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**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

Photoinduced oxidation of sea salt halides by aromatic ketones: a source of halogenated radicals

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

The interactions between benzophenone triplet state and halide anion species (Cl^- , Br^- and I^-) have been studied by laser flash photolysis (at 355 nm) in aqueous solutions at room temperature. The decay of the triplet state of benzophenone was followed at 525 nm. Triplet lifetime measurements provided rate constants, k_q ($\text{M}^{-1} \text{s}^{-1}$), close to diffusion controlled limit for iodide ($\sim 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), somewhat less for bromide ($\sim 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and much lower for chloride ($< 10^6 \text{ M}^{-1} \text{ s}^{-1}$). The halide (X^-) quenches the triplet state, and a product, having a transient absorption at 355 nm and a lifetime much longer than that of the benzophenone triplet state, is formed. This transient absorption feature matches those of the corresponding radical anion (X_2^-). We therefore suggest that such reactive quenching can be a photosensitized source of halogen in the atmosphere and represents a driving force for the chemical oxidation of the oceanic surface.

1 Introduction

Oceans cover about 70% of the Earth's surface and provide a surface where exchange of gases and energy take place through complex mechanisms. This complexity is, in addition, increased by the fact that the ocean's surface microlayer is particularly enriched in various and quite complex organics as revealed by chemical analysis, showing the presence of amino acids, proteins, fatty acids, lipids, phenols, PAHs, and humic-type components (Cincinelli et al., 2001a, b). Such a complex chemical mixture is naturally reactive and its decomposition leads to the formation of a variety of functional groups, such as carbonyl and carboxylic acids (Sempere and Kawamura, 2003). The implications of the presence of such light-absorbing organics and the possible photochemical reactions are not yet well understood in the sea surface microlayer. But clearly, the presence of such photoactive compounds at the air/sea interfaces could give rise to photosensitized processes (Becker et al., 1995; Canonica et al., 2000,

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2005, 2006; Das et al., 1981; Ivanov et al., 2005; Lathioor and Leigh, 2001; Lathioor et al., 1999; Leigh et al., 1996) which may also affect chemistry in the marine boundary layer (MBL) (Reeser et al., 2009). In this latter study, we showed that chlorophyll may be a photochemical source of halogenated radicals or the driving force for ozone deposition at low wind speed (Clifford et al., 2008).

Halide anions are highly abundant in the marine boundary layer (MBL) both in salty water and sea salt aerosols (Finlayson-Pitts, 2003). The predominant anion is chloride (with concentrations approaching 0.5–5.6 M); followed by bromide (~10 mM) and iodide being the less abundant (~1 μM) (von Glasow et al., 2003; Schweitzer et al., 2000). While the halide anions are very stable, their corresponding oxidized forms (i.e., halogen atoms) are highly reactive and play an important role in the oxidation capacity of the MBL as discovered for the Arctic boundary layer (Barrie et al., 1988). Different halogen atom sources have been suggested, basically involving heterogeneous chemistry of NO_y or O₃ on sea-salt aerosols or the photolysis of halogenated organics. The photochemical reactions of ozone at the air-sea interface may also be a significant source of molecular chlorine (Oum et al., 1998). Independently of their sources, the halogen atoms then initiate a set of catalytic cycles destroying tropospheric ozone (especially for Br and I cycles) or oxidizing hydrocarbons (as observed for Cl). Clearly, the importance of the halogen reactions in the lower troposphere during springtime is now recognized (Ariya et al., 1999).

Despite their importance, halogen atom sources in the MBL are still an open question which requires further attention. A recent study by Reeser et al. (2009) identified that halide anions (X⁻) can be photochemically oxidized to the corresponding radical anions (X₂⁻) at the air/sea interface due to a chemical reaction involving chlorophyll. This oxidation process occurred under visible illumination (up to 700 nm) and was facilitated by the presence of ozone. This study, considering chlorophyll as a proxy for the oceanic surface layer, clearly showed that photosensitized reactions may oxidize halides into atomic halogens.

The validity of such a complex proxy may be somehow questioned being highly un-

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**A. Jammoul et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

stable in salty water; however photosensitized reactions may also be initiated by other species present in the surface microlayer (especially carbonyl containing compounds). In the present study benzophenone (BP) has been selected as a proxy for the aromatic carbonyl, found in sea surface microlayer. Excited triplet states of aromatic ketone have been widely studied in photochemistry (Blanchi and Watkins, 1974; Encinas et al., 1985; Encinas and Scaiano, 1981; Grewer and Brauer, 1994; Haselbach et al., 1991; Jacques et al., 1997; Kajii et al., 1987). The absorption of UV and visible light can initiate photosensitized reactions. Numerous studies on aromatic ketones on photoinduced charge transfer or/and energy transfer (Benitez et al., 1997; Haag et al., 1984; Huang and Shu, 1995; Poznyak and Vivero, 2005; Wu and Masten, 2002) were investigated. In this case, following light absorption, benzophenone is capable of generating reactive oxidant species, such as singlet oxygen $O_2(^1\Delta_g)$ (Mehrdad et al., 2002a, b), ketyl radical and others, which can oxidize a wide range of organic compounds (Blanchi and Watkins, 1974; Encinas et al., 1985; Encinas and Scaiano, 1981; Grewer and Brauer, 1994; Haselbach et al., 1991; Jacques et al., 1997; Kajii et al., 1987). This has especially be recognized for the fate of organic matter in aquatic environments (Haag et al., 1984).

By applying laser flash photolysis, we do aim to investigate the interactions between benzophenone (again a possible proxy for the aromatics in the oceanic surface layer) and halide anions by determining bimolecular rate constants for the quenching of excited benzophenone (BP*) by halide anions and their mixtures.

2 Experimental

2.1 Laser flash photolysis

Transient absorption kinetics following excitation of benzophenone containing solutions were studied using a laser flash photolysis apparatus of standard design (Reeser et al., 2009). A frequency-tripled pulsed Nd:YAG laser (355 nm) was used as the photolysis

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

source. During these experiments, the laser was operated with an output of 35 mJ per pulse ($\sim 90 \text{ mJ/cm}^2$). The laser output passed through the 4 mm length of a 0.45 mL quartz flow cell, which was mounted about 40 cm away from the laser head and was maintained at ambient temperature. The body of the cell was blackened so that only its windows were transparent to radiation. The near-Gaussian density profile of the laser beam led to a fairly uniform irradiation of solutions in the flow cell. All connections to the cell were either glass or PTFE tubing, ensuring a “clean” liquid flow. The samples were pumped through the cell using a peristaltic pump, replenishing the cell content after the required laser pulses.

Transient species produced by the pulsed laser beam were monitored by means of time resolved absorption spectroscopy. A 150 W high pressure Xenon arc lamp was used as analyzing light. The attenuated lamp output passed through the long axis of the cell and illuminated the entrance slit of a 1/4 m monochromator equipped with a 2400 grooves/mm grating, then was detected by a photomultiplier (Hamamatsu H7732-10). The PMT signal was passed through a high-speed current amplifier/discriminator, and the AC component recorded on a 100 MHz storage oscilloscope. The digitized signal was then transferred to a microcomputer using an IEEE-488 connection. Typically 32 measurements of the intensity measured at $1 \mu\text{s}$ following the laser pulse were averaged at each wavelength to generate a transient absorption spectrum. The full transient absorption spectrum was then reconstructed from the steady and transient signals. For construction of an absorption spectrum, measurements were repeated every 10 nm; for the kinetics experiments three wavelengths – 525 nm, 370 nm and 340 nm – were employed for observing the decays of BP triplet state.

All experiments were carried out under pseudo first order conditions, with a large excess of the quencher with respect to the initial BP concentrations. The decay of triplet excited state of BP can be described as follows (in presence of a quencher):

$$\frac{d[{}^3\text{BP}]}{dt} = -k_1[{}^3\text{BP}] \quad \text{with} \quad k_1 = k_2[\text{Quencher}] \quad (1)$$

The combination of the Beer–Lambert law with (1) leads to the following equation:

$$\log \left(\frac{I_0}{I} \right) = -k_1 t \quad (2)$$

The pseudo first order rate constant, k_1 , is obtained from the slope of a linear fit of the transient signals, plotted logarithmically as suggested in Eq. (2). In Fig. 1a shows a typical decay curve of the BP triplet state in presence of 6 mM of sodium bromide at 298 K and pH=8. A good linear fit to the data is obtained as demonstrated in Fig. 1b, indicating that the reaction takes effectively place under pseudo first order conditions.

All the experiments were performed at room temperature in the range 295–300 K. Aqueous solutions containing 1 mM of BP were deoxygenated with a stream of Argon for 20 min. All solutions were freshly prepared using 18 M Ω (Millipore) water. The chemicals used in this study were obtained from: benzophenone (Aldrich, 99%), sodium chloride (Aldrich, 99+%), sodium bromide (99+%), sodium iodide (99+%), sodium hydroxide solution (32%; Riedel-de Haën); all were used without any further purification.

2.2 Flow tube experiments

A wetted-wall flow tube reactor followed by ion chromatography measurements was also used to determine whether halogen species were released into the gas phase as products of the suggested photosensitized reactions of BP with salt solutions. The experimental setup of the wetted wall flow tube is described in detail elsewhere (Clifford et al., 2008). A vertically-mounted Pyrex tube, 70 cm long and 1 cm internal diameter, was maintained at constant temperature using circulating thermostated water at 296 K through its outer jacket. Reagent solutions containing 100 μ M of BP, 0.01 M of sodium bromide and 0.5 M of sodium chloride at pH=1 (acidified with hydrochloric acid) were injected at the top of the flow tube and evenly distributed by an annular reservoir dispenser system, leading to a homogeneous downward flow. A synthetic air flow of 200 mL/min was passed along its length. The flow tube was then irradiated using 4

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**A. Jammoul et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

fluorescent UV tubes (Black-Light-Blue OSRAM Sylvania TLD15W/08), with output in the range 340–420 nm and $\lambda_{\text{max}}=365$ nm. The gas extracted from the flow tube passed through a bubbler containing 150 ml of water at pH=13, basified with sodium hydroxide. Any halogen molecules released into the gas phase during a reaction within the flow-tube should then react with the hydroxyl anions in basic solution to give X^- and XO^- . This is a crude but efficient way of assessing qualitatively the presence of gaseous halogens such as X_2 molecules (X being any of the investigated halides), finally identified by ion chromatography.

A Dionex DX-120 ion chromatograph instrument equipped with a Dionex AS40 autosampler and a conductimeter detector was used for these measurements. The determination of anions (X^-) was performed using a (PAC ion AS14A) column (4 mm×250 mm) and a mixture of $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ (8 mM/1 mM) as eluent at a flow rate of 1 mL/min.

3 Results and discussion

3.1 Quenching rate

Excited triplet states of aromatic ketones are known to be strong oxidants; this has been studied with different electron donating compounds such as phenol (Canonica et al., 2000, 2006; Leigh et al., 1996) and oxygen (Mehrddad et al., 2002a, b). Immediately after the laser pulse a new spectrum, displayed as solid symbols in Fig. 2, showing two absorption maxima around 310 and 525 nm, was observed. These transient absorption features do correspond to the absorption spectra of the benzophenone triplet state previously reported (Bensasson and Gramain, 1980).

Monitoring the decay rate of both absorption bands enables the determination of the lifetime of the triplet state. First of all, these decay rates were observed to be mono-exponentials, leading to a triplet lifetime $\tau_0=6.0\pm 0.5$ μs (simply defined as the inverse of the first order rate constant) in the absence of quenchers. Figure 2 shows that

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

most of the absorption of benzophenone triplet state is disappeared 8 μs after the laser pulse (empty triangles). In the presence of halide anions, the decay of the BP transient absorption measured at 525 nm remains monoexponential, but becomes significantly more rapid with increasing anion concentration. The measured dependence of the decay rate on the halide anion concentration is displayed in Fig. 3 for the quenching of triplet BP by Cl^- , Br^- , I^- and a mixture of Br^-/Cl^- at ambient temperature and $\text{pH}=8$. From the slopes of the pseudo-first order decay rate k_1 (s^{-1}) of ^3BP vs. the halide concentration (Fig. 3), the quenching rate constant, k_q , may be determined using Eq. (3):

$$k_1 = k_q[\text{X}^-] + ct_e \quad (3)$$

The corresponding quenching rate constants obtained for the different quenchers are summarized in Table 1. The k_q values are in reasonable good agreement with the values obtained by Hurley et al. (1988) and Shizuka et al. (1982) in aqueous and acetonitrile media. The slight difference (20–50%) is probably due to an ionic strength effect (Douglas et al., 1990; Morrison et al., 1996) or to a solvent effect (Burget and Jacques, 1998; Gutierrez, 2008). The large magnitude of the k_q values determined for iodide and bromide strongly suggests that benzophenone quenching by these anions is highly efficient and potentially close to rate diffusion constant (especially for iodide); on the other hand quenching by chloride is much less efficient.

In order to approach more realistic oceanographic conditions, a mixture of a smaller amount of bromide and an excess of chloride was studied. Solutions are prepared with 100 μM BP containing a fixed concentration of sodium chloride (0.01 M) and varying concentration of sodium bromide (from 0 to 6 mM). Under these conditions, the measured triplet state quenching rate constant is 1.5 times faster than with bromide alone. This slight change could be due to the ionic medium variation or to coupled Cl/Br chemistries.

To test whether benzophenone triplet state deactivation by the anions can be explained by an electron transfer mechanism, we seek for a correlation between the measured quenching rates constants and the associated free energies. Electron transfer

between a halogen anion and the triplet state of benzophenone can be decomposed into different steps. First, the species diffuse together, allowing the formation of a contact complex $^{1,3}(\text{BP}^* \cdots \text{X}^-)$. Then, an intramolecular electron transfer takes place leading to an ion pair $^{1,3}(\text{BP}^{\bullet-} \cdots \text{X}^\bullet)$. At this point, two fates are possible: charge separation, leading to the separated radical ($\text{BP}^{\bullet-} \cdots \text{X}^\bullet$) or a return to the initial state (back electron transfer). The deactivation can take place by this mechanism only if the free energy of the electron transfer is negative (or very close). This quantity may be calculated using the Rehm-Weller equation (Eq. 4) (Burget and Jacques, 1998; Gutierrez, 2008):

$$\Delta G_{\text{ET}} = F(E(\text{X}^-/\text{X}) - E_{1/2}(\text{BP}) - E_T(\text{BP})) + C \quad (4)$$

where $E(\text{X}^-/\text{X})$, $E_{1/2}$ and E_T correspond, respectively to the oxidation potential of the anion X^- , the reduction potential, and the triplet state energy of the benzophenone photosensitizer: $E_{1/2}(\text{BP}) = -1.3 \text{ V}$ and $E_T(\text{BP}) = 3 \text{ V}$ (Murov et al., 1993). The entropic variation and the coulombic term (C) are considered here as negligible.

The calculated values of ΔG_{ET} are shown in Table 1. The formation of charge transfer complex is thermodynamically favorable ($\Delta G_{\text{ET}} < 0$) for iodide and unfavorable ($\Delta G_{\text{ET}} > 0$) for chloride. In the case of bromide the ΔG_{ET} is near to zero. These results are consistent with the measured values of k_q i.e., a rapid electron transfer (quenching) has been measured for the better electron donor iodine, a somewhat lower rate for bromide, and a much slower rate for chloride, which displays unfavorable thermochemistry.

3.2 Transient absorption of products in solution

The electron transfer mechanism proposed above implies the formation of iodine and bromine atom radicals as products. To test this, we carried out transient absorption experiments in order to observe the radical X^\bullet and the benzophenone ketyl radical, $\text{Ph}_2\text{C}^\bullet - \text{O}^-$. The identification of radical products was only carried out with iodide and

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

bromide solutions, since the initial experiments showed that no radical products were observed following the excitation of benzophenone in solutions containing chloride.

3.2.1 Iodide

The ketyl and iodine radicals were not observed in aqueous media having BP concentrations of 0.1 mM. However, at a much lower benzophenone concentration (1 μM), a transient absorption spectrum with a maximum at 380 nm was measured; this has previously been assigned to the iodine anion radical $\text{I}_2^{\bullet-}$ (Devonshire and Weiss, 1968). The observation that $\text{I}_2^{\bullet-}$ is only formed at very low BP concentrations may be due to a solvent effect on the quenching rate. A possible reaction can occur between the iodine radicals and benzophenone, therefore preventing the $\text{I}_2^{\bullet-}$ formation. On the other side, we looked at the formation of iodine radicals in acetonitrile media. Immediately following the laser pulse, we observed clear indications of $\text{I}_2^{\bullet-}$ formation under these conditions. A strong, very long-lived feature appeared at 385 nm as shown as the solid line in Fig. 4. The transient signal observed at 525 nm (due to absorption by the triplet state of BP) is shown as well, for comparison. The feature observed at 385 nm is ascribed to $\text{I}_2^{\bullet-}$ which exhibits absorption bands at 385 and 725 nm (Devonshire and Weiss, 1968). $\text{I}_2^{\bullet-}$ is expected to be the only absorbing species at this wavelength; it has a reported lifetime of approximately 25 μs (Devonshire and Weiss, 1968). Thus, we conclude that either acetonitrile solvent may promote electron transfer between triplet benzophenone and iodine anion or that halogen radical formation is more stabilized (longer lived) in acetonitrile than in aqueous solution.

3.2.2 Bromide

The formation of a new transient species has been clearly observed subsequent to the quenching of benzophenone by the bromide anion. The spectra of the observed transients in solutions containing BP (0.1 mM) and Br^- (2 mM) is shown in Fig. 5 at 1 and 8 μs after the laser pulse at 355 nm. The absorption maxima lie around 350

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

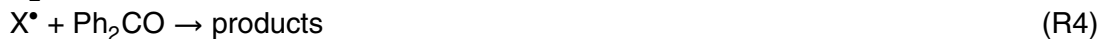
Printer-friendly Version

Interactive Discussion

and 525 nm. The transient absorption spectrum is characterised by a broad band feature, from 450 to 600 nm with a corresponding to ³BP and benzophenone ketyl radical (Bensasson and Gramain, 1980; Sakamoto et al., 2004) and an intense band at low wavelength (<400 nm). After 8 μs when the triplet benzophenone is relaxed, the absorption at 350 nm is still apparent and long-lived (with a life time of ca. 15±0.5 μs) and may corresponds to bromine radical anion Br₂^{•-} (Ershov and Janata, 2003; Ershov et al., 2002; Grodkowski and Neta, 2002; Hurley et al., 1988; Zehavi and Rabani, 1972). This radical anion is known to absorb light from 300 to 400 nm with maximum absorption at 355 nm.

3.3 Reaction mechanisms

The results presented above are consistent with a mechanism in which oxidation is initiated by an electron transfer from the anion X⁻ to the excited triplet state of BP, yielding a halogen radical X[•] and a deprotonated ketyl radical (Ph₂C[•]O⁻). We propose that all the observations presented above can be explained with the following mechanism:



In the presence of a large excess of X⁻, the halogen radical X[•] may react with X⁻ ions and form X₂^{•-} radical anions (R2). The X[•] and X₂^{•-} radicals are strong oxidants and may react with the surrounding organic compounds by electron transfer and H-abstraction (R3 and R4) with rates that depend on the difference in the redox potentials of the reagents (Gilbert et al., 1988; Hasegawa and Neta, 1978; Martire et al., 2001).

In solution containing both sodium chloride and small amounts of sodium bromide, one would expect that the faster reaction with bromide (see Table 1) might dominate over reaction with chloride, except when the Cl^-/Br^- ratio is below $\sim 10^{-3}$. Indeed, in mixed chloride-bromide solutions, it appears that the quenching of ^3BP is dominated by the bromide anion, as inferred from the rapid deactivation rate. In this case, the mechanism of Br_2 and BrCl formation may be via the sequence below (Ershov et al., 2002).



This reaction mechanism produces, by a photosensitized process, atomic halogen as recently highlighted in the case of illuminated chlorophyll reacting with salts. The present confirms this previous study and underlines that such process may occur with different photosensitizers.

5 3.4 Formation of gas phase products

We investigated the possible production of gas phase X_2 or XY (X being another halide), implied by reaction (R6) above, using the flowtube apparatus. At its exit, both X_2 and XY will react in the alkaline bubbler with the hydroxyl anion (OH^-), giving rise to bromide or chloride anions which are then detectable by ion chromatography.

10 The formation of X_2 or in the flow-tube was monitored at 295 ± 2 K as a function of the injector position (which is proportional to the residence time in the tube), using a solution containing a $[\text{Cl}^-]:[\text{Br}^-]$ molar ratio of 50:1. The result is shown in Fig. 6. We observe the presence of X^- anions, which strongly implies the formation of X_2 . The concentration initially increases with the exposure time of the BP/salt solution to illumination, but then is seen to decrease at long exposure time, though we did not make
15 any measurements using an irradiation time of more than 6 s. It is possible that, at the longer exposure times halogen molecules were still released into the gas phase, but at a concentration below the instrumental limit of detection of 15 ppbv, corresponding

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to 0.1 mg/L in solution. This decay could be simply observed by the heterogeneous chemistry of the gaseous dihalogens at the air/liquid interface in this wetted-wall flow tube. Alternatively it could be that the longer exposure times give rise to photochemical or evaporative loss of the benzophenone, thereby reducing its ability to act as a photosensitizer. To explore this issue, we measured the UV-visible absorption spectrum for solutions containing a benzophenone – halide anion mixture at different times of irradiation. We found that the amount of benzophenone decreased by 60% after 6 s of irradiation. This is mainly due to the volatility of benzophenone and its low solubility in water. On the other hand, this may also be due to reaction of BP with the reactive halogenated species formed following the electrons transfer.

4 Conclusions

In the present paper we have demonstrated that photosensitized reactions may occur in the sea surface microlayer due to the presence of photochemical agents. According to the proposed mechanism, chemistry may be initiated by interactions between triplet state benzophenone and halide anions. We have measured the quenching rate constant of triplet BP by different sea salts; while chloride is not strongly reactive with the triplet state of BP, deactivation is very fast with iodide and somehow less for bromide. The magnitude of the quenching rate constant follows a trend given by the values of the free energy for electron transfer. Thus electron transfer was shown to be the probable mechanism for the oxidation of sea salt anions by triplet BP. This mechanism leads to the formation of halogen molecules in the gas phase. We expect that such a photosensitized process initiated by carbonyl compounds may be relevant in the chemistry of the sea surface microlayer, not only for sea salt but also for any organic compound having a one electron oxidation potential. This has important implications for the chemistry in the MBL, because the activation of halides in seawater containing chlorophyll or organic carbonyl provides a catalytic loss mechanism for ozone. The latest measurements (Environmenta, 2009) show that the halogen may participate to decreasing

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

ozone levels in the lower atmosphere over tropical oceans and probably above most other oceans. Indeed, the source of tropospheric gas-phase halogen is known to be heterogeneous in nature (Knipping et al., 2000). The omission of halogen sources and their chemistry in atmospheric models may lead to significant errors in calculations of global ozone budgets. The mechanism presented above could represent such a source for model calculations. We are currently undertaking experiments to quantify its potential importance.

Finally, the reaction of Cl (and, potentially, other halogens present as halides in seawater) or OH with organic compounds at the ocean's surface may be a source of halogenated or partially oxidized organic compounds, which might participate in new particle formation and growth in the MBL.

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Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**A. Jammoul et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**A. Jammoul et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**A. Jammoul et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Photoinduced oxidation of sea salt halides by aromatic ketones

A. Jammoul et al.

Table 1. Rate constants for quenching of benzophenone triplet by different sea salt halogens and mixture of anions, oxidation potentials for the anions, the free energy of the electron transfer ΔG , and a comparison of the quenching rate constant with the previous study. The errors given as 95% confidence intervals estimated from the data fits by Table curve program.

Quencher	Conditions	K_q ($M^{-1} s^{-1}$)	$E(X^-/X)$ (V) (Alfassi et al., 1987)	ΔG_{ET} (eV)
I^-	pH=5.5 water	$(8.2 \pm 0.8) \times 10^9$ this work	1.33	-0.46
	pH=11 water	2.3×10^9 (Hurley et al., 1988)		
	acetonitrile/water	3.5×10^9 (Shizuka and Obuchi, 1982)		
Br^-	pH=8 water	$(3.5 \pm 0.3) \times 10^8$ this work	1.93	0.14
	pH=11 water	2.2×10^8 (Hurley et al., 1988)		
	acetonitrile/water	5.0×10^7 (Shizuka and Obuchi, 1982)		
Cl^-	pH=5.5 water	$(7.3 \pm 2.1) \times 10^5$ this work	2.6	0.81
	pH=11 water	$\sim 8.0 \times 10^4$ (Hurley et al., 1988)		
	acetonitrile/water	2.2×10^5 (Shizuka and Obuchi, 1982)		
Br^-/Cl^-	pH=5.5 water [Cl^-]=0.01 M	$(5.1 \pm 0.9) \times 10^8$ this work		

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

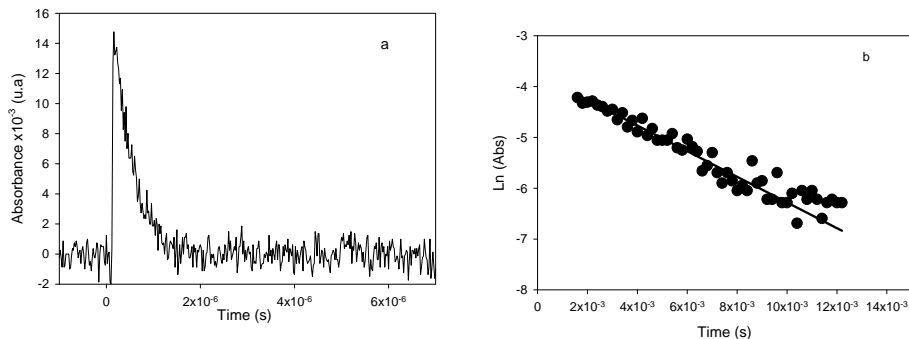


Fig. 1. (a) Transient absorption decay of the benzophenone triplet state ($\lambda_{\text{obs}}=525$ nm) in deoxygenated aqueous solutions in presence of 4 mM of bromine. (b) Typical pseudo first order decay observed in the study of the $^3\text{BP}+\text{Br}^-$ reaction. The experimental conditions were as follow: $[\text{BP}]=100\ \mu\text{M}$, $\text{pH}=8$ at ambient temperature and the number of laser shots averaged were 32.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

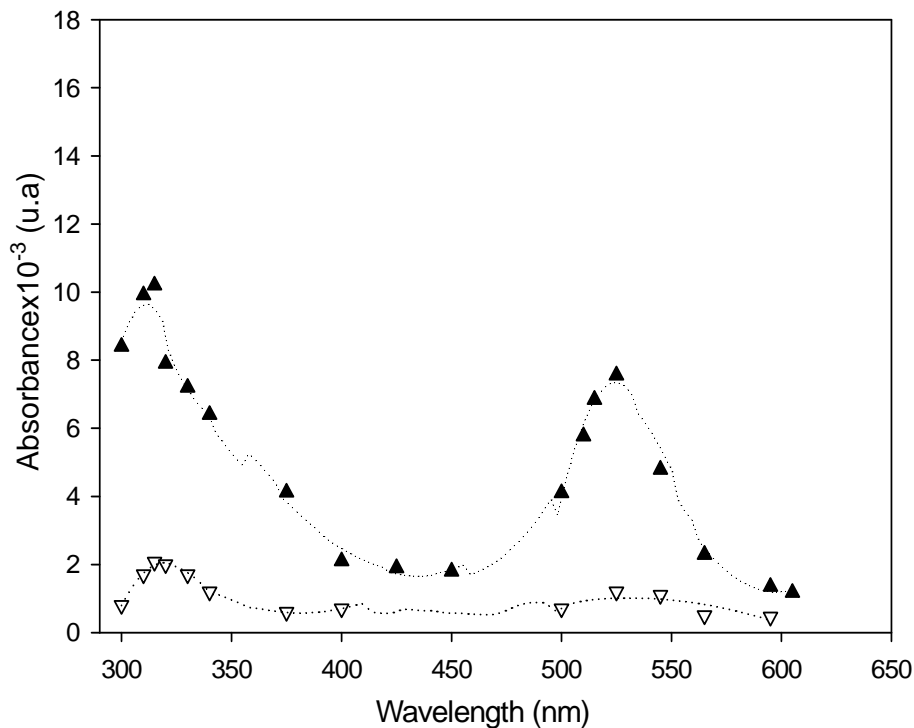


Fig. 2. Transient absorption spectra of aqueous deoxygenated solutions of BP (0.1 mM) at room temperature recorded after the 355 nm laser pulses. The filled and empty triangles represent, respectively the BP triplet state at the end of pulse and 8 μ s after the pulse.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

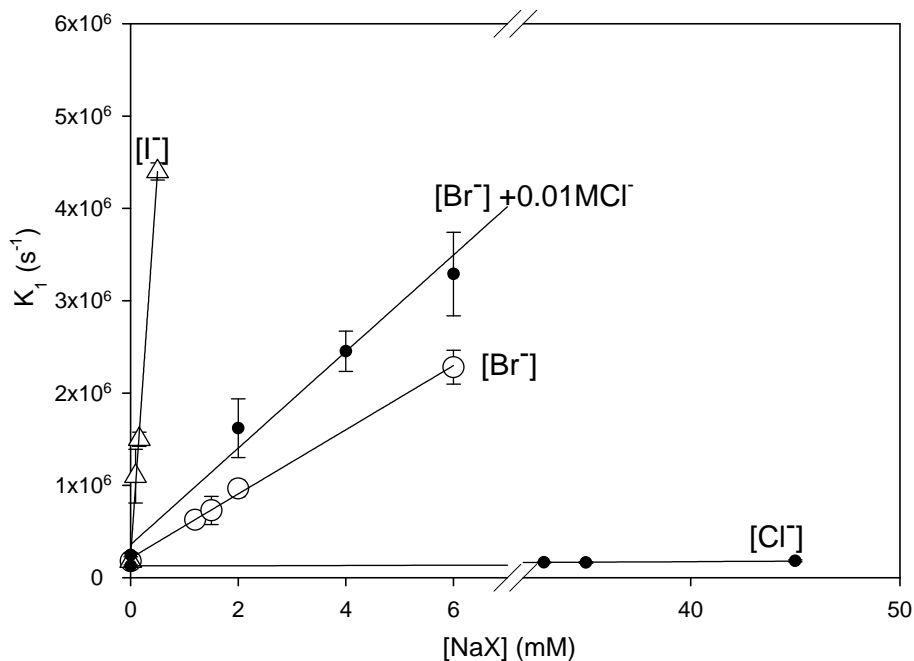


Fig. 3. Stern–Volmer plot of the pseudo-first order rate constants as a function of the anion concentrations for the quenching of BP triplet state in deoxygenated aqueous solutions monitored at 525 nm at room temperature. Benzophenone concentration (0.1 mM) laser energy 25 mJ. The error bars are given as triple the standard deviation of the least squares slope from analysis.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

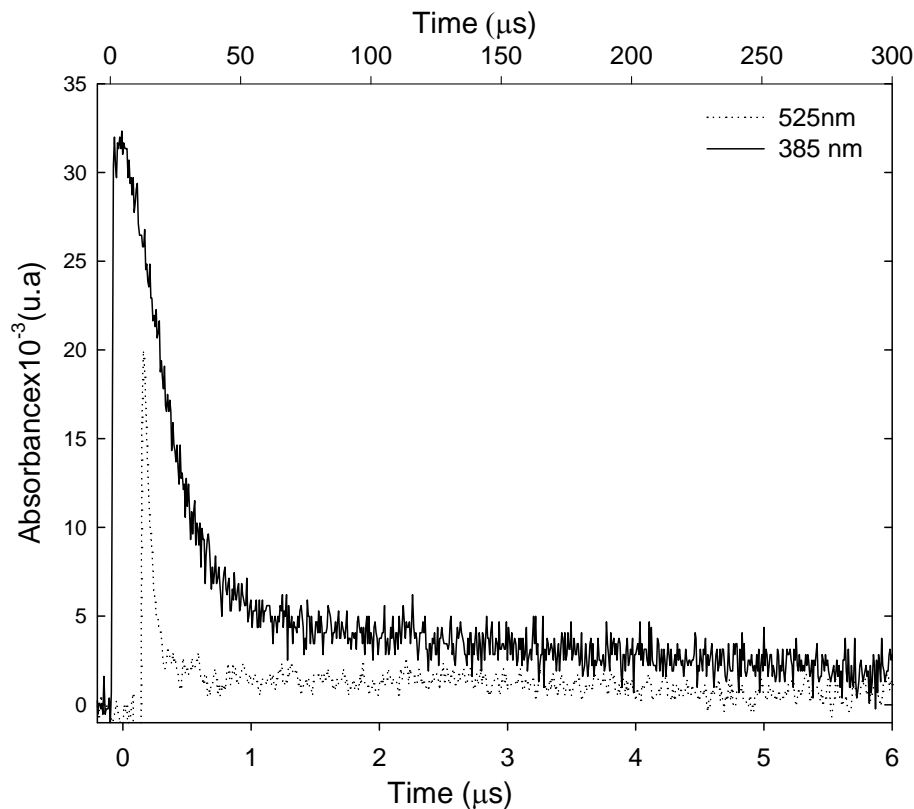


Fig. 4. Transient decay at 525 nm (dotted line) and 385 nm (solid line) obtained after flashing at 355 nm a deoxygenated solution containing 0.1 mM of benzophenone and 0.5 mM of potassium iodide in acetonitrile media.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

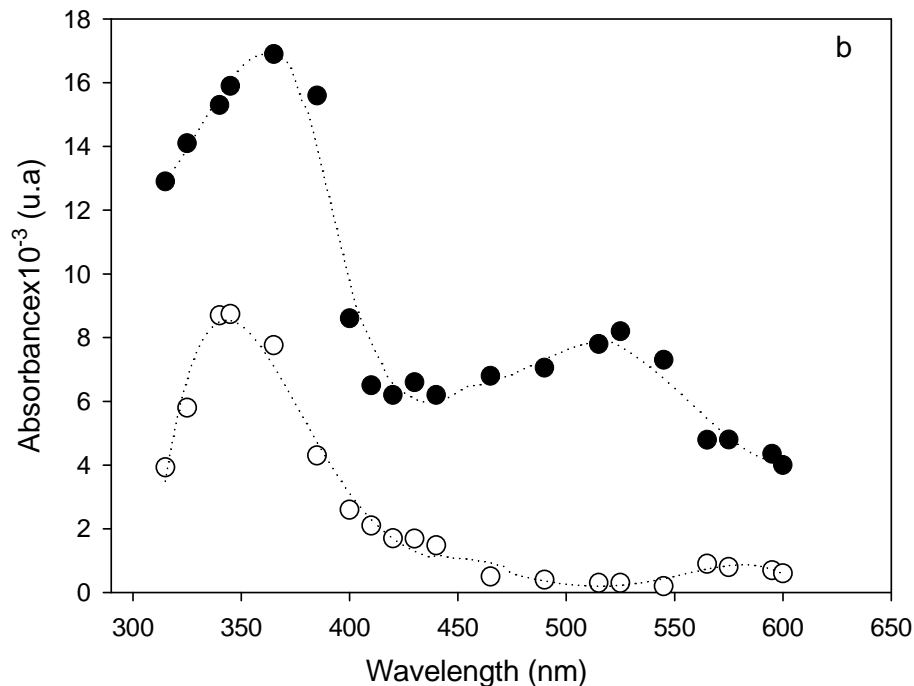


Fig. 5. Transient absorption spectra of aqueous deoxygenated solutions of BP (0.1 mM) and NaBr (2 mM) at room temperature recorded after laser excitation ($\lambda=355$ nm). The filled circles represent the initial spectrum (1 μ s after the pulse) of (BP+Br⁻) and the empty circles represent the absorption spectrum of the new transient 8 μ s after the pulse.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Photoinduced
oxidation of sea salt
halides by aromatic
ketones**

A. Jammoul et al.

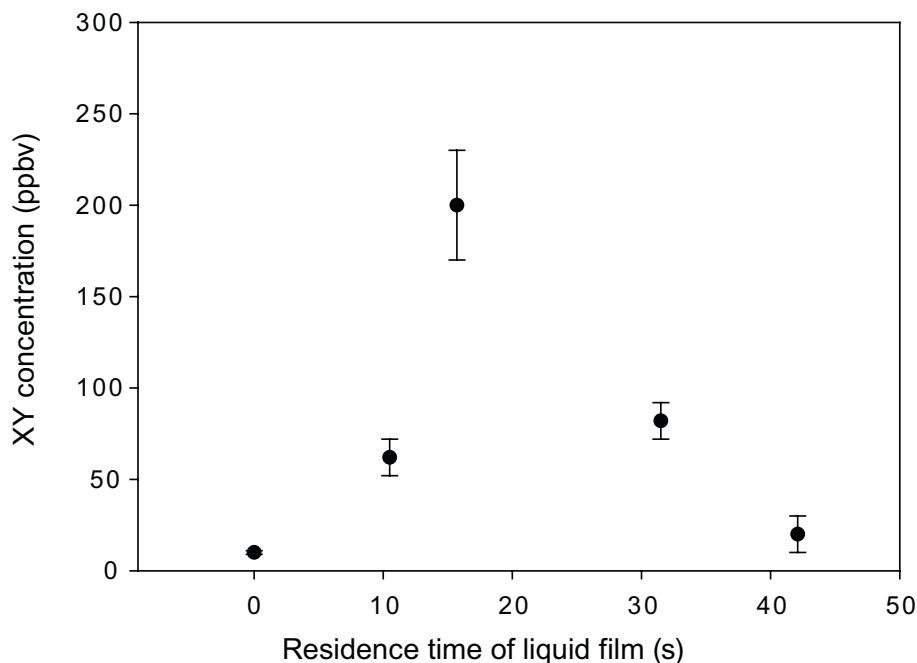


Fig. 6. Kinetics of the gaseous dihalogen production as a function of residence time of gases in the irradiated flowtube. The experiments are performed under UV irradiation (spectral irradiance 1.2×10^{15} photons $\text{cm}^{-2} \text{s}^{-1}$ in the 340–420 nm range) and the conditions were as follow: ambient temperature, [BP]=100 μM , [NaBr]=0.01 M, [NaCl]=0.5 M.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)