
EMISSION OF I₂ INTO THE ATMOSPHERE BY THE UPTAKE OF OZONE (O₃) BY IODIDE (I⁻) AT SEAWATER SURFACE

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ABSTRACT:

In the presence of sunlight, Iodine (I₂) is emitted by the uptake of ozone on iodide (I⁻) solution at the sea surface with an uptake coefficient (γ) of $(7.3 \pm 0.2) \times 10^{-7}$ at a temperature of 293 K which could potentially be a source of I₂ to the atmosphere. The measured I₂ flux for the seawater and atmospheric level concentrations of I⁻ (i.e. 100 nM) and ozone (35 ppb) is $(2.9 \pm 0.1) \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ which is ~ 5 times larger than the modelled flux at Cape Verde i.e. $6.0 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$.

KEYWORDS: Iodide----- iodine oxide particles (IOP) -----Oxidation-----Ozone-----Iodine

INTRODUCTION

Recently, it has also been reported that oxidation of iodide (I⁻) at the sea surface resulting from uptake of ozone (O₃) could enhance the emission of I₂ into the MBL (Martino et al., 2009; Sakamoto et al., 2009; Hayase et al., 2010). Also, the ubiquitous presence of the H₂O₂ 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 (I₂) (Kupper et al., 1998; Carpenter, 2003; Pradhan et al., 2010). Emission of I₂ to the atmosphere by the uptake of O₃ and H₂O₂ 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; O'Dowd and De Leeuw, 2007; Mahajan et al., 2010). The recycling of iodine back to the gas phase would also increase the overall O₃-depleting potential of iodine.

In this paper a series of laboratory studies to elucidate the mechanism for the oxidation of aqueous I⁻ in the presence of sunlight, and the subsequent emission of I₂. A series of IOP formation and detection experiments were conducted to investigate three potentially important processes likely to participate in the emission of I₂ to the atmosphere from seawater or sea salt aerosol by the uptake of O₃ on an aqueous I⁻ were conducted.

EXPERIMENTAL

The experimental setup was to study the oxidation of I⁻ in the presence of sunlight and the emission of I₂ to the gas phase shown in figure 1. The subsequent emission of I₂ from I⁻ was measured indirectly by its photo-oxidation in a second cell in the presence of O₃, leading to iodine oxide particle (IOP) formation and detection using an electrical mobility spectrometer (EMS VIE10: Tapcon GmbH). Nitrogen gas (N₂) was flowed through the cell to flush out the I₂ produced which was then transported to the IOP generation cell. At this point an additional flow of N₂ and an O₃ flow were added to the generation cell. Ozone (O₃) was generated using a mercury pen lamp adjacent to a flow of oxygen (O₂). A tungsten lamp was used to photolyse the I₂ molecules to produced iodine atoms and hence IOPs were produced by the reaction of iodine atom and O₃.

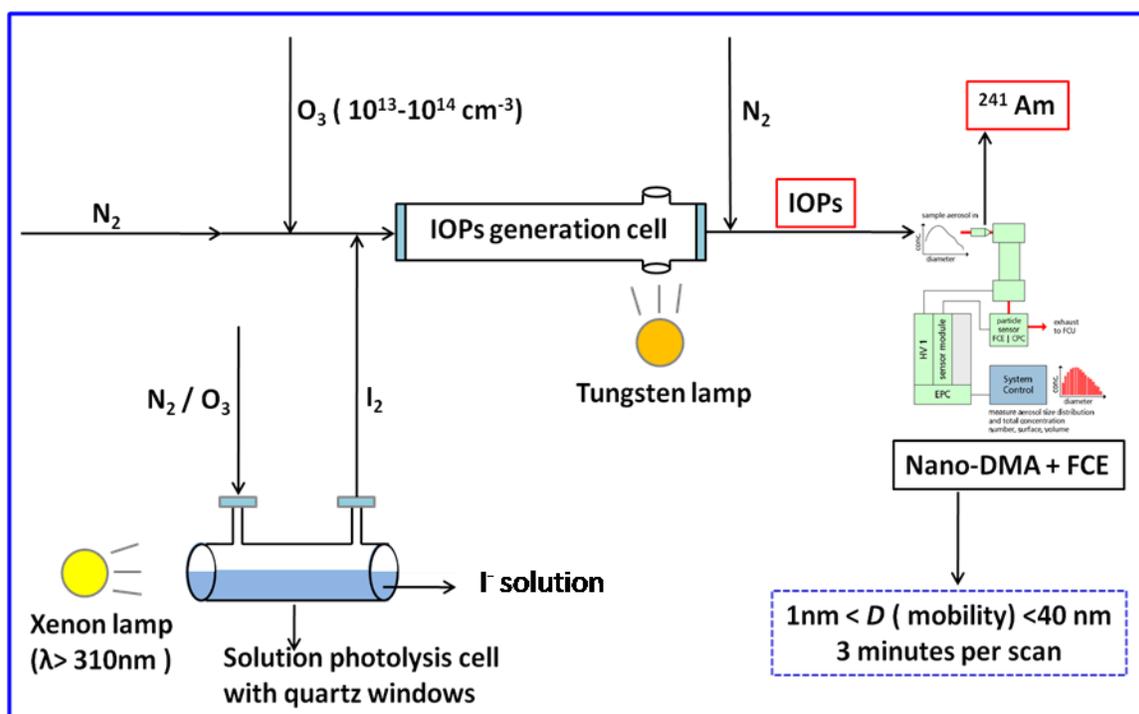


Figure 1: Schematic of experimental set-up used to study the oxidation of I^- and subsequent emission of I_2 .

RESULTS AND DISCUSSIONS

Oxidation of I^- and the emission of I_2 by the uptake of O_3 on I^- solution

A set of experiments were conducted to measure the I_2 emitted in the form of IOPs formation using the EMS from the oxidation of I^- under either dark or irradiation of visible light ($\lambda > 310$ nm). I_2 was measured by the EMS following conversion of IOPs. However, no indication for the emission of I_2 in the dark was seen. The solution was then irradiated using near UV-visible light. The effect of O_3 uptake on 1.0×10^{-7} M I^- solution at room temperature (293 ± 1 K) for the emission of I_2 from the surface of seawater. A mixture of N_2 and O_3 was flowed through the headspace of the solution cell to flush out any I_2 produced by the uptake of O_3 on I^- . Any I_2 produced was then transported to the IOP generation cell.

Figure 2 shows the effect of O_3 uptake on 1.0×10^{-7} M I^- solution, with increased IOP formation occurring as the O_3 concentration is increased whereas, figure 3 shows the variation of IOP mass with increasing the O_3 concentration.

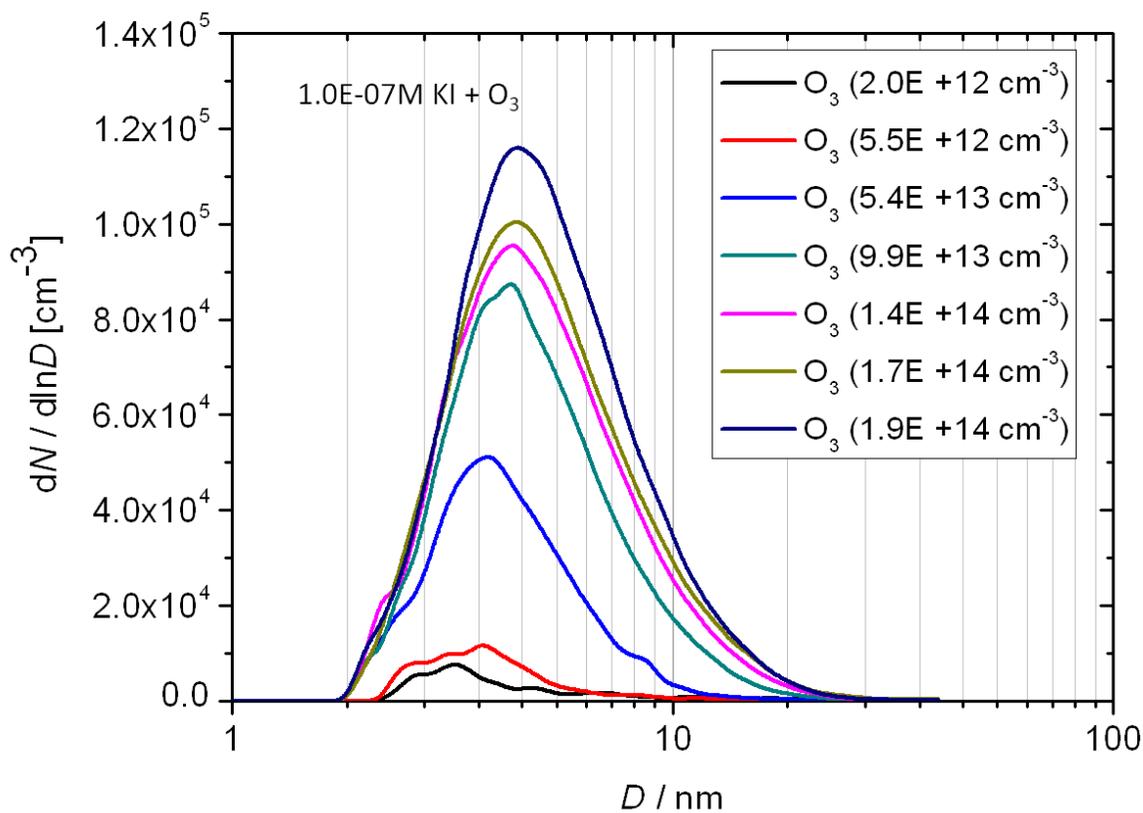


Figure 2: Size distribution of Iodine oxide particles (IOPs) formed due to the uptake of O₃ into an I⁻ solution.

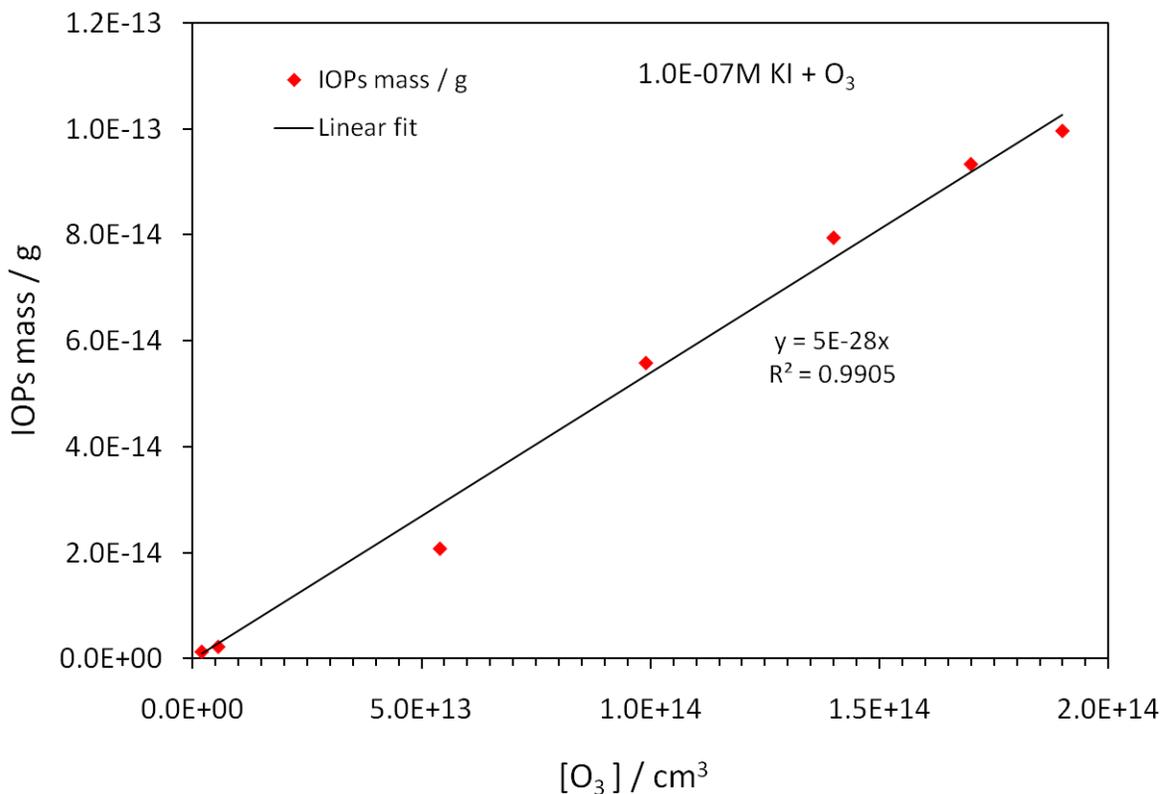
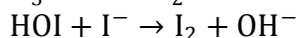
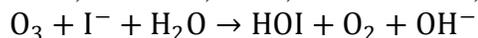


Figure 3: Variation of IOP mass with increasing concentration of ozone on I⁻ solution.

Figure 2 and 3 shows that both particles size distribution and IOP mass increase as the concentration of O_3 is increased. This indicates that more I_2 is emitted with increasing O_3 concentration and emission of I_2 by the uptake of O_3 on aqueous I^- solution, consistent with the following mechanism (Bichsel and von Gunten, 1999; Liu et al., 2001; Martino et al., 2009; Sakamoto et al., 2009):



Uptake coefficients [the probability that an O_3 molecule strikes the aqueous I^- surface returns an I_2 molecule to the gas phase (Garland et al., 1980; Garland and Curtis, 1981; Gallagher et al., 2001; Mahajan et al., 2010)] of O_3 on I^- solution were then calculated from the IOP mass measured in the experiments and plotted in Figure 4.

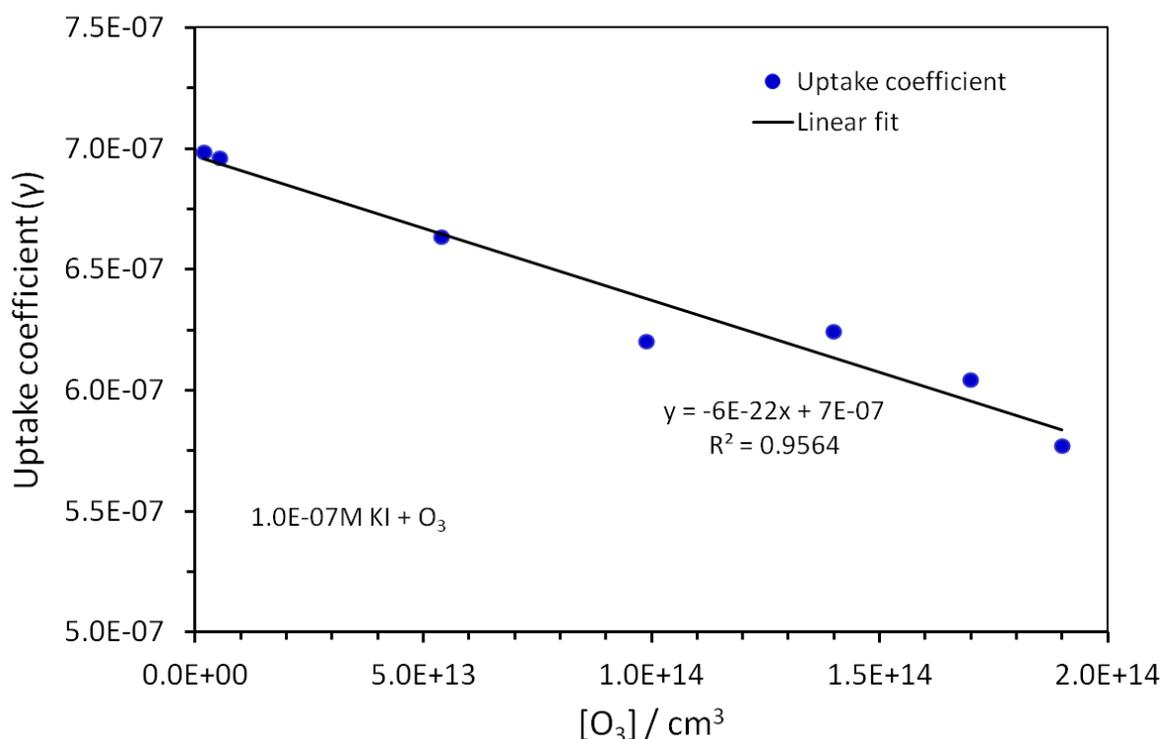


Figure 4: Variation of uptake coefficients of O_3 on $1.0 \times 10^{-7} M I^-$ solution.

Figure 4 shows that uptake coefficient of O_3 decreases linearly with increasing concentration of O_3 . Using the fitting equation in the Figure 4, the uptake coefficient of an atmospherically relevant concentration of O_3 (i.e. 35ppb) (Mahajan et al., 2009; Mahajan et al., 2010) was evaluated. The evaluated value of uptake coefficient was found to be $(7.3 \pm 0.2) \times 10^{-7}$. The I_2 flux (which is defined as the uptake coefficient $\times O_3$ concentration) was then evaluated using O_3 concentration and uptake coefficient. The I_2 flux was evaluated as $(2.9 \pm 0.1) \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ which is ~ 5 times larger than the modelled flux at Cape Verde i.e. $6.0 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ (Mahajan et al., 2010). However, this flux is only due to I^- solution at a temperature 293 K. Further study will be needed to see any effects of salinity (Cl^-), DOM, and temperature to define the I_2 flux in real matrix.

CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

From these laboratory experiments, the following insights can be drawn regarding the emission of iodine by the uptake of O_3 by I^- at seawater surface. Iodine (I_2) is emitted by the uptake of ozone on iodide (I^-) solution at the sea surface with an uptake coefficient (γ) of $(7.3 \pm 0.2) \times 10^{-7}$ at a temperature of 293 K which could potentially be a source of I_2 to the atmosphere. The measured I_2 flux for the seawater and atmospheric level concentrations of I^- (i.e. 100 nM) and ozone (35 ppb) is $(2.9 \pm 0.1) \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ which is ~ 5 times

larger than the modelled flux at Cape Verde i.e. $6.0 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$. However, further study will be needed to see any effects of salinity (Cl), DOM, and temperature to compare the I_2 flux in real matrix.

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REFERENCES

1. Bichsel, Y., von Gunten, U., 1999. Oxidation of Iodide and Hypoiodous Acid in the Disinfection of Natural Waters. *Environmental Science & Technology* 33, 4040-4045.
2. Carpenter, L.J., 2003. Iodine in the marine boundary layer. *Chemical Reviews* 103, 4953-4962.
3. Gallagher, M.W., Beswick, K.M., Coe, H., 2001. Ozone deposition to coastal waters. *Quarterly Journal of the Royal Meteorological Society* 127, 539-558.
4. Garland, J.A., Curtis, H., 1981. Emission of Iodine From the Sea Surface in the Presence of Ozone. *Journal of Geophysical Research-Atmospheres* 86, 3183-3186.
5. Garland, J.A., Elzerman, A.W., Penkett, S.A., 1980. The Mechanism for Dry Deposition of Ozone to Seawater Surfaces. *Journal of Geophysical Research-Atmospheres* 85, 7488-7492.
6. Hayase, S., Yabushita, A., Kawasaki, M., Enami, S., Hoffmann, M.R., Colussi, A.n.J., 2010. Heterogeneous Reaction of Gaseous Ozone with Aqueous Iodide in the Presence of Aqueous Organic Species. *The Journal of Physical Chemistry A* 114, 6016-6021.
7. Kupper, F.C., Schweigert, N., Gall, E.A., Legendre, J.M., Vilter, H., Kloareg, B., 1998. Iodine uptake in Laminariales involves extracellular, haloperoxidase-mediated oxidation of iodide. *Planta* 207, 163-171.
8. Liu, Q., Schurter, L.M., Muller, C.E., Aloisio, S., Francisco, J.S., Margerum, D.W., 2001. Kinetics and Mechanisms of Aqueous Ozone Reactions with Bromide, Sulfite, Hydrogen Sulfite, Iodide, and Nitrite Ions. *Inorganic Chemistry* 40, 4436-4442.
9. Mahajan, A.S., Oetjen, H., Saiz-Lopez, A., Lee, J.D., McFiggans, G.B., Plane, J.M.C., 2009. Reactive iodine species in a semi-polluted environment. *Geophysical Research Letters* 36.
10. Mahajan, A.S., Plane, J.M.C., Oetjen, H., Mendes, L., Saunders, R.W., Saiz-Lopez, A., Jones, C.E., Carpenter, L.J., McFiggans, G.B., 2010. Measurement and modelling of tropospheric reactive halogen species over the tropical Atlantic Ocean. *Atmospheric Chemistry and Physics* 10, 4611-4624.
11. Martino, M., Mills, G.P., Woeltjen, J., Liss, P.S., 2009. A new source of volatile organoiodine compounds in surface seawater. *Geophysical Research Letters* 36.
12. McFiggans, G., Coe, H., Burgess, R., Allan, J., Cubison, M., Alfarra, M.R., Saunders, R., Saiz-Lopez, A., Plane, J.M.C., Wevill, D.J., Carpenter, L.J., Rickard, A.R., Monks, P.S., 2004. Direct evidence for coastal iodine particles from Laminaria macroalgae - linkage to emissions of molecular iodine. *Atmospheric Chemistry and Physics* 4, 701-713.
13. O'Dowd, C.D., De Leeuw, G., 2007. Modelling iodine particle formation and growth from seaweed in a chamber. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* 365, 1753-1774.
14. O'Dowd, C.D., Hoffmann, T., 2005. Coastal new particle formation: A review of the current state-of-the-art. *Environmental Chemistry* 2, 245-255.
15. Pradhan, M., Kyriakou, G., Archibald, A.T., Papageorgiou, A.C., Kalberer, M., Lambert, R.M., 2010. Heterogeneous uptake of gaseous hydrogen peroxide by Gobi and Saharan dust aerosols: a potential missing sink for H_2O_2 in the troposphere. *Atmospheric Chemistry and Physics* 10, 7127-7136.
16. Sakamoto, Y., Yabushita, A., Kawasaki, M., Enami, S., 2009. Direct Emission of I_2 Molecule and IO Radical from the Heterogeneous Reactions of Gaseous Ozone with Aqueous Potassium Iodide Solution. *The Journal of Physical Chemistry A* 113, 7707-7713.
17. Saunders, R.W., Plane, J.M.C., 2005. Formation pathways and composition of iodine oxide ultra-fine particles. *Environmental Chemistry* 2, 299-303.