LABORATORY STUDIES OF PHOTOCHEMICAL REDUCTION OF IODATE (IO$_3^-$) TO IODIDE (I$^-$) IN SEA WATER

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In the presence of humic acid, IO$_3^-$ photo-chemically transforms to aqueous I$^-$ and soluble iodinated humic acid and the fixing of iodine within humic structures is likely to occur at aromatic 1, 2 diol groups. Spectroscopic analysis identified ~ 20% of reduced iodate in the form of 'free' I$^-$ with lifetime ~ 2 days for IO$_3^-$ in marine aerosol. The remaining [I$^-$] concentration (average of ~ 80%) is assumed to have been taken up by humic acid and form the soluble iodinated humic acid. This lifetime of IO$_3^-$ in marine aerosol is consistent with the THAMOD model predictions.

INTRODUCTION

Iodine exists in open seawaters mainly in the inorganic forms iodate (IO$_3^-$) and iodide (I$^-$) (Wong and Zhang 2008). While the concentration of IO$_3^-$ predominates in deep water, I$^-$ concentrations increase toward the surface. The primary precursor for iodine oxide particle (IOP) formation in the coastal marine boundary layer (MBL) is iodine (I$_2$) (Saiz-Lopez, Plane *et al*. 2006) originating from exposed macroalgae. In contrast, recent field measurements of IO above the open ocean suggest that biogenic organic-iodine emissions cannot account for the observed levels (Read, Mahajan *et al*. 2008; Mahajan, Oetjen *et al*. 2009; Mahajan, Plane *et al*. 2010). Therefore, it is assumed that IO$_3^-$ is reduced to I$^-$ in seawater which is converted to, and emitted as I$_2$ to the atmosphere which may contribute to observed levels of I$_2$ in the MBL. Previous studies have shown that dissolved organic matter (DOM) plays an important role in photo-reduction of IO$_3^-$ to I$^-$ (Tsunogai and Sase 1969; Spokes and Liss 1996). Dissolved organic forms have been studied in detail with both volatile (*i.e.* organo-iodides such as CH$_3$I or CH$_2$I$_2$), and non-volatile fractions being identified (Klick and Abrahamsson 1992; Cook, Carpenter *et al*. 2000; Huang, Ito *et al*. 2005). Although the volatile forms (organo iodides and I$_2$) are present at very low levels (< 10^{-3} μM) (Wong and Cheng 2001) and can pass into the atmosphere via transfer across the water surface, and then participate in a number of processes including secondary aerosol formation (O'Dowd, Jimenez *et al*. 2002; Saunders and Plane 2005; O'Dowd and De Leeuw 2006; O'Dowd and De Leeuw 2007), the non-volatile species are not so well characterized.

Recent measurements have shown that a significant fraction of organic iodine present in the marine aerosol is in the form of dissolved organic iodine (DOI) (Aguer, *et al*. 1999 Baker 2005; Gilfedder, Lai *et al*. 2008), most likely originating from the sea surface micro-layer (Clark 2000). This has led to the suggestion of a possible reaction between DOI and the aqueous species hypoiodous acid (HOI), which would recycle I$^-$ within aerosol and also

enhance the release of I_2 into the gas phase (Pechtl, Schmitz *et al*. 2007) , but the exact identification of such material remains largely unknown. Humic acids are likely to be an important class of compound, for which iodine has been shown to readily be taken up and fixed into a non volatile form (Francois 1987; Keppler, Biester *et al*. 2003; Reiller, Mercier-Bion *et al*. 2006). Humic acids are found in both terrestrial and marine environments and represent a group of multi-functional organic compounds including carboxyl and hydroxyl groups, for which no single molecular structure or weight exists. They are soluble in water and are chromophores which participate in photo-sensitised chemical reactions in natural waters (Zafiriou, Joussotdubien *et al*. 1984; Clark 2000; Clark, Debruyn *et al*. 2008; Clark, De Bruyn *et al*. 2009). Whilst a number of techniques have been used to attempt to identify the mechanism by which iodine is taken into such compounds (Wong and Cheng 1998; Warner, Casey *et al*. 2000), to date no solid picture has emerged to fully characterise the chemical pathways leading to the formation of iodinated humic substances and emission of I_2 to the atmosphere.

Recently, it has also been reported that oxidation of iodide (I^-) at the sea surface resulting from uptake of ozone (O_3) could enhance the emission of I_2 into the MBL (Martino, Mills *et al*. 2009; Sakamoto, Yabushita *et al*. 2009; Hayase, Yabushita *et al*. 2010). Also, the ubiquitous presence of the H_2O_2 in the lower troposphere can lead to uptake at the seawater surface and into aerosol, with the potential for oxidation of I^- through to molecular iodine (I_2) (Kupper, Schweigert *et al*. 1998; Pradhan, Kyriakou *et al*. 2010). Emission of I_2 to the atmosphere by the uptake of O_3 and H_2O_2 would be a potentially important source of precursor for the production of secondary aerosol in the form of iodine oxide nanoparticles, as observed in numerous field and laboratory studies (McFiggans, Coe *et al*. 2004; O'Dowd and Hoffmann 2005; Saunders and Plane 2005). The recycling of iodine back to the gas phase would also increase the overall O_3-depletiing potential of iodine.

In this paper a series of laboratory studies to elucidate the mechanism for the reduction of aqueous IO_3^- to I^- in the presence of humic acid and sunlight, and the subsequent emission of I_2. A series of UV-visible spectroscopic and IOP formation and detection experiments were conducted to investigate three potentially important processes likely to participate in the emission of I_2 to the atmosphere from seawater or sea salt aerosol: (i) the role of dissolved organic materials (*i.e.* humic acid) in the reduction of IO_3^- to I^- in the form of 'free' aqueous ions and also fixed iodinated humic form, (ii) the effect of salinity (Cl^-) and H_2O_2 on the reduction process, and (iii) the role of surrogate compounds of humic acid (i.e. catechol) in the reduction of IO_3^- to I^-.

In order to see what happens to the produced I^- by the reduction of IO_3^- in the aerosol, preliminary experiments of the uptake of O_3 on an aqueous I^- were also conducted.

Experimental

Experiments were carried out in two steps. First, a UV-visible spectroscopic study of the reduction of IO_3^- to I^- in the presence of light and humic acid. A fresh 10^{-4} M $NaIO_3$ (Sigma-Aldrich, $\geq$ 99.5%) aqueous solution was prepared, to which a humic acid solution was added. The humic acid solution was prepared using an untreated commercially available compound (Sigma-Aldrich – 53680) by stirring a small amount of the solid in ultra-pure water (18MΩ) for typically 2-3 hours, and then filtering off any undissolved matter. The solution was then placed into a cylindrical glass cell (volume of 132 cm^3), mounted with quartz windows for subsequent photolysis using a 1000W Xenon arc lamp (ozone-free Oriel 'Solar Simulator'). The lamp beam was filtered using (a) a water filter to remove IR wavelengths and thus prevent

heating of the solution, (b) a solar mass filter to 'shape' the lamp spectrum to mimic the solar spectrum at the base of the atmosphere, and (c) a cut-off filter to remove any of the small output of the lamp at $\lambda < 310$ nm. The solution was continually exposed to the filtered lamp beam for a 20 hour period at room temperature (293 ± 1 K). An aliquot was extracted from the solution cell for subsequent spectroscopic analysis and UV-visible spectra were taken every 2 hours using a Perkin-Elmer spectrometer (Lambda 900) at 0.5 nm intervals between 200 nm and 600 nm using 1 cm quartz cuvettes. These experiments were performed both in the dark and using the solar simulator. A complete schematic experimental set-up is shown in Figure 1.
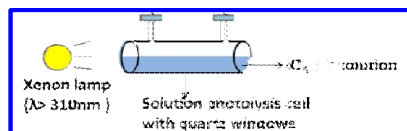

Fig. 1. Schematic of experimental set-up used to study the reduction of IO_3^- to I^-

This experimental set-up was first used to detect any IOP formation resulting from an irradiated 1.0×10^{-4} M IO_3^-/humic acid solution to establish whether oxidation of I^- to I_2 occurs. Separate experiments were also carried out in which 6.6×10^{-5} M H_2O_2 (equivalent to the aqueous concentration which would be in equilibrium with a realistic atmospheric gas phase mixing ratio of 0.8 parts per billion) (Jackson and Hewitt 1999; Wong and Zhang 2008) and 0.5 M NaCl (an equivalent concentration to that in seawater) (Lide 2009) solutions were added to the IO_3^- / humic acid solution prior to irradiation to see the effect of these species on emission of I_2.

RESULTS AND DISCUSSIONS

UV-visible study of the reduction of IO_3^- to I^- Initially, the solutions of IO_3^- and humic acid were irradiated separately to identify any change in the individual spectra. Figures 2 & 3 show the time-resolved spectra of IO_3^- and humic acid solutions respectively on irradiation for a 10 hour period.
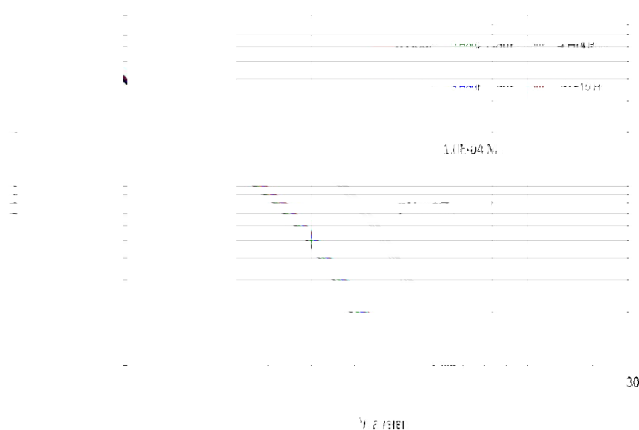

Fig. 2. UV-visible spectra of an irradiated 1.0E-04M NaIO$_3$ solution
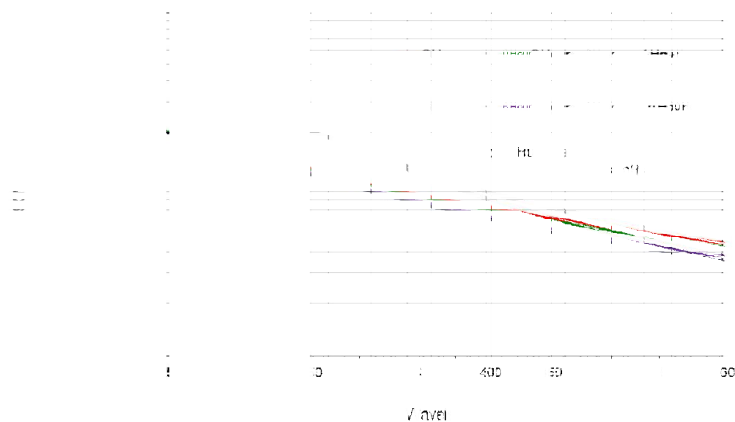
Fig. 3. UV-visible spectra of an irradiated humic acid solution

These figures clearly show that there is no significant change upon irradiation of the two individual solutions.

A mixed solution of 1.0×10^{-4} M IO_3^- + humic acid was then irradiated and spectra were taken at every 2 hours. Figure 4.4 shows time-resolved solution spectra between 200 and 600 nm, and at 200 – 300 nm (inset), with the thick sky blue line indicating the initial (*i.e.* before photolysis) solution mixture (*t* = 0 hour) spectrum and the thick red line, the final (*t* = 20 hours) spectrum that was acquired.
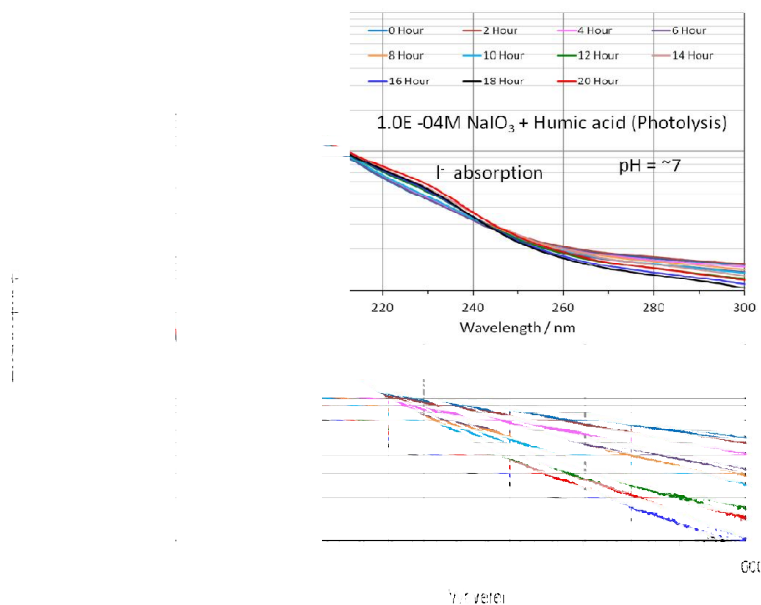

Fig. 4. Time-resolved UV-visible absorption spectra taken of an irradiated IO_3^- + humic acid mixed solution.

Figure 4 shows a steadily increasing absorption between ∼ 210 nm and 240 nm, consistent with the formation of I^-, which absorbs strongly in this region, peaking at ∼ 225 nm (molar extinction coefficient $\varepsilon \sim 1.4 \times 10^4$ M^{-1} cm^{-1}, compared with ε at 225 nm for IO_3^- of ∼ 10^3 M^{-1} cm^{-1} (Awtrey and Connick 1951). Absorption in the visible region is exclusively due to humic

acid (Frimmel 1994; Aguer, Richard *et al*. 1999), and shows a continually decreasing absorption at all wavelengths in this region with time.

In order to determine the change in concentration of reactants and products with time, a least squares optimised spectral fitting analysis was performed using reference spectra taken of the initial iodate and humic acid solutions, and of a prepared 1.0×10^{-4} M KI solution. Firstly, the humic acid reference spectrum was fitted to the visible part of the photolysed solution spectra and then iodate and iodide reference spectra were fitted at 225 nm.

For humic acid, it was not possible to quantify the concentration throughout the photolysis experiments as neither the molecular weight nor molar extinction coefficients are known for the substance. Therefore figure 5 (a) is a plot of absorbance at 225 nm for the three species as a function of photolysis time for the data fitted for the same experiments as described above i.e. initial $[IO_3^-] = 1.0 \times 10^{-4}$ M.

Figure 5 (b) shows the variation in the fraction of detectable I^- in solution at each time period *i.e.* the ratio of $[I^-]_t/([IO_3^-]_t-[IO_3^-]_0)$.
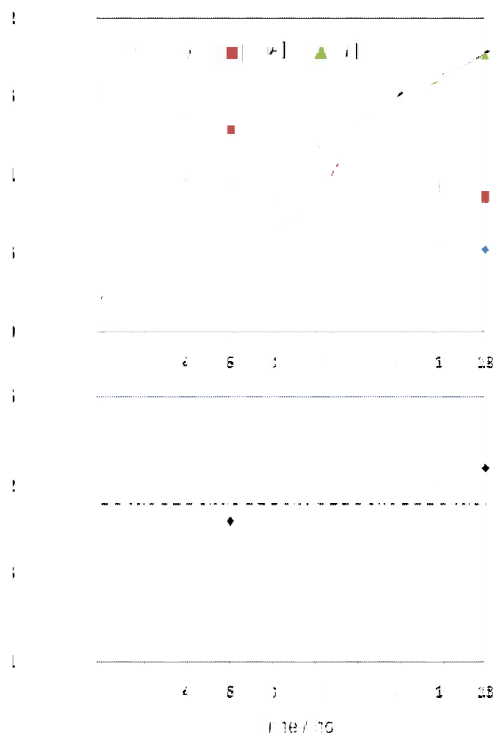

Fig. 5. (a) – Variation of measured absorbance of IO_3^-, humic acid [HA], and I^- with photolysis time at 225 nm, obtained by spectral fitting of the individual components. The solid black lines indicate linear fits of the I^- data points, whilst the dashed black line indicates the increase resulting from a combination of the 2 hour photolysis period and the overnight, dark reaction in the stored solution. (b) – Calculated fraction of I^- in solution as a result of photo-sensitised iodate reduction (dashed line indicates the average value of ~ 0.19.

It is clear from figure 5 that both humic acid and iodate absorbances (concentrations) are seen to steadily decrease with time with a final $[IO_3^-]$ after 18 hours of 5.3×10^{-5} M, whilst the $[I^-]$ concentration in solution increases to 1.3×10^{-5} M after 18 hours. The decrease in iodate concentration with time throughout the experimental time-scale described in Figure 4.5 (a) is shown in Figure 4.6, with an iodate loss rate (slope) of 1.2×10^{-5} s^{-1}.
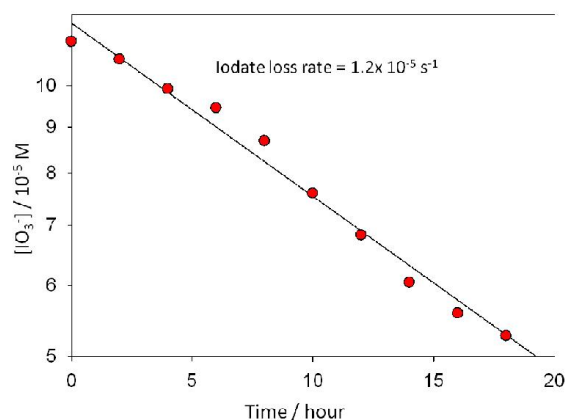
Fig. 6. A linear fit of the decrease in iodate concentration with time.

The loss rate shown in the Figure 6 corresponds to a lifetime of ∼ 2 days for iodate in aerosol. The concentration of [I⁻] after 18 hours represents ∼ 20% of the iodine which has undergone conversion from the initial iodate form. This fraction is seen to be fairly constant with time, with an average of 0.19 as indicted by the dashed line in the bottom panel. The remaining [I⁻] concentration (average of ∼ 80%) is assumed to have been taken up by humic acid and form the soluble iodinated humic acid (Reiller, Mercier-Bion *et al*. 2006). However, there are no definitive absorption features evident in the mixed solution spectra to verify this. The conversion fraction of iodate into [I⁻] and iodinated humic acid is consistent with the modelling work performed using THAMOD for predictions for Cape Verde. Figure 7 shows the modelling predictions of the conversion of iodate into [I⁻] and organic fraction.
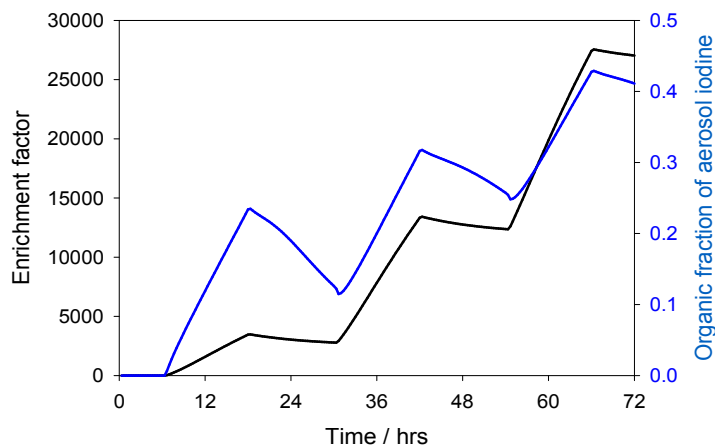

Fig. 7. Variation of enrichment factor with time. The enrichment factor represents the total aerosol iodine concentration to seawater (450 nM).

From the figure 7 it clear that a typically enrichment factor ∼ 5000-10000 is consistent with a lifetime of 40 hours (∼ 2 days) and the organic fraction increases to 40% after 4 days.

This lifetime accounts for the enrichment of iodate in marine aerosol, and explains why aged aerosol has less iodate relative to organic iodine.

Conclusions

From these laboratory experiments, the following insights can be drawn regarding the transformation of iodine species in seawater and within atmospheric aerosol. Firstly, IO_3^- (oxidation state = +5) is reduced into I^- (oxidation state = −1) on photolysis with visible light ($\lambda > 310$ nm) in the presence of aqueous humic acid solution. The action of visible light on humic acid produces solvated electrons (e^-_{aq}) and H_2O_2. Solvated electrons (e^-_{aq}) reduce IO_3^- to I^-, which is then oxidised to I_2 by H_2O_2.

Secondly, the spectral fitting analysis has shown that only ~ 20% of the reduced IO_3^- is in the I^- form and the difference, ~ 80% of reduced IO_3^-, forms iodinated humic acid, not amenable to direct spectroscopic detection. This indicates that the dissolved organic iodine will be the major reservoir of reduced iodine in seawater.

Acknowledgements

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