Atmospheric Iodine Chemistry

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There has been growing interest in the impact of reactive iodine species in the troposphere and lower stratosphere (Saiz-Lopez et al., 2012a), following observations of iodine oxide radicals (IO and OIO) at coastal (Alicke et al., 1999; Saiz-Lopez et al., 2007; Saiz-Lopez and Plane, 2004) and open ocean (Read et al., 2008; Prados-Roman et al., 2015a; Mahajan et al., 2012; Grossmann et al., 2013) locations, as well as in the free troposphere (Dix et al., 2013; Volkamer et al., 2015). Iodine alters the oxidizing capacity of the atmosphere by destroying ozone (O_3) and by changing odd hydrogen (OH, HO_2) and nitrogen oxide (NO, NO_2) radical chemistry. Furthermore, the higher iodine oxide species (I_2O_x, $x \geq 2$) condense spontaneously to form ultrafine iodine oxide particles (IOPs) which may grow by the uptake of water and acids (e.g. H_2SO_4) to form cloud (or ice) condensation nuclei and hence impact climate on a regional or global scale (Saunders et al., 2010; Huang et al., 2010; Gomez Martin et al., 2013). IOP formation is also of concern in nuclear reactor accidents (Dickinson et al., 2014).

Recent work has shown that the major source of iodine is the emission of HOI and I_2 from the sea surface, resulting from the uptake of O_3 and its reaction with iodide (I^-) ions (Carpenter et al., 2013; MacDonald et al., 2014). There is therefore a potentially significant negative feedback between enhanced iodine emissions and O_3 in polluted outflows from continents (Prados-Roman et al., 2015b). Because the major sources of iodine - whether iodocarbons or I^- ions - are biogenic (Saiz-Lopez et al., 2012a; Carpenter et al., 2003), there are probable feedbacks between iodine chemistry and climate (Saiz-Lopez et al., 2012b).

The iodine paradox is this: if iodine oxides condense so readily to form new particles, how are species such as IO and OIO able to persist in the atmosphere and cause O_3 depletion? This problem is most obvious in Antarctica, where we measured some of the highest levels of IO seen anywhere on Earth in air that had freshly advected over sea ice, but also recorded significant levels of IO *in air which had spent several days over the interior of the continent* (Saiz-Lopez et al., 2007). Satellite observations have shown substantial levels of IO close to the South Pole (Schönhardt et al., 2008). More recently, aircraft measurements have recorded surprisingly high levels of IO in the free troposphere over the tropical Pacific (Dix et al., 2013; Volkamer et al., 2015), which are consistent with rapid convective transport of iodine species from the marine boundary layer. Rapid vertical transport in the tropics should also cause a significant injection of active iodine into the lower stratosphere, where iodine is far more O_3-depleting than Br or Cl. However, somewhere along the way in the upper troposphere the iodine "disappears". This is an important mystery that needs to be solved.

The figure below is a simplified schematic of atmospheric iodine photochemistry, based upon current knowledge of gas- and condensed-phase processes. Dashed lines represents photolysis, and dotted lines illustrate phase equilibration with aerosols (IX = I_2, ICl and IBr). I atoms, produced from the photolysis of I_2, HOI or an iodocarbon (e.g., CH_2I_2), are oxidized to IO by O_3, followed by the IO self reaction which has two important channels:

$$IO + IO \rightarrow OIO + I \quad \text{(R1a)}$$

$$IO + IO \rightarrow IOIO \quad \text{(R1b)}$$

At atmospheric pressure and 295 K, OIO and the asymmetric dimer IOIO are produced with branching ratios of ~ 40% and 60%, respectively (Gomez Martin et al., 2007). However, theoretical calculations (Kaltsoyannis and Plane, 2008) on the dimer show that it is relatively unstable and decomposes to OIO + I in ~ 0.1 s at 295 K. The OIO that is produced in reaction 1 may then recombine with IO or itself (Gomez Martin et al., 2013):

$$OIO + IO \rightarrow I_2O_3 \quad \text{(R2)}$$

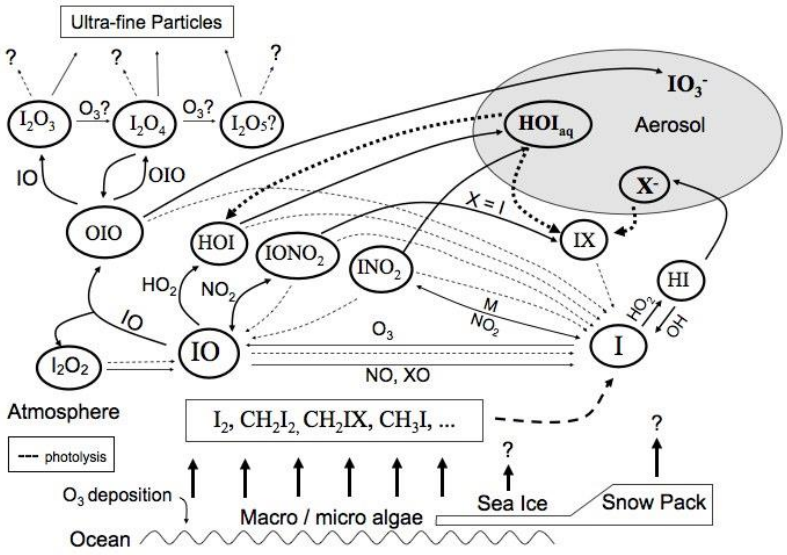
$$OIO + OIO \rightarrow I_2O_4 \quad \text{(R3)}$$

Some I_2O_5 may also be produced by further oxidation of I_2O_4 in the presence of O_3. The higher oxides can then undergo one of the three fates: photolysis, polymerization to form IOPs, or uptake on pre-existing marine aerosol (where the resulting iodate (IO_3^-) ions are photochemically reduced in the presence of humic material (Saunders et al., 2012)). **Understanding how these processes compete is probably the remaining major uncertainty in the gas-phase chemistry of iodine.**

The photolysis cross sections

$$I_2O_x\ (x = 2\text{-}5) + h\nu \rightarrow \text{products (IO, OIO etc.)} \quad \text{(R4-R7)}$$

are crucial for explaining the longevity of IO and OIO in the boundary layer and free troposphere (Saiz-Lopez et al., 2008; Saiz-Lopez et al., 2012a). Gas-phase measurements of the photolysis cross sections and photolysis products of these molecules is now possible following the successful use of Laser Photo-ionization Time-of-Flight Mass Spectrometry (LP-ToF-MS) at Leeds to detect the higher oxides for the first time (Gomez Martin et al., 2013). Furthermore, electronic structure calculations have recently been combined with RRKM theory to show that dimerization of I_2O_4 is probably the key step in IOP nucleation (Gomez Martin et al., 2013), although other polymerization reactions may be significant. The rate coefficients for these reactions now need to be measured.



Objectives:

The goal of this project will be to use a combination of laboratory measurements and atmospheric modelling to solve the “iodine paradox”. Specific objectives:

1. Measure the photolysis cross sections and products of I_2O_3, I_2O_4 and I_2O_5
2. Measure rate coefficients for the polymerization reactions of these higher oxides
3. Use the results of the laboratory studies to assess the impact of iodine chemistry in the troposphere and lower stratosphere. Initially, the 1-D model boundary layer THAMO (Saiz-Lopez et al., 2008; MacDonald et al., 2014) will be used, followed by the global chemical transport model TOMCAT/SLIMCAT (Hossaini et al., 2013).

There may also be the opportunity to participate in fieldwork, carrying out measurements of iodine species under the supervision of Dr Alfonso Saiz-Lopez (director of the Department of Atmospheric Chemistry and Climate at CSIC in Madrid).

Potential for high impact outcome:

Understanding the impacts of iodine in the free troposphere and lower stratosphere – where iodine is much more ozone-depleting than chlorine or bromine, and observations and models disagree significantly – is a high impact topic. Furthermore, as iodine source emissions increase because of increasing wind stress at the ocean surface and increasing boundary layer ozone, and the strength of convective transport is forecast to increase, this subject will become even more important in the future.

Training:

This project will provide a high level of specialist scientific training in: (i) laboratory kinetic and photochemistry studies, using advanced laser and mass spectrometry techniques; (ii) development of the chemistry within a world-leading atmospheric chemistry-climate model.

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