the aqueous surface is observed due to the production of reactive halogen atoms via oxidation of the halides by photoexcited chlorophyll. If chlorophyll behaves this way at the air−aqueous interface, then it is likely that other photoactive organic molecules which are present in the SML also act as photosensitizing agents and give rise to similar halogen (and perhaps NO_x) releasing mechanisms. This suggestion is supported by recent results of Jammoul et al., who observed the production of halogens (implied by the formation of X_2^- and XY^-) during the photosensitized oxidation of halides by benzophenone in various aqueous media.[15,16] Those authors also measured the production of gas-phase Cl_2 and ClBr, confirming that this type of halide oxidation provides an important route for the release of halogenated species and molecular halogens[16] to the MBL. This general mechanism would be expected to be most important as a source of iodine species because the iodine atom is the least likely to react with the photoactive organic species, as in reaction 4, but is the most likely to be oxidized. We are currently working on methods to measure the halogenated products of this reaction to further understand and possibly verify the reaction mechanism.

Conclusions

The loss of chlorophyll at the air−sea interface is enhanced in the presence of actinic radiation. The reaction kinetics are linearly dependent on the concentration and identities of the halides present. Halides have the greatest influence on chlorophyll loss at the air−water interface, with bromide being the most effective, followed by chloride, and then iodide. The loss of chlorophyll is governed by two reactions, oxidation of anionic species by chlorophyll cations (or excited-state chlorophyll) followed by reaction of chlorophyll with the newly formed halogen atom. The low reactivity of iodine atoms, NO_2, and NO_3 toward organics suggests that these species could be released into the MBL. Further measurements of products are required to test these hypotheses and determine the influence which this and similar reactions occurring with other photoactive organic compounds in the SML have on chemistry in the MBL. This chemistry is particularly important in coastal regions where waters are most enriched with phytoplankton. If this reaction is a potential source of NO_x, then this is also important because it could influence local NO_x chemistry.

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