

LABORATORY STUDIES OF THE BEHAVIOUR PHOTOCHEMICAL REDUCTION OF IODATE (IO_3^-) TO IODIDE (I^-) IN SEA WATER: EMISSION OF IODINE TO THE ATMOSPHERE

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Photo-chemically reduction of IO_3^- to aqueous I^- occurs in presence of humic acid in sea water. The fixing of iodine within humic structures is likely to occur at the aromatic 1,2 diol groups (i.e. likely to catechol analogue). Transfer of I_2 to the gas phase from the reduction of IO_3^- to I^- , shows the oscillatory behaviour of the 'Bray-Liebhafsky' reaction and is enhanced in the presence of H_2O_2 and salinity (Cl⁻). The reduction of IO_3^- to I^- shows second-order reaction kinetics in the presence of H_2O_2 with a rate constant $(1.87 \pm 0.01) \times 10^{-1} \text{ mol}^{-1} \text{ L sec}^{-1}$. The lifetime of the conversion of IO_3^- to I_2 in the aerosol is at least several days. These iodinated humic acids are stable with respect to photolysis at visible wavelengths and consequently are likely to account for a significant proportion of dissolved, non-volatile iodine-containing organic material occurring within marine waters and aerosols.

KEYWORDS : Iodine oxide particles-----UV-Visible Spectroscopy-----Reduction----- IO_3^- ----- I_2 .

INTRODUCTION

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) (Baker, 2005; Gilfedder *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 *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 *et al.*, 2003; Reiller *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 (Zafirou *et al.*, 1984; Clark, 2000; Clark *et al.*, 2008; Clark *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 *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 *et al.*, 2009; Sakamoto *et al.*, 2009; Hayase *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 *et al.*, 1998; Pradhan *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 *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 -depleting potential of iodine.

This paper describes 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, experiments of the uptake of O_3 on an aqueous I^- were also conducted.

EXPERIMENTAL

Experiments were conducted 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 (18M Ω) 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 cm³), 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. A complete schematic experimental set-up is shown in Figure 1. The experiments were also conducted on the reactions between with 10^{-4} M $NaIO_3$ solution and a number of 'surrogate' compounds with potentially reactive functional groups found within humic acids such as catechol (1, 2 benzenediol), benzoquinone, salicylic acid and phthalic acid to identify any key species which may be involved in the humic acid-iodate reactions.

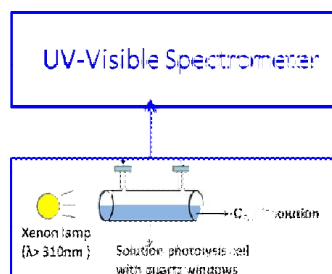


Fig. 1. Schematic of experimental set-up used to study the behavior of reduction of IO_3^- to I^- .

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 0.5M 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

Spectroscopic studies were conducted of the dark and light reactions between iodate solutions and a number of 'surrogate' compounds with potentially reactive functional groups found within humic acids (shown in Figure 2), to identify any key functional groups which may be involved in the humic acid-iodate reaction (Stevenson, 1994). These compounds included catechol (1, 2 benzenediol), benzoquinone, salicylic acid and phthalic acid.

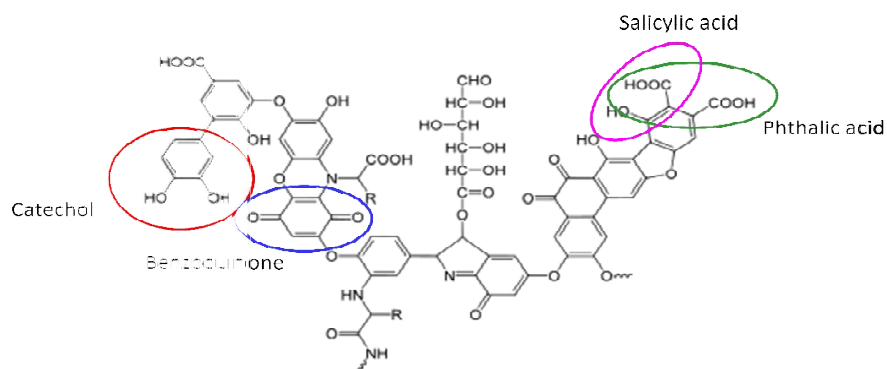


Fig. 2. The molecular structure of a 'model' humic acid compound [taken from Stevenson, (1994)].

Salicylic acid and phthalic acid did not show any detectable reaction with iodate in either the dark or light experiments. Benzoquinone similarly showed no reaction with iodate in the absence of visible light. It is converted to the 2, 5 dihydroxy form on photolysis (Ahmed and Khan, 2000) which has a small visible absorption peak at 480 - 490 nm, giving rise to a distinct pink colouration to the initial colourless solution. However, there was no evidence for any subsequent reaction of this species with iodate.

Finally, UV-visible spectra of a catechol solution were studied under dark and light conditions. Initially, 1.0×10^{-4} M catechol solution was irradiated for 6 hours and UV-Vis spectra were taken at every 2 hours period (shown in figure 3) to check any spectral change.

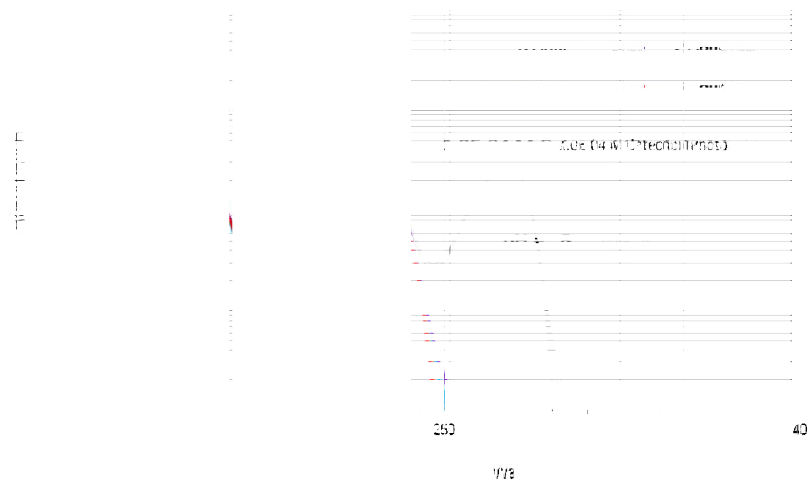


Fig. 3. UV-visible spectra of 1.0×10^{-4} M catechol solution irradiated for a period of 6 hours.

Figure 3 shows that there is no change in the spectrum of the catechol solution upon irradiation. Therefore, catechol itself does not undergo photolysis at visible wavelengths.

Figures 4 and 5 show UV-Vis spectra taken every 2 hours under dark and light conditions, respectively, for a 20 hour period at room temperature from a mixed solution of 1.0×10^{-4} M NaIO_3 and 1.0×10^{-4} M catechol.

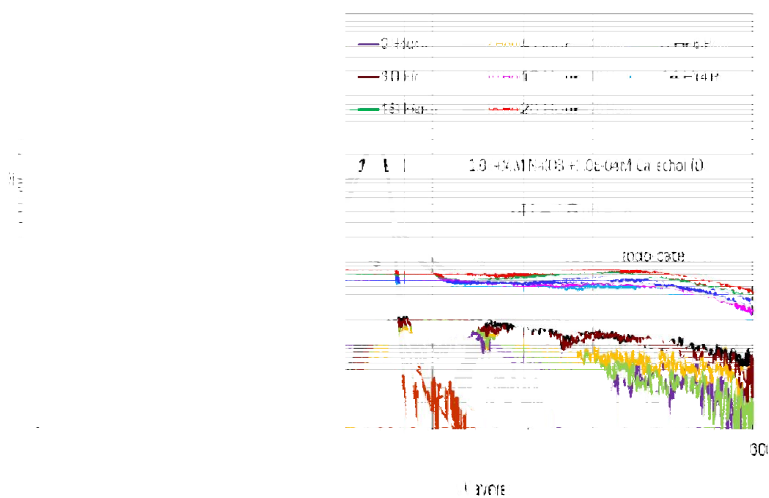


Fig. 4. UV-visible spectra of a mixed solution of 1.0×10^{-4} M NaIO_3 and 1.0×10^{-4} M catechol, taken every 2 hours under dark conditions.

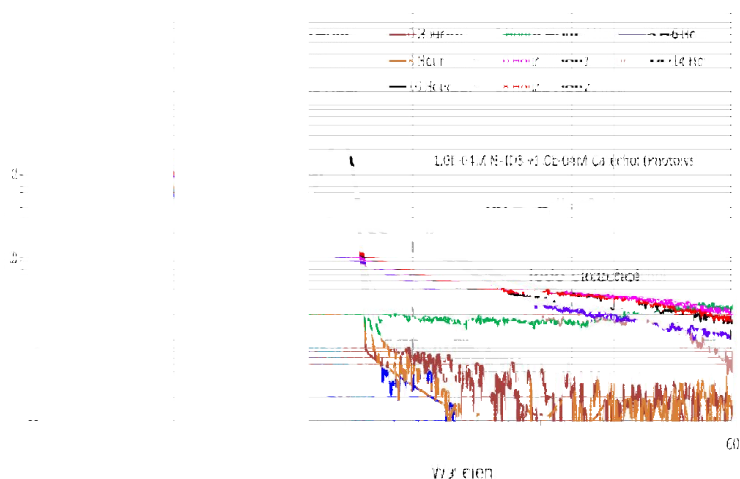


Fig. 5. UV-visible spectra of a mixed solution of 1.0×10^{-4} M NaIO_3 and 1.0×10^{-4} M catechol, taken at every 2 hours in light.

From the figure 4 it is clear that the aqueous solution of IO_3^- and catechol undergoes a dark reaction, with broad absorption peaks of I_3^- at ~ 350 nm and iodo-catechol at ~ 520 nm (Awtrey and Connick, 1951; Nagy *et al.*, 2003; Reiller *et al.*, 2006). Both absorption peaks increase with time, and the formation of I_3^- indicates that both I^- and I_2 are produced in the solution (Schmitz, 2000; Reiller *et al.*, 2006).



The absorption peak of iodo-catechol indicates that the same absorption feature (as in the case of IO_3^- and humic acid) is produced, and a fraction of iodine is substituted at this functional group.

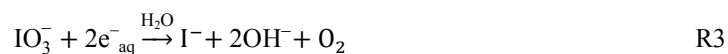
Figure 5 shows that on photolysis the absorption of iodo-catechol decreases and absorption of I_3^- increases. This indicates that the iodo-catechol is photolysed in light and releases I^- back into solution (Sharma and Kharasch, 1968), which enhances the formation of I_3^- .

To find out the exact pathway for the reduction of IO_3^- to I^- and subsequent release of I_2 in the presence of humic acid/catechol and light, the following mechanism was proposed.

Firstly, the photolysis of humic acid (HA) in water releases electrons under irradiation at near-UV/visible wavelengths (Zepp *et al.*, 1987; Frimmel, 1994; Aguer *et al.*, 1999), which then become solvated.



IO_3^- is a known effective scavenger of solvated electrons (e_{aq}^-) (Anbar and Hart, 1965; Barat *et al.*, 1972; Abbé *et al.*, 1980; Spokes and Liss, 1996) and therefore it is reduced to I^- as follows;

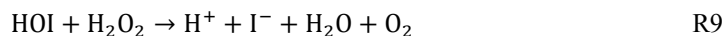


Humic acid is also known to produce H_2O_2 in the presence of light as; (Cooper *et al.*, 1988; Clark *et al.*, 2008)

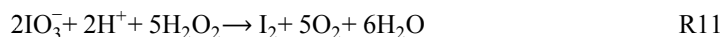




The H_2O_2 produced in solution could then react with Γ^- to form H^+ ions and releases I_2 in solution as; (Kupper *et al.*, 1998)



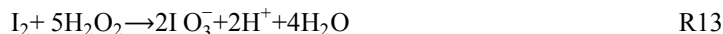
The emission of I_2 from the above proposed mechanism can be represented as follows (Treindl and Noyes, 1993; Vilcu *et al.*, 1998, 2000; Schmitz, 2010);



A fraction of the Γ^- produced in the reacts the humic acid to form iodinated humic acid (Radlinger and Heumann, 2000; Warner *et al.*, 2000; Reiller *et al.*, 2006; Steinberg *et al.*, 2008):



The I_2 released in the reaction can also be oxidised by H_2O_2 to recycle into IO_3^- as (Treindl and Noyes, 1993; Noyes *et al.*, 1995; Vilcu *et al.*, 2000);



Thus, H_2O_2 can act as both an oxidising and reducing agent in the reaction, and is the key intermediate for the reduction process. The reduction process shows second-order reaction kinetics in the presence of $6.6 \times 10^{-5} \text{ M}$ H_2O_2 (an atmospherically relevant concentration in seawater) (Jackson and Hewitt, 1999; Wong and Zhang, 2008). Figure 6 shows the variation of the 1:1 ratio of the concentrations of IO_3^- and H_2O_2 with time and a linear fit to the data points.

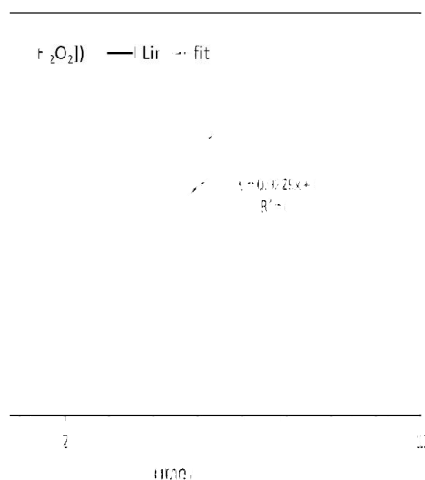
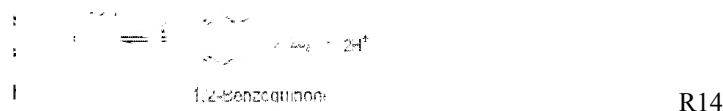


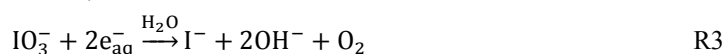
Fig. 6. The variation of 1:1 ratio of the concentrations of IO_3^- and H_2O_2 with time and the second order linear fit of the reaction.

Using the fitting parameters in Figure 6, the second order rate constant of the reduction process was calculated as $1.87 \times 10^{-1} \text{ mol}^{-1} \text{ L sec}^{-1}$.

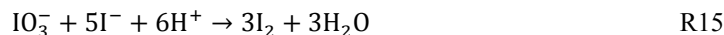
In the case of catechol, the reduction process occurs via the following steps. First, catechol in water produces solvated electrons (e_{aq}^-) under either dark or light (Nematollahi and Rafiee, 2004):



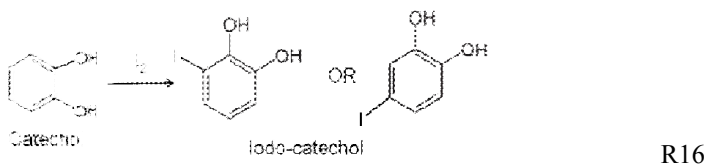
Solvated electrons (e_{aq}^-) reduce IO_3^- to I^- (Anbar and Hart, 1965; Barat *et al.*, 1972; Abbé *et al.*, 1980; Spokes and Liss, 1996):



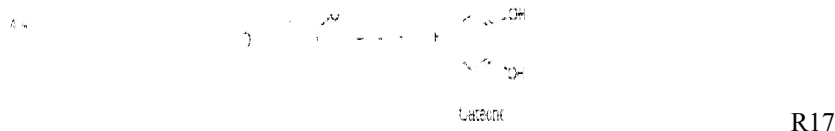
Since, H^+ ions are also produced in the solution, I_2 and I_3^- can form via the following reactions (Schmitz, 1999, 2000; Reiller *et al.*, 2006):



The I_2 product also undergoes a substitution reaction with catechol, forming iodo-catechol (Nolan and O'Connor, 2008):



Under irradiation, iodo-catechol regenerates the iodine back into solution (Sharma and Kharasch, 1968):



CONCLUSIONS

The laboratory experiments were performed in this studies show that the fixing of iodine within humic structures is likely to occur at the aromatic 1, 2 diol groups (*i.e.* like the catechol analogue) and the emission of I_2 to the gas phase from the reduction of IO_3^- to I^- , shows the oscillatory behaviour of the 'Bray-Liebafsky' reaction. This reduction process is enhanced in the presence of H_2O_2 and salinity (Cl^-). H_2O_2 is the key intermediate to explain the oscillatory behavior in the emission of iodine (I_2) from the reduction process. The reduction of IO_3^- to I^- shows second-order reaction kinetics in the presence of H_2O_2 with a rate constant

$(1.87 \pm 0.01) \times 10^{-1} \text{ mol}^{-1} \text{ L sec}^{-1}$. The lifetime of the conversion of IO_3^- to I_2 in the aerosol is at least several days.

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