From the measurement of halogenated species to iodine particle formation

Xucheng He
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Ohjaajat: Mikko Sipilä
Matti Rissanen

Tarkastajat: Markku Kulmala
Tuukka Petäjä

UNIVERSITY OF HELSINKI
DEPARTMENT OF PHYSICS
PL 64 (Gustaf Hällströmin katu 2)
00014 Helsingin yliopisto
Halogenated species have significant impact on atmospheric composition, including catalytic ozone destruction and influence on HOx and NOx cycles. Halogens are also involved in marine and coastal new particle formation, a process that can ultimately affect Earth’s radiation balance. However, the exact processes governing halogen chemistry and halogen new particle formation have been puzzling the community for years.

One of the major difficulties in understanding these processes has been the lack of techniques able to measure inorganic halogenated radicals and stable species simultaneously both in laboratory and in ambient conditions. This is because previous spectroscopic and mass spectrometric methods utilized could only measure one, or a few halogenated species at once, while most of the halogenated species existing in the atmosphere were likely un-measurable. Here we present new chemical ionization (CI) mass spectrometric methods to measure over 20 halogenated species simultaneously at ambient pressure. These species include halogen oxides, halogen acids, nitrogen containing halogen species, halogen radicals and molecular halogens, covering the major categories present in the ambient atmosphere. The methods will further be deployed into field measurements in various locations around the world to better understand the impact of halogenated species to the atmosphere.

A recent study revealed homogeneous nucleation processes by (HIO3) (brackets here indicate all the isomers). However, the exact formation mechanism of (HIO3) has not been investigated in laboratory experiments. We deployed the above mentioned new measurements methods to study the formation mechanism of (HIO3) in dedicated flow tube experiments. The results show that OIO and OH radical could form (HIO3) as indicated by previous quantum mechanism calculations. In addition, two novel (HIO3) formation pathways from photo-oxidation of CH2I2 and molecular iodine were suggested. One pathway shows that the homogeneous bimolecular reaction of CH2IOO could form (HIO3), while the other suggests either iodine radical or iodine monoxide could react with ozone and water vapor to form (HIO3). These findings could potentially explain the large amount of (HIO3) observed.

Beside from coastal areas, the first ambient data showing the existence of (HIO3) in various locations in the world, including a boreal forest site, a wet land site, Greenland and Antarctica are also presented here. These findings indicate that the (HIO3) might be involved in nucleation processes in locations other than coastal areas.

More than (HIO3), sulfuric acid is known for its active role in atmospheric nucleation over different environments. However, the knowledge of its gas phase oxidation processes is not complete. Our laboratory results imply that iodinated species might be able to oxidize SO2 to sulfuric acid through some yet unknown mechanisms. Further studies are needed to understand the exact mechanisms in the oxidation processes and how important this mechanism could be in the ambient atmosphere.
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0.1 Terminology in the thesis

Br$_y$: total gas phase inorganic bromine
I$_y$: total gas phase inorganic iodine
VOC: volatile organic compounds
VOIC: volatile organic iodine compounds
(X) for example (HIO$_3$) means no specific isomer is defined. This only means the molecular expression
UVC: pen mercury lamp
UVA: two fluorescent ultraviolet lamps connected to a controller. The peak spectra is roughly around 350 nm.
sccm: unit for flow speed. Standing for standard cubic centimeter per minute
H$_2$O: when this term is used in the plots. This means humidified nitrogen or humidified synthetic air flow
Mass defect: the difference between the exact mass and nominal mass of a compound
MBL: marine boundary layer
ODE: ozone depletion events
CTM: chemical transport model
CIMS: chemical ionization mass spectrometer
CI: chemical ionization
APi-TOF: atmospheric pressure interface time of flight mass spectrometer
CI-APi-TOF: chemical ionization APi-TOF
BrCI: bromide based CI-APi-TOF
ICI: iodide based CI-APi-TOF
NCI: nitrate based CI-APi-TOF
IMR: ion-molecule reaction chamber
slm: standard liter per minute
sccm: standard cubic centimeter per minute
PTFE: Polytetrafluoroethylene
MFC: mass flow controller
DMS: dimethyl sulfide
DMSO: dimethyl sulfoxide
UVA: two UVA fluorescent lamps connected by a controller
sCI: stabilized Criegee intermediate
LOD: limit of detection (detection limit of an instrument)
CCN: cloud condensation nuclei
MS: mass spectrometry
DOAS: differential optical absorption spectrometer
LP-DOAS: long path differential optical absorption spectrometer
AMS: aerosol mass spectrometer
RHS: reactive halogen species. Includes Cl, ClO, OClO, HOCl, Cl₂, BrCl, ClNO₂, Cl, HCl, Br, BrO, HOBr, Br₂, I, I₂, HOI, IO, OIO
RIS: reactive iodine species. Includes I, I₂, HOI, IO, OIO
1. Introduction

Halogen species play an important role in changing atmospheric composition. The discovery of how halogen radicals, for example, chlorine atoms, could deplete ozone in stratosphere, led to the 1995 Nobel Prize in Chemistry to Paul Crutzen, Mario Molina and F. Sherwood Rowland. However, at their time, the importance of tropospheric halogens wasn’t yet discovered, until the first implication got from the high Arctic, where ODEs were found in 1980s. Bromine species were later on blamed for this phenomenon. Since then, the sources of gas phase bromine containing compounds and the chemistry of their gas phase reaction became a hot topic which led to a deeper understanding of their emission and fates. Interest was also given on gas phase iodine containing species due to their active role in marine new particle formation processes, as well as their dominant role in catalytic destruction of ozone over other halogen species, in marine boundary layer (Sherwen et al., 2016b).

1.1 Global impact of halogens

1.1.1 Tropospheric halogen induced ozone depletion

A large amount of tropospheric ozone loss occurs in tropical marine boundary layer (Read et al., 2008). This phenomenon had been thought due to the fast photolysis of ozone in presence of substantial amount of water vapor. However, Read et al. (2008) found that the daytime destruction of O₃ could not be explained by known mechanisms without the presence of halogen chemistry. They concluded that halogen chemistry plays an essential role in ozone destruction in tropical Atlantic marine boundary layer, while neglecting halogen chemistry would lead to significant error in estimating global ozone budgets.

A key process in initiation of halogen chemistry is the photolysis of molecular halogens ($X₂$), which can be represented as

$$X₂ + hv \rightarrow 2X$$ (1.1)

The $hv$ in the equation represents solar radiation.

The most significant fact that makes reaction (1.1) important is that the absorption
spectra of three molecular halogens are within the range of near-UV (Saiz-Lopez et al., 2004; Simpson et al., 2015), which means at the surface level, their photolysis rates are still significant.

After the photolysis of dihalogens, two reactive halogen radicals are produced, which further undergo reaction

\[ X + O_3 \rightarrow XO + O_2 \]  \hspace{1cm} (1.2)

The photolysis of the produced halogen monoxides, especially bromine monoxide and iodine monoxide is rather rapid, normally at the order of seconds to minutes (Kanaya et al., 2003). The reaction can be represented as

\[ XO + hv \rightarrow X + O \]  \hspace{1cm} (1.3)

which produces an oxygen atom and a halogen atom. The oxygen atom reacts with oxygen molecule in the atmosphere to produce \( O_3 \) through

\[ O + O_2 \rightarrow O_3 \]  \hspace{1cm} (1.4)

to create a null cycle, in which the ozone concentration is not affected. However, the lifetime of chlorine monoxide is much longer, which makes the null cycle mentioned above not valid for chlorine.

Nevertheless, the importance of the halogen atoms and halogen oxides lies in their ability in depleting ozone in the atmosphere. For example, the reactions

\[ XO + XO \rightarrow X_2 + O_2 \]  \hspace{1cm} (1.5)

\[ XO + XO \rightarrow X + X + O_2 \]  \hspace{1cm} (1.6)

\[ XO + XO \rightarrow OXO + X \]  \hspace{1cm} (1.7)

could lead to the catalytic ozone depletion. As the reactions (1.5) and (1.6) produce equal amount of dihalogens or halogen atoms, while the ozone is converted to \( O_2 \). The reaction (1.7) produces half the amount of halogen atoms which reacted with ozone which also destroys ozone. In addition, the varied fates of \( OXO \) radical could either deposit on particles or surfaces, or recycle back to iodine radical or iodine monoxide to further deplete ozone.

The second catalytic cycle to deplete \( O_3 \) involves reactions with \( HO_2 \) radical through

\[ X + O_3 \rightarrow XO + O_2 \]  \hspace{1cm} (1.8)

\[ XO + HO_2 \rightarrow HOX + O_2 \]  \hspace{1cm} (1.9)

\[ HOX + hv \rightarrow X + OH \]  \hspace{1cm} (1.10)
These reactions convert one HO₂ radical and one O₃ to one OH radical. This means this cycle not only catalytically destroys O₃ but also reduces the HO₂/OH ratio in the atmosphere.

The third cycle involves NOₓ, which can influence ozone levels in polluted environments. The processes in this cycle could be found in

\[
\begin{align*}
    \text{net : } & \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \\
\end{align*}
\]  

(1.11)

After the photolysis of iodine precursors, iodine radical reacts with ozone to produce halogen monoxide. Halogen monoxide can react with NO₂ to produce XONO₂. The rapid photolysis of XONO₂ produces a halogen radical and NO₃ radical, which decompose to NO and O₂ under solar radiation. The net effect of this cycle converts two ozone molecules to three oxygens molecules.

The relative importance of three halogens are different over various regions in the world. Saiz-Lopez et al. (2007); Saiz-Lopez and Blaszczak-Boxe (2016) concluded that the iodine is more important in destroying ozone over coastal Antarctica areas, while bromine’s role is comparatively less. However, over Arctic sea ice, bromine dominates in ozone destruction while the role of iodine is absent (Simpson et al., 2007).

However, halogens are not only destroying ozone. A study suggested that chlorine emissions (Cl₂ and HOCl) and Cl– from sea-salt could increase the O₃ concentrations, as the rapid photolysis of ClINO₂ could lead to the production of NO₂ which further releases an oxygen atom to form O₃ with Oxygen molecule. These processes are effective in, for example, polluted coastal environments.

### 1.1.2 Effects of halogen on NOₓ and organics

As shown by the third cycle in last section, halogens change the NO to NO₂ ratio, as well as reduce the NOₓ concentrations by hydrolysis of XNO₃. These coupled effects perturb NOₓ concentrations in the atmosphere, and indirectly influence O₃ budget (von Glasow et al., 2004).

Halogens are also involved in the oxidation of VOCs (mainly Br and Cl). In the modeling results of Sherwen et al. (2016b), the oxidation loss of ethane (C₂H₆), propane(C₃H₈) and acetone (CH₃C(O)CH₃) by chlorine radicals are calculated to be 27%, 15% and 14% respectively.
on a global scale. It was also suggested that the losses of other VOCs due to chlorine is globally small. However, it should be noted that in the modeling results of Sherwen et al. (2016b), the chlorine emission is at the lower limit, while in the real atmosphere it might be more important.

1.1.3 Halogen containing aerosols

Aerosols play an important role in earth’s climate system because of their direct or indirect roles in interacting with solar or terrestrial radiations (Russell et al., 1994). Aerosols could also serve as cloud condensation nuclei (CCN) which further forms clouds to influence the radiation balance of the globe (Andreae and Rosenfeld, 2008).

Marine is an important source of halogen-containing aerosols in the atmosphere. Wind stress at the sea surface could result in primary aerosol production (O’Dowd and de Leeuw, 2007) which contains chloride. Secondary aerosol formation involves, first, that new particle formation occurs via the nucleation of stable small clusters. Following the new particle formation processes, small clusters could further condense on the formed aerosols to grow the aerosol size. The second way that could grow the aerosols is via heterogeneous reactions and aqueous phase oxidation of dissolved gases in the aerosols (O’Dowd and de Leeuw, 2007). In marine environment, sulfur species were speculated the major chemical component involved. Later studies revealed that iodine oxides were associated with regular new particle formation events in coastal areas (O’Dowd et al., 1998). In this work, we only discuss about iodine particle formation processes in coastal areas.

1.2 Sources of halogen compounds

Halogenated species have significant impact on atmospheric composition, including catalytic ozone destruction and influence on HO\textsubscript{X} and NO\textsubscript{X} cycles (Sherwen et al., 2016b; McFiggans et al., 2000; Chameides and Davis, 1980). Halogens are also involved in marine and coastal new particle formation, a process that can ultimately affect Earth’s radiation balance. To estimate the impact of halogenated species in a global scale, we need to understand their global distribution and sources.

Most of the emissions of Br and I are from the tropics, while the emission of chlorine species are more widely distributed. Due to the longer lifetime of the source compounds of bromine than that of iodine, bromine compounds are more equally spread throughout the atmosphere than iodine. This also suggests the importance of bromine compounds in higher atmosphere might be more significant (Sherwen et al., 2016b). For iodine species specifically, the major oceanic sources of atmospheric iodine are iodocarbons produced by marine biota and physical processes, such as aerosol mediated halogen release (Gravestock et al., 2010) and I\textsubscript{2}
(and iodocarbons) from reaction of dissolved organic matter with iodide and ozone (Martino et al., 2009). However, the relative importance of different halogenated species are diverse over various landscapes in the world. Halogen sources are discussed in the following sections according to landscape types, with a focus on iodine species.

### 1.2.1 Open ocean sources

Oceans cover 71% of the Earth’s surface and it is important to understand the halogen emissions from the sea water. In the sea water, chloride and bromide are abundant. However, different with bromide and chloride, iodide is much less abundant because of its role as a nutrient in biological processes (Simpson et al., 2015). The organic iodine species are thus believed to be more abundant in oceans (Carpenter, 2003; Saiz-Lopez et al., 2012). Thus, the processes leading to the emission of halogenated species are very different for iodinated species to that of chlorinated and brominated species (Simpson et al., 2015).

It is know that the biota can produce halogenated organic compounds, for instance, alkyl bromides and alkyl iodides (Simpson et al., 2015), which have atmospheric lifetimes from minutes to months (Saiz-Lopez et al., 2012). Jones et al. (2010) suggested that the maximum concentrations of volatile organic iodine compounds (VOIC) over open oceans were located in $15 - 25^\circ$N region. Also the same study implied that the CH$_2$ClI concentration is much higher in shelf water and upwelling system, potentially due to some biological processes producing VOIC in these waters. Their results also show that the dihalomethanes, which mainly consist of CH$_2$ClI, CH$_2$I$_2$ and CH$_2$IBr, produce comparable sources of reactive iodine compared to that of CH$_3$I, which has been previously thought the main VOIC source. It is worth noting that CH$_2$I$_2$ has a short atmospheric lifetime of about 5 mins and the estimation of its concentration over sea surface is thereby important. This is because if there is a hot spot of CH$_2$I$_2$, the rapid photolysis of CH$_2$I$_2$ could impact the local ozone concentration and particle formation processes. The local effects of other abundant VOICs are comparably smaller due to their relatively slow photolysis in the atmosphere, as their atmospheric photolysis lifetime range from hours (CH$_3$I) to days (CH$_3$I).

Alkyl chloride and alkyl bromide are the major natural chlorine emissions (Khalil et al., 1999) and bromine emissions respectively (Ordóñez et al., 2012). However, for iodine species, Carpenter et al. (2013) suggested a mechanism of emitting molecular iodine and HOI gases through the reaction of O$_3$ with the iodide ion in the ocean surface water. More specifically, according to modeling results, hypoiodous acid is emitted at a rate 10 times that of molecular iodine. The hypoiodous acid emission is thus believed the largest iodine emission from the sea water compared to molecular iodine and organoiodide emissions Sherwen et al. (2016a). At the meantime, this work challenges previous assumption that marine biological processes are
the main source of oceanic iodine sources (Simpson et al., 2015) as the heterogeneous reaction producing hypoiodous acid and molecular iodine from open ocean does not require biological processes.

1.2.2 Coastal sources

Macroalgae in coastal areas have periodic stress because of tidal activities. That is when the tide retreat, they are exposed to the air, and when the tide springs, they are submerged by the salty sea water. A relationship of a low tide and halogen emission from the macroalgae was observed by Carpenter et al. (1999). At the time CH$_3$I was measured the most abundant iodine emission. However, the most important species controlling gas phase iodine radical production are CH$_2$I$_2$ and CH$_2$BrI because of their rapid photolysis rates which produce iodine radicals more efficiently than CH$_3$I. On average, CH$_2$I$_2$ and CH$_2$BrI are about 10% to 20% of the concentration of CH$_3$I. However, McFiggans et al. (2000) suggested that the alkyl iodide could not solely explain the observed iodine oxides concentrations observed in Mace Head, a coast site in Ireland. Saiz-Lopez (2004b) measured a significant I$_2$ emission from a coastal area (Mace Head) with response to the exposure of the macroalgae while the tide was low. They proposed that the I$_2$ should be the major iodine species emitted by the macroalgae. However, the technique they were using was a long path differential optical absorption spectrometer (LP-DOAS) with 8.2km absorption path and the measurements were 20 m above the sea level. The point source of I$_2$ could be much higher than that.

1.2.3 Polar sources

The involvement of halogenated compounds in polar ozone depletion events (ODEs) is recognized for long. Differential optical absorption spectrometer (DOAS) measurements (Hausmann and Platt, 1994) confirmed the hypothesis from Barrie et al. (1988), that the halogens caused the ozone depletion events (ODE) in Arctic regions. The existence of halogens were later on confirmed also in other areas of the Arctic (Tuckermann et al., 1997; McElroy et al., 1999) and Antarctica (Kreher et al., 1997).

The first IO concentrations in Neumayer-station in coastal Antarctica was reported by Frieß et al. (2001), and was again measured by Saiz-Lopez et al. (2007). Later, Mahajan et al. (2010) reported IO concentration in Arctic. Allan et al. (2015) deployed an aerosol mass spectrometer (AMS) in Greenland and found the particle composition consisted iodine species. This indicates a potential iodine source in that region, which was not clear at the time. According to these theories reactive inorganic iodine compounds seem to have much higher concentration in the Antarctic than the Arctic, potentially due to the environmental
differences between the poles (Saiz-Lopez et al., 2012).

Jones et al. (2009) reported high vertical column densities of BrO in coastal Antarctica by satellite, which also has correlation with high wind events. They proposed that the blowing snow and the snow pack are the source of reactive bromine species. Laboratory experiments were carried out and Pratt et al. (2013) found molecular bromine increased significantly when the ozone was injected to the snow sample, which suggests that the snow may be a source of bromine containing compounds in ozone depletion events in Arctic spring time. However, BrO measurements over other landscapes with effective measurement over detection limits are few, with only two measurements existing by 2015 (Saiz-Lopez, 2004a; Coburn et al., 2011; Simpson et al., 2015). Considering the ability of bromine species to change atmospheric composition, and their ability deplete aerosols (Sander et al., 2003), it is necessary to measurement bromine species over wider areas in the world, in order to understand their role in the atmosphere better.

1.2.4 Free troposphere

There are currently very few measurements of halogens in the free troposphere, altitude range from about 2 km to 18 km. Prados-Roman et al. (2011) measured vertical profiles of BrO. Puentedura et al. (2012) observed IO on a mountain-top station on Izana mountain in Atlantic Ocean.

1.2.5 Sources on unique locations

Some unique geographic locations also have intensive halogen chemistry (Simpson et al., 2015). Albeit their relative contribution to the regional and global tropospheric composition is minor, investigating these processes could provide valuable insight into related marine boundary layer (MBL) halogen chemistry. For instance, high level bromine monoxide was observed in a volcanic plume (Bobrowski et al., 2003). Moreover, Dead Sea (Hebestreit, 1999), Great Salt Lake (Stutz et al., 2002) and dry salt plains (Hönninger, 2004) appear to produce high levels of halogens oxides.

1.3 Halogen modeling

Global models have been deployed to investigate quantitatively the effect of halogens in ozone deduction. von Glasow et al. (2004) compared the results from a chemical transport model (CTM), with and without the inclusion of bromine species, to investigate the effect of bromine species on ozone deduction. The results showed that the inclusion of 2 ppt BrO could result in a reduction of 18% zonal mean ozone mixing ratio, and up to 40% deduction of ozone
regionally. As deeper understandings of the sources and the chemistry of halogens have been achieved during the past decade, it is needed to implement the up to date knowledge into the CTM and then further investigate the global impacts of halogens. Only recently, chemistry mechanisms of the three halogens (Cl, Br and I) were implemented into the GEOS-Chem model. The model was applied to study the impact of tropospheric halogens on atmospheric oxidants and composition. This model includes the emission of inorganic iodines from the oceans, anthropogenic and biogenic sources of halogenated gases, gas phase chemistry, ans an assessment of heterogeneous halogen chemistry (Sherwen et al., 2016b). Their results show that the addition of halogen chemistry reduce the global tropospheric $O_3$ burden by 18.6%. The inclusion of the halogen chemistry resulted in a better agreement with the ozone observation compared to a scheme without halogen chemistry. The relative importance of the three halogens in catalytic ozone destruction were found different at the same study.

Bloss (2005) and Sommariva et al. (2006) found with observationally constrained models that the $\text{IO} + \text{HO}_2$ reaction accounted for up to 40% of the loss of $\text{HO}_2$, but only up to 15% of the source of OH from the photolysis of HOI. However, the inclusion of a complete set of halogen chemistry is essentially very important. The missing of any of the three halogens will potentially lead to a mis-estimation of their global effects. For example, Sherwen et al. (2016a) estimated the effect of iodine compounds to the OH is increasing by 1.8%. OH concentration globally. However, Sherwen et al. (2016b) renewed the results with inclusion of the three halogens in his model, which resulted in a decrease of by 8.2% as discussed in last section.

Beside from global modeling, Gantt et al. (2017) used a regional model to simulate coastal area ozone concentrations over the US. The study shows that the role of halogens in ozone deduction occurs in two ways. The first pathway involves a reaction between sea surface iodide with gas-phase ozone. The second one is by reaction between gas phase iodine and bromine with ozone.

Although an inclusion of halogens in global chemical transport model has been used to study the impact of halogens on the atmospheric composition, the uncertainties of the model results are still very high. For example, IO concentration retrieved by satellite could not be reproduced in Sherwen et al. (2016b), which the authors attributed to the lack of polar-specific processes in the GEOS model. These discrepancies are due to our limited understanding regarding to the sources and fates of the halogens in the atmosphere. These uncertainties include the poor to missing knowledge about the photolysis of iodine compounds, and the sources of organic and inorganic iodine species, and the heterogeneous processes involving halogens (Sherwen et al., 2016a). Little experimental data and parameters about physical and chemical properties for the aerosols containing halogens are provided.

In order to fully understand the impact of halogens on tropospheric composition, sig-
significant improvements in measurement techniques are needed. In addition, more field studies are required to understand the sources of halogens and laboratory studies to understand the halogen chemistry are required.

1.4 Objectives and structure of this work

1.4.1 Objectives

As described by the preceding sections, halogenated species have influence on atmospheric composition. These include iodine particle formation, catalytic ozone destruction and impact on HO\textsubscript{x} and NO\textsubscript{x} cycles. However, the exact processes governing halogen chemistry and halogen new particle formation have been puzzling the community for years. One of the major difficulties in understanding these processes has been the lack of techniques able to measure inorganic halogenated radicals and stable species simultaneously both in laboratory and ambient conditions. This is because previous spectroscopic and mass spectrometric methods utilized could only measure one, or a few halogenated species at once, while some of the important halogenated species existing in the atmosphere were likely un-measurable.

Thus, the first question that needs to be answered is that whether we could expand our capability in measuring some of the important halogenated species that were not directly measurable. These species include for example HOI, which currently is believed the major iodine emission from oceans (Saiz-Lopez et al., 2012). In addition, preferably the instrument could measure different halogenated species simultaneously. In this way one instrument would be capable of measuring multiple halogenated species which would otherwise take several instruments. This advance would potential enable easier deployment of the instrument to field studies which are urgently needed to understand the impact of halogenated species on atmospheric composition (Sherwen et al., 2016b).

Second, the formation mechanism of (HIO\textsubscript{3}) remains relatively unknown, though, (HIO\textsubscript{3}) was recently revealed to be the compound that triggers iodine nucleation (Sipilä et al., 2016). It is needed to understand the formation mechanism of (HIO\textsubscript{3}) to be able to determine to what extent the (HIO\textsubscript{3}) could be formed globally.

Iodine particle formation is mostly believed a coastal and polar phenomenon as described in previous sections. Two reasons support this assumption. First, the major sources of iodine species are marine and polar origins. Second, most iodine species are normally reactive in chemical and/or photolytic processes. These characteristics make them play an minor role in the atmosphere in locations without iodine emissions. However, as (HIO\textsubscript{3}) is an iodine reservoir species that is not chemically reactive and was suggested to participate in particle
formation processes. The third question would be to figure out whether the existence of (HIO$_3$) is restricted to coastal and polar regions, or it is more widely distributed than expected.

Fourth, OH radical alone fails to explain all the sulfuric acid present in Mace Head (Berresheim et al., 2014). Additional oxidants would be needed to explain the large concentration of sulfuric acid present there. Though, IO was suggested too slow to explain the missing oxidants. It is necessary to investigate whether other iodine species could trigger the formation of sulfuric acid from SO$_2$.

In conclusion, the four questions that will be answered in this work is:

1) whether it is possible to measure multiple halogenated species, including some of the yet un-measurable ones, simultaneously with one instrument?
2) how does (HIO$_3$) form?
3) does (HIO$_3$) exist in other environments than coastal and polar regions?
4) could iodine species oxidize SO$_2$ to form sulfuric acid?

1.4.2 Structure of this work

In the instruction chapter, the impact of halogenated species on atmospheric composition and the sources of halogen compounds in different environments were reviewed. Preceding works on halogen global modeling and its quantitative results were discussed.

In the halogen measurements chapter, basic principles of mass spectrometry will be presented. An instrument used to measure halogenated species will be described in details. The experimental setup deployed to study iodine chemistry is to be presented and explained. Peak determination of some anions measured by iodide chemical ionization will be discussed.

In the iodine chemistry chapter, photo chemical processes that are involved in the experiments will be discussed. Three proposed formation mechanisms of (HIO$_3$) will be presented together with experimental proofs. Indications from laboratory experiments that iodine species might be able to oxidize SO$_2$ to form sulfuric acid will be explained.

In the iodine particle formation chapter, previous literatures and the development of the iodine particle formation theories will be reviewed. Experiments on macroalgal incubation and their relevance to iodine emissions will be discussed. First results show that (HIO$_3$) exist in a wide range of environments will be presented.

In the conclusion and future work chapter, conclusions of this work and future work in potential doctoral studies will be discussed.
2. Halogen measurements

Currently our understanding of the emission and fate of halogenated species in the atmosphere is limited by their sparse ambient observations. Also, it is nearly impossible to accurately simulate and predict their effects on atmospheric composition. This is essentially caused by the limitation of the current field deployable measurement techniques. The majority of the measurements of halogenated species use spectroscopic or mass spectrometric methods.

Direct measurement of elevated chlorine in coastal regions were made by a chemical ionization mass spectrometer (CIMS) in 1998 (Spicer et al., 1998) and modeling results suggested a potential release of chlorine from sea salt aerosols over coastal regions (Vogt et al., 1996). Liao et al. (2012) and Peterson et al. (2017) applied an iodine I– CIMS method to measure Br$_2$, BrO and HOBr from ambient. Custard et al. (2016) applied a iodide CIMS in measuring Cl$_2$, Br$_2$, BrO and ClO. Pratt et al. (2013) used a iodide CIMS method to measure molecular bromine from an outdoor snow chamber experiments. The bromine monoxide measurement was also compared with differential optical absorption spectroscopy (DOAS) measurements (Liao et al., 2011). DOAS deployed in atmospheric research is used to measure atmospheric trace gases (Platt and Stutz, 2008). Lawler et al. (2011) used a bromide ion based CIMS method to detect Cl$_2$ and HOCl compounds, where the HOCl measurement represented the first ambient measurement of this species. However, the models could not reproduce the observations in this study, indicating there might be incomplete understandings of the emission of chlorinated species from chloride in the sea water (Simpson et al., 2015). Enami et al. (2016) reported measurements of a few iodine containing species using an electrospray mass spectrometer.

However, most instruments used previously could only detect a single or a few halogenated species at a time. Here we present mass spectrometry methods that can measure over 20 different inorganic halogenated species simultaneously directly from atmospheric pressure gas mixture.
2.1 Mass Spectrometry

Mass spectrometry (MS) is a method to ionize neutral molecules to be able to measure the mass to charge ratios of the produced ions (de Hoffmann and Stroobant, 2007). Typically a mass spectrometer consists four principal parts: sample inlet, ion source, mass analyzer and detector. The products of the measurement is normally a mass spectrum. A mass spectrum is a plot of ion signals measured by the instrument versus their mass to charge ratios.

The first part is a sample inlet. It is used to feed the sample, which can be solid, liquid or gas, to the instrument. In some applications, the sample inlet could also be coupled with gas chromatography to separate gas vapors in the mixture.

The second part is the ion source, it is used to convert part of the sample into ions, either negative or positive. Depending on the phase (solid, liquid or gas), there are various methods to ionize the sample (Peacock et al., 2017). Ionization methods are the key to determine what kind of ions could be produced and further measured. For liquid and gas samples, electron ionization and chemical ionization are two typical methods used. Electron ionization deploys shooting energetic electrons onto the sample molecules to produce ions. In chemical ionization, a reagent gas in excess level is injected to the ion source to absorb most of the electrons created entered the ion source. The formed reagent ions and the reagent gas form an ionization plasma. The sample reacts with this plasma to create ions. Chemical ionization is a lower energy process than electron ionization, which results in lower or sometimes no fragmentation.

After the ionization of the sample, the ions are guided into a mass analyzer. Mass analyzer could separate the signals of the ions according to their mass-to-charge ratio. Different mechanisms are employed to achieve this aim. However, there are two fundamental law governing this process. The first one is Lorenz’s law denoted in (2.1a) and Newton’s second law of motion as shown in (2.1b). The $F$ is the force applied to the ion, $Q$ is the number of charge the ion carries, $E$ is the electric field, $\mathbf{v} \times \mathbf{B}$ is the vector cross products of velocity of the ion and the magnetic field. Equating the two equations could yield classic equation of motion for charged ions, as denoted by (2.1d). If the initial states of the charged ions are provided as well as the conditions of strength of the electric and magnetic field, the classic equation of motion for charged ions could be solved. And the mass to charge rations of the ions could be derived from the motion of the ions. Further, in a time of flight mass spectrometer, the vector cross products of velocity of the ion and the magnetic field could be ignored. This is because in the time of flight part, electric field alone supplies the energy for guiding the movement of the ions.
\[ F = Q(E + v \times B) \]  \hspace{1cm} (2.1a)

\[ F = ma \]  \hspace{1cm} (2.1b)

\[(m/Q)a = E + v \times B \] \hspace{1cm} (2.1c)

\[(m/Q)a = E \] \hspace{1cm} (2.1d)

The last part of the mass spectrometry is a detector. A detector could record an ion when passes by or hits the detector. Normally, a kind of electron multiplier is deployed to amplify the signal an ion produced. The products of a scanning mass spectrometer is a mass spectrum.

### 2.2 Chemical ionization methods in halogen measurements

Atmospheric Pressure interface Time Of Flight Mass Spectrometer (APi-TOF) has been designed to measure natural ions in the atmosphere (Junninen et al., 2010). A chemical ionization inlet was constructed and deployed to measure sulfuric acid in the ambient air (Eisele and Tanner, 1993). Kurtén et al. (2011) modeled the possible effect of sulfuric acid clustering with amines using a new designed chemical ionization inlet that has similar principle as the inlet in (Eisele and Tanner, 1993). Both inlets utilize nitric acid as the reagent ion. Jokinen et al. (2012) combined the inlet by Kurtén et al. (2011) with APi-TOF to measure sulfuric acid and compared the results with quadrupole CIMS which led to a good agreement. The developed technique was called CI-APi-TOF afterwards. Moreover, nitric acid based CI-APi-TOF could measure compounds called Highly Oxygenated Molecules (HOMs) which are important in secondary organic aerosol (SOA) formation (Ehn et al., 2014). Later on, HIO\(_3\) and I\(_2\)O\(_5\) were measured by Sipilä et al. (2016) which were proposed to participate in the particle formation events in Mace Head.

However, in the above mentioned studies, the deployed chemical ionization method was always nitric acid based chemical ionization, which has been shown lacking the ability to measure halogenated species other than (HIO\(_3\)), iodine pentoxide and iodosous acid. A new chemical ionization method which would be suitable for measuring more halogenated species, especially reactive halogens would be needed to resolve the role of halogens in the ambient atmosphere using mass spectrometric methods. Low pressure iodide based chemical ionization has been applied to measure halogenated species in various locations (Peterson et al., 2017; Custard et al., 2016; Pratt et al., 2013; Liao et al., 2012; Lawler et al., 2011). A low pressure iodide chemical ionization mixes air sample with charged reagent ion in an ion-molecule reaction (IMR) chamber under turbulent conditions to charge the molecules in the air sample. An IMR chamber is
a chamber with low pressure (normally operated at a 100 mbar level). The charged reagent ion are produced by passing clean nitrogen flow carrying reagent gas (in this case methyl iodide) in a polonium source to produce charged oxygen and nitrogen ions which further transfer charge to produce negatively charged iodide ion. Iodide ion is the reagent ion in this system. These studies show that the low pressure iodide system can measure several halogenated species with Q-CIMS. Recent development of the API-TOF mass spectrometer enables us to measure different molecular masses simultaneously, while the Q-CIMS could only measure one unit mass at a time. Coupling the low pressure iodide chemical ionization with the API-TOF has shown its ability in measuring organics as well as some halogenated species (Lee et al., 2014). However, an inherent problem of using the low pressure iodide chemical ionization method is that iodine radicals are also produced while the regent molecule is charged by a Polonium source. This is because the sample flow is turbulently mixed inside the IMR chamber with the reagent carrier flow. The potential problem of using low pressure iodide chemical ionization is that some of the halogenated species could react with iodine radicals as shown by reactions (2.2) (Bedjanian et al., 1996, 1997a; Jenkin et al., 1990; Bedjanian et al., 1997b; Dolson and Leone, 1982; van den Bergh and Troe, 1976).

\[
\begin{align*}
I + \text{OCIO} & \rightarrow IO + \text{ClO} & (2.2a) \\
I + \text{BrO} & \rightarrow IO + \text{Br} & (2.2b) \\
I + \text{ClO} & \rightarrow IO + \text{Cl} & (2.2c) \\
I + I & \rightarrow I_2 & (2.2d) \\
I + \text{Cl}_2\text{O} & \rightarrow I\text{Cl} + \text{ClO} & (2.2e) \\
I + \text{Cl}_2 & \rightarrow I\text{Cl} + \text{Cl} & (2.2f) \\
I + \text{INO}_2 & \rightarrow I_2 + \text{NO}_2 & (2.2g)
\end{align*}
\]

2.2.1 Atmospheric pressure iodide and bromide chemical ionization mass spectrometry

In this study, we investigate the possibility of using atmospheric pressure iodide and bromide based chemical ionization with CI-API-TOF, to simultaneously measure a series of halogenated species. The self-made schematic of the instrument is shown in Figure 2.1. The instrument couples a coaxial Eisele type chemical ionization inlet with a soft x-ray source, which is used to charge neutral molecules, and an API-TOF, which is used to measure the produced ions. The cylindrical chemical ionization inlet mainly has three parts. The first part is a 3/4” inlet which lets roughly 10 standard liter per minute (slm) gas sample flow to go through. The second part
is the ionization chamber which is illuminated by a soft X ray to charge the reagent gas to produce reagent ion. The flow coming out of the sampling inlet and the flow in the ionization chamber are laminar. This means the flows are well separated from each other and are not mixed. The flow from the ionization chamber is called sheath flow and the flow from the sampling line sample flow. The third part is an IMR chamber, which allows reaction of the charged reagent ion and the neutral molecule. The IMR chamber is connected to a negative electric field to force the negative reagent ion from the sheath flow into the sample flow. This design prevents the contact of the reagent gas and uncharged radicals (for example, iodine radical or bromine radical) with the air sample. Thus, the reactions shown in (2.2) which could change the composition of the neutral molecules in the air sample are largely reduced in this coaxial inlet.

At the connection part of the coaxial inlet and the APi-TOF, excess flow of the total mixed flow is sucked out to balance the flow system. This is because the combined sheath flow and sample flow are around 40 slm while the APi-TOF only sucks about 1 slm flow. The APi part is used to focus the ion beam and at the meantime to lower the pressure of the sample flow stage by stage until it reaches below $10^{-5}$ mbar in the third chamber. The TOF part has a pressure of roughly $10^{-6}$ mbar, and is used to guide the movement of the ions to be detected by the multichannel plate (MCP) detector.

2.3 Experimental setup

The experimental setup used to measure halogenated species and investigate iodine chemistry is shown in Figure 2.2. Note that the experiments done in this study were carried out with various setups and conditions. For example, at some occasions the UVA and/or the Green light were dismantled and the flow tube was covered by shelter to prevent the laboratory lights from penetrating. Moreover, the gas feeding system was always under change as different chemical system required different gases in the system. However, the principles of all the experiments are similar to the one will be discussed here. Thus, unless it is worth noted, the exact experimental setups will not be specifically described in the following texts. Figure 2.2 here would be a reference for all the experiments below.

The main parts of the experimental setup consist of two CI-API-LTOFs, a flow tube, ozone monitor and dew point meter and light sources. CI-API-LTOF is an identical mass spectrometer to CI-API-TOF, except the TOF part of the instrument is changed to a LTOF (long TOF). LTOF nearly doubles the mass resolution of a normal APi-TOF instrument. It is a newer generation of APi-TOF instrument. Two chemical ionization (CI) inlets are connected by a Y shaped flow divider to the flow tube. The flow tube is a one meter long quartz tube
with an diameter of about 7 cm. Thus the inner volume of the flow tube is approximately 4 liters. With a flow ranging from 7 slm to 20 slm, the reaction time in the flow tube is around from 34 s to 12 s. At the connection part between the Y shaped flow divider and the two sampling tubes which are connected to the CI-APi-TOFs, an ozone monitor and a dew point meter are also connected to the system to measure the ozone concentration and the humidity in the sample gas in the flow tube. The other end of the flow tube is connected to an aluminum box. The aluminum box is used to house a pen mercury lamp to shelter the UV of the pen mercury lamp. A quartz tube is passing the aluminum box to allow the illumination of the pen mercury lamp to the gas flow in the quartz tube before its injection to the flow tube. Before the aluminum box, gas is fed by Polytetrafluoroethylene (PTFE) tubes connected by stainless steel connectors to enable the feeding of different precursors gases. The PTFE tubes are connected to mass flow controllers (MFC) with different flow speed controllability.

In addition, two green light fluorescent lamps with major lights of 528 nm connected to one controller and two UVA fluorescent lamps with major lights of 350 nm connected to
Figure 2.2: Instrumental setup for the experiments performed in this study.

one controller are fixed over and above the flow tube to initial photo-chemical reactions inside the flow tube. The green fluorescent lamp is effective for photolysing molecular iodine and molecular bromine and the UVA lamp is effective for photolysing CH$_2$I$_2$ and Cl$_2$. This is because the absorption cross sections of CH$_2$I$_2$ and Cl$_2$ are in favor of the spectra of the UVA lamp and the I$_2$ and Br$_2$ are in favor of the Green lamp as shown by Figure 2.3. Pen mercury lamp mainly has two major wavelength of 184.5 nm and 254 nm to enable the photolysis of molecular iodine, CH$_2$I$_2$, water vapor and oxygen molecule.
2.4 Measurement of halogenated species

2.4.1 Iodide CI-APi-TOF

The schematic shown in Figure 2.1 is a Bromide CI-APi-TOF (BrCl). However, if the reagent molecule is changed to an iodide ion source, in this case from CH₂Br₂ to C₂H₅I, it becomes an Iodide CI-APi-TOF (ICI). Experiments were carried out to investigate the ability of ICI in measuring halogenated species. A mixture of CH₂I₂, water vapor and synthetic air was flushed through a flow tube illuminated by a pen mercury lamp to initiate photo-oxidation of iodine species. The photolysis of water vapor and oxygen in the carrier flow produces OH radical, HO₂ radical and ozone while the photolysis of CH₂I₂ produces reactive iodine species, such as iodine radical, molecular iodine and iodine monoxide. By checking the resulting mass spectra of the ICI instrument, we could get a qualitative picture how many iodinated species the ICI could measure. Surprisingly, the ICI could measure 14 different iodinated species while any instrument that had been deployed in the field measurements reported only measurements of only a single one, or a few iodinated species.

The mass defect plot of the results is shown in Figure 2.4, subplot B. Mass defect is the
difference of the exact mass and nominal mass of a molecule or an ion. However, it should
de noted that ICI has backgrounds signals for iodine species. This is because at the time soft
X-ray is breaking the reagent molecule, iodine radical could also be produced in the ionization
chamber which could react with ozone and NOx, if they present in the sheath flow, to produce,
for example, iodine oxides or nitrogen containing iodinated species. The produced iodine oxides
could be charged by iodide ion in the ionization chamber which further being forced by negative
electric field to the center of the IMR chamber and being measured by the APi-TOF. The
background signals generally are not avoidable while using ICI to measure iodinated species.
However, the reaction time for these reactions is normally short, thus the background signals
from the instrument are small for laboratory experiments, however, significant for ambient
measurements. Thus, careful examination of the background should be made and zeroing
method should be applied when using ICI to measure iodinated species in the field. Moreover,
chlorine containing contamination were found in the mass spectra in the same experiments.
The source of the contamination is not known. However, the best guess would be that it came
from the sample of CH₂I₂ or from the purity 5.0 nitrogen or synthetic air gases. The measurable
chlorinated species and some bi-halogen species are plotted in mass defect plots in Figure 2.4,
subplot B. In total 10 different chlorinated species and bi-halogen species were measured. This
indicates that the ICI can be applied to detect these species too. The measurements of the
chlorinated species are less problematic than iodinated species, as the background of them are
normally below noise level of the ICI instrument as they could not be produced in the sheath
flow without input of chlorine and bromine precursors.
Figure 2.4: Mass defect plots from iodide CI-APi-TOF measuring halogenated species. An arrow that starts from a dot to a ion composition shows the ion composition of that dot in the mass defect plot. A) iodinated species measured by Iodine CI-APi-TOF. B) Chlorinated species and bi-halogen species measured by Iodine CI-APi-TOF.
2.4.2 Bromide CI-API-TOF

In order to avoid the background signals of iodinated species while using ICI to measure them, an attempt was also given to BrCI. Bromide chemical ionization has been used to measure HOCl and Cl₂ by Lawler et al. (2011) and HO₂ radical by Sanchez et al. (2016). The technique used by these studies was low pressure bromide chemical ionization system with Q-CIMS. In our study, atmospheric pressure coaxial Eisele type inlet was coupled with an API-TOF to investigate the ability of BrCI in measuring halogenated species. A mixture of molecular chlorine, molecular iodine and molecular bromine together with humidified nitrogen flow and synthetic air flow were mixed in a flow tube. The synthetic air flow was passed through an ozone generator to produce ozone if needed. A physical on/off switch was used to control the ozone generator. The flow tube was under the illuminated by two UVA fluorescent lamps and two green fluorescent lamps. Thus, photo-oxidation processes of the three halogens and also inter-halogen reactions could be initiated in the flow tube. In total 18 different halogenated species were measured by BrCI, covering the majority of the interesting halogenated species in the atmosphere as these species are most actively participate in the ozone depletion events.

![Mass defect plot from Bromide CI-API-TOF measuring halogenated species. An arrow that starts from a dot to a ion composition shows the ion composition of that dot in the mass defect plot.](image)

**Figure 2.5:** Mass defect plot from Bromide CI-API-TOF measuring halogenated species. An arrow that starts from a dot to a ion composition shows the ion composition of that dot in the mass defect plot.
The development of the atmospheric pressure iodide and bromide chemical ionization mass spectrometry not only enable us to measure some of the un-measurable halogenated species like HOI, but also makes it possible to measure over 20 different halogenated species simultaneously. This fulfills our first aim as suggested by section 1.4.

2.5 Peak determination

2.5.1 Ozone detection

HIO$_3$NO$_3^-$ and IO$_3^-$ are speculated to be produced from

\[
(HIO_3) + (HNO_3)_n NO_3^- \rightarrow IO_3^- + (HNO_3)_n HNO_3 \quad n = 0,1,2 \quad (2.3a)
\]

\[
\rightarrow HIO_3NO_3^- + (HNO_3)_n \quad (2.3b)
\]

in nitrate chemical ionization (NCI). In ICI, the similar processes, if happening, should form via

\[
(HIO_3) + I^- \rightarrow IO_3^- + HI \quad (2.4a)
\]

\[
\rightarrow HIO_3I^- \quad (2.4b)
\]

However, no significant amount of HIO$_3$I$^-$ was measured by ICI while a large amount (HIO$_3$) was measured by NCI, indicating the charging process through reaction (2.4b) might not be happening or is not efficient enough. As for IO$_3^-$ in ICI, beside from produced by (2.4a), another possibility is that this anion is produced by reaction between ozone and I$^-$ anion. In the same experiments as described by Table 2.1, the IO$_3^-$ signals were recorded by ICI in parallel to the NCI and the signals from ICI are plotted in Figure 2.6. The lines describing measurements under different experimental conditions seem to be converged to each other regardless of the experimental conditions, while the IO$_3^-$ anion in NCI seems to behave rather differently. The correlation of the normalized IO$_3^-$ signal to ozone concentration tends to be linear in ICI. These imply that the neutral precursor/s behind the IO$_3^-$ in ICI might be partly ozone, as the reaction (2.4a) could not be excluded totally.
Table 2.1: Experimental conditions in run 25. The experiment number is the same as shown in the legend of Figure 2.6. 0 in CH$_4$ column means no input of CH$_4$. 0 in UVC column means there is no pen mercury lamp turned on. 1 in UVC column means only the filtered pen mercury lamp is turned on. The filtered pen mercury lamp is filtering the light of the pen mercury lamp so that only light with a wavelength of 184.9 nm could penetrate through the filter. 2 in the UVC column means not only a filtered pen mercury lamp is turned on, but also a bare full power pen mercury lamp is turned on in the aluminum box (refer to Figure 2.2 for the position of the aluminium box)

<table>
<thead>
<tr>
<th>Experiments</th>
<th>O$_2$, ppm</th>
<th>H$_2$O, ppm</th>
<th>I$_2$, ppb</th>
<th>CH$_4$ ppm</th>
<th>Ozone, ppb</th>
<th>UVC</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1569</td>
<td>0.4707</td>
<td>0</td>
<td>0-30</td>
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</tr>
<tr>
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<td>1569</td>
<td>0.4707</td>
<td>0</td>
<td>0-30</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>10500</td>
<td>1569</td>
<td>0.4707</td>
<td>0</td>
<td>0-30</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>10500</td>
<td>1569</td>
<td>0.4707</td>
<td>2500</td>
<td>0-30</td>
<td>2</td>
</tr>
<tr>
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<td>2500</td>
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</tr>
<tr>
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<td>10500</td>
<td>1569</td>
<td>0.4707</td>
<td>2500</td>
<td>0-30</td>
<td>0</td>
</tr>
</tbody>
</table>

2.5.2 I$_2$– in iodide CI

The I$_2$– peak in ICI could be formed by
I + I⁻ → I₂⁻ \hspace{1cm} (2.5a)
\[ \text{I}_2 + \text{I}⁻ \rightarrow \text{I}_2⁻ + \text{I} \] \hspace{1cm} (2.5b)

The reaction (2.5a) represents the detection of I radical, while the reaction (2.5b) represents the detection of iodine molecular. This is a critical difference between the systems, as the I radical is the major precursor of various iodine containing compounds whereas the iodine molecule is relatively un-reactive. In order to figure out the neutral precursor of I₂⁻ peak in iodide Cl, a set of experiments were performed under dark condition (Finnish winter plus no laboratory lights on). The experimental conditions are shown in Table 2.2. The O₂ and H₂O concentrations were kept unchanged, while the I₂, CH₄ and the intensity of pen mercury lamps were changed according to experimental conditions. The correlation between I₃⁻ signal and I₂⁻ is shown in Figure 2.7. The legend shows the different experimental conditions. Ozone means only ozone was additionally added to the system aside from the O₂ and H₂O. UVC1 means the filtered pen mercury lamp was on and the UVC2 means both the filtered pen mercury lamp and the other not filtered one were on. A filtered mercury lamp means that a mercury lamp is kept in a closed light housing with only on whole covered by a light filter. The light filter could only let lights with wavelength 184.9 nm to penetrate. In this way, it would be easier to quantify the light intensity. CH₄ means 2500 parts per million (ppm) of CH₄ was added to the system.

**Table 2.2:** Experimental conditions in run 27. The experiment number is the same as shown in the legend of Figure 2.7. 0 in CH₄ column means no input of CH₄. 0 in UVC column means there is no pen mercury lamp turned on. 1 in UVC column means only the filtered pen mercury lamp is turned on. The filtered pen mercury lamp is filtering the light of the pen mercury lamp so that only light with a wavelength of 184.9 nm could penetrate through the filter. 2 in the UVC column means not only a filtered pen mercury lamp is turned on, but also a bare full power pen mercury lamp is turned on in the aluminum box (refer to Figure 2.2 for the position of the aluminium box).

<table>
<thead>
<tr>
<th>Experiments</th>
<th>O₂, ppm</th>
<th>H₂O, ppm</th>
<th>I₂, ppb</th>
<th>CH₄ ppm</th>
<th>Ozone, ppb</th>
<th>UVC</th>
</tr>
</thead>
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<td>0</td>
<td>10-14</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
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<td>470</td>
<td>0-0.4707</td>
<td>0</td>
<td>10-14</td>
<td>1</td>
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<tr>
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<td>10-14</td>
<td>2</td>
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<tr>
<td>4</td>
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<td>10-14</td>
<td>2</td>
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<tr>
<td>5</td>
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<td>0-0.4707</td>
<td>2500</td>
<td>10-14</td>
<td>1</td>
</tr>
</tbody>
</table>
The experiments 3 and 4 show clearly higher I$_2^-$ concentrations than the other runs. This is because the photolysis of I$_2$ by UVC2 produces vast amounts of iodine radicals in the system. This difference in the ratio between I$_3^-$ and I$_2^-$ between turning on the bare pen mercury lamp and not indicates that the neutral precursor of I$_2^-$ is at least partly iodine radical. As in first experiments with no light sources on, the existence of I$_2^-$ signal indicates the reaction (2.5b) might be happening to a lesser extent as well. The complex ion chemistry involved in using iodide ion to detect iodinated species can potentially interfere the interpretation of the results from ICI. Moreover, the other influence that could be observed is that there are nearly no differences between turning on the UVC1 and off. This is because the filtered pen mercury lamp was not efficient enough to photolyse molecular iodine.
3. Iodine chemistry

Chameides and Davis (1980) realized the potential of iodinated species in ozone destruction and they also observed how halogen species strongly shift HO$_\text{x}$ and NO$_\text{x}$ cycles. However, at the time, kinetic data and reactive iodine fluxes from various sources were significantly lacking. These limitations made the assessment of the effect of iodine chemistry on the tropospheric composition difficult. Since after, our understandings of the atmospheric sources and fates of organic and inorganic iodine compounds and their kinetics have been revised considerably. Nevertheless, open questions remain in some key aspects of iodine chemistry.

IO is an important compound that serves as an intermediate in catalytic ozone destruction (refer to section 1.1). IO is also an efficient oxidizer that converts dimethyl sulfide (DMS) into dimethyl sulfoxide (DMSO) and hence influences the global sulfate budget (Nakano et al., 2003). The formation of IO is also the initial step in forming higher iodine oxides, for example, OIO, I$_2$O$_2$, I$_2$O$_3$, I$_2$O$_4$ and I$_2$O$_5$. To explain the observed IO concentration in Mace Head, multiple studies have been performed to investigate the sources and the chemistry involved in producing and maintaining the IO concentration. Stutz et al. (1999) applied a box model without aerosol phase chemistry, to reproduce the measured 6 pptv IO in Mace Head. They found that the second ozone destruction cycle, which involves HO$_2$ (reactions (1.8) to (1.11)), destroyed 12.5 ppb ozone per day. At the meantime, the first ozone destruction cycle which involves the IO self-reaction would lead to about 3.8 ppb ozone destroyed per day (Saiz-Lopez et al., 2012).

McFiggans et al. (2000) applied a box model with the chemical scheme based on Vogt et al. (1999) but without detailed aerosol chemistry. They used field measurements to constrain the model, and they also implemented the iodine fluxes into the model. The concentrations of IO for Mace Head and Tenerife were well reproduced. The results also showed that at that certain modeling condition, the iodine chemistry could be as important as HO$_\text{x}$ chemistry for ozone destruction. Moreover, they showed that the uptake of iodine to aerosol particles could lead to a significant concentration of iodine in aerosols. Further, Peters et al. (2005) showed that with observed alkyl iodides as the only iodine precursors, they could reproduce the observed IO concentration. However, previously Saiz-Lopez (2004b) had suggested that molecular iodine should account for the source of iodinated species and new particles in Mace Head. Saiz-Lopez
et al. (2012) suggested that even with a small amount of I$_2$, the iodine chemistry could be significant, which is due to the fast photolysis of I$_2$ under ambient conditions.

IONO$_2$ is generally thought to be a reservoir for iodine. However, Stutz et al. (2007) measured up to 24 pmol mol$^{-1}$ OIO under high NO$_x$ condition, during the daytime. This has two important implications for gas-phase iodine chemistry. First, it suggested that there might be a recycling pathway of iodine from IONO$_2$ which would make it an inefficient reservoir of iodine. Second, it indicates that OIO should be a photo-stable compound while Ashworth et al. (2002) measured the photolysis life time of OIO is to be about 1 s. The disagreements between these studies warrant further investigation to confirm.

In order to solve the discrepancies in iodine chemistry, more laboratory experiments aiming to solve them need to be done. As described in the last chapter, new mass spectrometric methods have been developed and deployed in laboratory experiments for the first time. These methods have been utilized in current work to investigate several aspects of the iodine chemistry: (1) the formation mechanisms of (HIO$_3$), (2) reactive iodine as a gas-phase sulfur dioxide oxidant and the formation mechanism of iodine oxides. The novel results are shown on the following sections.

### 3.1 Photo-dissociation of relevant gases

Before going to results of the performed iodine chemistry experiments, it is necessary to discuss the photo-dissociation of relevant compounds involved in the experiments. Some of the experiments utilize pen mercury lamps (UVC) to photolyse CH$_2$I$_2$, O$_2$ and H$_2$O. The photolysis of CH$_2$I$_2$ is initiated by the dissociation of one iodine atom from the molecule, shown by

$$
\text{CH}_2\text{I}_2 + \text{hv} \rightarrow \text{CH}_2\text{I} + \text{I} 
$$ (3.1)

After the photo-dissociation, a CH$_2$I radical is formed, which further reacts with O$_2$ to form an excited complex, CH$_2$IOO$^\#$ as shown in

$$
\text{CH}_2\text{I} + \text{O}_2 \rightarrow \text{CH}_2\text{IOO}^\#
$$ (3.2)

This complex further stabilizes to form either a peroxy radical (reaction (3.4)) or a criegee biradical (reaction (3.3)) (Stone et al., 2013).

$$
\text{CH}_2\text{IOO}^\# \rightarrow \text{CH}_2\text{OO} \text{(Criegee)} + \text{I} \tag{3.3}
$$

$$
\text{CH}_2\text{IOO}^\# + \text{M} \rightarrow \text{CH}_2\text{IOO} \text{(Peroxy)} + \text{M} \tag{3.4}
$$

The photolysis of H$_2$O under UVC produces one OH and one HO$_2$ by

$$
\text{H}_2\text{O} + \text{hv} \rightarrow \text{OH} + \text{H} \tag{3.5}
$$
\[
H + O_2 \rightarrow HO_2
\] (3.6)

The OH radical produced will be converted to HO_2 radical in the presence of CO by
\[
CO + OH \rightarrow CO_2 + H
\] (3.7)

and (3.6). Thus, the role of CO is not only in scavenging OH, but also in producing HO_2. CO will be utilized in some of the experiments to investigate the effect of OH radical in the formation mechanism of (HIO_3).

The photo-dissociation of \(O_2\) in the presence of UVC produces \(O_3\) as shown by
\[
O_2 \rightarrow O(^3P) + O(^3P) \quad \lambda_{\text{threshold}} = 242\text{nm} 
\] (3.8)
\[
O_2 \rightarrow O(^1D) + O(^3P) \quad \lambda_{\text{threshold}} = 175\text{nm} 
\] (3.9)

Two energy states of oxygen atom could be produced, the majority giving ground state \(O(^3P)\) atom. However, to a lesser extent, \(O(^1D)\) is also produced, which is capable of producing OH radical.

After the oxygen atoms are produced from the photolysis of \(O_2\), the \(O(^3P)\) reacts with \(O_2\) to form \(O_3\) by
\[
O(^3P) + O_2 \rightarrow O_3 
\] (3.10)
while \(O(^1D)\) reacts with \(H_2O\) to form two OH radicals ( (3.11)). The residence time of the flow illuminated by the UVC is roughly 0.1s. The major production of OH in this system is the photolysis of \(H_2O\). Thus, in the experiments, the OH/HO_2 ratio is roughly unity.
\[
O(^1D) + H_2O \rightarrow OH + OH 
\] (3.11)

### 3.2 Formation mechanism of (HIO_3)

The importance of (HIO_3) in iodine nucleation was recently revealed by Sipilä et al. (2016), which resulted in the urgency to investigate the formation mechanism of HIO_3. Only quantum chemical mechanisms have been previously used to investigate the possible formation pathways by Plane et al. (2006) and Drougas and Kosmas (2005). There are no previous experimental characterization of gas-phase iodic acid, or its isomers.

Previous studies had shown ClO could react with HO_2 to form (HClO_3) (Francisco and Sander, 1996), as presented in
\[
\text{ClO} + \text{HO}_2 \rightarrow (\text{HClO}_3) 
\] (3.12)

For bromine, Guha and Francisco (1998, 1999) calculated the likelihood of
\[
\text{BrO} + \text{HO}_2 \rightarrow (\text{HBrO}_3) 
\] (3.13)
which turned out that the pathway was possible. Due to the importance of iodine chemistry in the atmosphere as discussed in previous chapters and the observation of HIO$_3$ by Sipilä et al. (2016), there is a need to investigate if the same reaction is possible for IO and HO$_2$ radical. The first calculation on this mechanism was done by Drougas and Kosmas (2005). They did calculations on the different isomers of (HIO$_3$), and found that the HOIO$_2$ was the most stable compound, followed by HOIOOI and then HOIOIO. HIO$_3$ was found the least stable compound among the four. They also indicated that the HOIO$_2$ might be a possible path in the atmosphere in low temperature and high pressure condition, shown by

$$\text{IO} + \text{HO}_2 \rightarrow \text{HOIO}_2$$  \hspace{1cm} (3.14)

The quantum chemical calculations studying the reaction between OIO and OH showed that one branch of the reactions

$$\text{OIO} + \text{OH} \rightarrow \text{HOIIIO}_2$$  \hspace{1cm} (3.15a)
$$\rightarrow \text{IO} + \text{HO}_2$$  \hspace{1cm} (3.15b)
$$\rightarrow \text{HOI} + \text{O}_2$$  \hspace{1cm} (3.15c)

could produce HOIO$_2$, as shown in (3.15a) (Plane et al., 2006). This reaction happens with the simple attachment of O in OH to the I in OIO, which produces the most stable isomer in (HIO$_3$) family (Drougas and Kosmas, 2005). Also, results from Drougas and Kosmas (2005) showed that the IO + HO$_2$ and HOI + O$_2$ potential surfaces contained significant barriers. Moreover, reactions (3.15b) and (3.15c) need to overcome significant energy barriers, which made the reaction (3.15a) the most likely pathway in reaction (3.15) at atmospheric conditions (Plane et al., 2006).

### 3.2.1 Formation of HIO$_3$ from HO$_x$ and iodine oxides

Though, calculated mechanisms suggested two pathways producing (HIO$_3$), there are no direct experimental data confirming these. In our study, flow tube experiments were carried out to investigate the possibility of the pathways suggested by Plane et al. (2006) and Drougas and Kosmas (2005). Typical experimental sequence are shown in Figure 3.1. The first vertical line on the plot marks the initial experimental condition, in this case, 3 standard cubic centimeter per minute (scm) nitrogen gas was used to carry CH$_2$I$_2$ vapor and 10 scm nitrogen to carry water vapor from evaporators to the UVC light source; 30 scm synthetic air, and 10000 scm nitrogen were used as carrier gases. The UVC was used to initiate photochemistry in the system as described in the last section. When roughly 4.8 $\times$ 10$^{17}$ molecules cm$^{-3}$ of CO was injected into the flow tube at stage 2 as marked by a vertical bar in Figure 3.1, nearly all the OH radical was scavenged by reaction (3.7), while, at the meantime, produced the same amount of HO$_2$
and thus doubled the HO$_2$ concentration in the system. During this, the (HIO$_3$) dropped by a factor of 3.5, while OH was scavenged. This indicates that the reaction (3.15a) should be forming (HIO$_3$), as the scavenging of OH radical caused significant drop in (HIO$_3$). On the other hand, the reaction (3.14) should be relatively slower than (3.15a). This is due to the fact that while OH is converted to HO$_2$, the reaction (3.14) is accelerated by a factor of 2 while (3.15a) is shut down. This means the deduction of (HIO$_3$) by reaction (3.15a) is much larger than the increase of (HIO$_3$) by (3.14), because the total effect of both reactions is the deduction of (HIO$_3$). However, no quantitative or relative reaction rates of the reactions (3.14) and (3.15a) have been derived by this stage.

![Figure 3.1: Time series of (HIO$_3$) normalized signals. The black vertical lines in the figure represent different experimental stages and the conditions. Right next to the vertical line, conditions that have been changed are marked. The first stage is the initial stage where all the conditions at that stage are written down. Starting from the second stage, only the changed conditions are written, while the other conditions not noted kept unchanged.](image)

### 3.2.2 Formation of HIO$_3$ from CH$_2$IOO

The photo-dissociation processes of CH$_2$I$_2$ radical were described in section 3.1. This photolysis process are initiated by the release of a CH$_2$I and an I radical at the first step. Promptly after the production of CH$_2$I radical, an oxygen molecule attaches onto the CH$_2$I radical to form the CH$_2$IOO$^\cdot$ intermediate which further stabilizes to either CH$_2$IOO, a peroxy radical or CH$_2$OO, a Criegee bi-radical. Stone et al. (2013) suggested 18% CH$_2$OO (reaction (3.3)) yield
at atmospheric pressure from the reaction of CH$_2$I and O$_2$, while the left of CH$_2$IOO$^\#$ follows reaction pathway given in (3.4).

The CH$_2$IOO peroxo radical could further react with itself to produce an oxygen molecule and two CH$_2$IO radicals as described by reaction

$$
\text{CH}_2\text{IOO} + \text{CH}_2\text{IOO} \rightarrow \text{CH}_2\text{IO} + \text{CH}_2\text{IO} + \text{O}_2
$$

(3.16)

However, whether this reaction is the only fate of CH$_2$IOO peroxo radical in (3.4) is an open question. Experiments were conducted to investigate the fate of CH$_2$IOO radical and its relation to the formation of (HIO$_3$).

**Figure 3.2:** (HIO$_3$) formation experiments CH$_2$I$_2$ experiments with various scavengers: the first step starts with the injection of a high level of CH$_2$I$_2$ in presence of water vapor and synthetic air. This is followed by turning on the UVA blacklight, injection of SO$_2$, turning on UVC, injection of acetic acid vapor, injection of CH$_4$ and finally injection of NO. N$_2$ means purity 5.0 nitrogen gas. H$_2$O means humidified nitrogen flow. SynAir means purity 5.0 synthetic air. UVA means UVA lamps. CH$_2$I$_2$ / N$_2$ means nitrogen flow carrying CH$_2$I$_2$. CH$_3$COOH means nitrogen flow carrying CH$_3$COOH. CH$_4$ means high purity CH$_4$ gas. NO means 50 ppm NO gas. UVC means pen mercury lamp. Ozone means a steam of synthetic air passing a ozone generator. The numbers after the gases and lamps indicators mean the flow rate injected into the system, unit in sccm. However, for ozone, the number after means the concentration of ozone with unit ppb. For UVA and UVC, 2 mean the lamps were on.

Figure 3.2 shows a typical CH$_2$I$_2$ experiments with different conditions to illustrate a new pathway forming HIO$_3$ from the photolysis products of CH$_2$I$_2$. The initial condition includes
synthetic air with water vapor and the injection of CH$_2$I$_2$ vapor carried by nitrogen flow. Both (HIO$_3$) and sulfuric acid are at a low level (below detection limit) at this stage. Further, UVA was turned on in between the first step and second step, where the (HIO$_3$) has a sudden increase around 21:34, to photolyse CH$_2$I$_2$ to produce reactive iodine species. However, the formation of (HIO$_3$) under these conditions could not be explained by previous theories. Formation of IO after the photolysis of CH$_2$I$_2$ may be possible by reaction (Welz et al., 2012)

$$\text{CH}_2\text{I} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{IO} \quad (3.17)$$

or reaction (Gravestock et al., 2010)

$$\text{CH}_2\text{IOO} + \text{I} \rightarrow \text{CH}_2\text{O} + \text{I} + \text{IO} \quad (3.18)$$

However, both mechanisms previously calculated by Plane et al. (2006) (3.15) and Drougas and Kosmas (2005) (3.14) need either OH radical or HO$_2$ radical to produce (HIO$_3$) (Plane et al., 2006; Drougas and Kosmas, 2005). Thus (HIO$_3$) production with this condition could not be explained by either of those mechanisms. The potential precursors for forming (HIO$_3$) are CH$_2$OO, a stabilized Criegee Intermediate (sCI), CH$_2$IOO peroxy radical, CH$_2$IO radical and I radical. In order to understand the reaction pathways, SO$_2$ was added to the system as an indicator for sCI and OH radical, as the OH and sCI are known oxidants for SO$_2$ (Mauldin III et al., 2012). Thus, we could use sulfuric acid as an indicator for the presence of sCI and OH radical. The SO$_2$ was added at step 2 in Figure 3.2. At step 3, a pen mercury lamp (UVC) which is directly illuminating the mixture of synthetic air, water vapor and CH$_2$I$_2$, was turned on. The photo-dissociation processes for related gases were discussed in section 3.1. We could observe considerable increases of both sulfuric acid and (HIO$_3$), which could be related to the presence of HO$_x$ radicals and the sCI produced by CH$_2$I$_2$.

At step 4, acetic acid which can be used as a sCI scavenger was added to the system to study the effect of sCI on the formation of sulfuric acid and (HIO$_3$). A roughly ten times drop of sulfuric acid was observed by adding acetic acid to the system, which showed a significant amount of sCI produced by CH$_2$I$_2$ was scavenged at that time. However, only about 10% decrease of (HIO$_3$) was observed. This indicates that the major oxidant for production of (HIO$_3$) under these conditions would not be sCI.

At step 5, CH$_4$ was further added to the system to scavenge OH radicals in the flow tube. Both sulfuric acid and (HIO$_3$) dropped by about 10%, showing OH initiated production of sulfuric acid and (HIO$_3$) are functioning in this experimental condition. The reason why the production of sulfuric acid wasn’t terminated by adding OH and sCI scavengers is that the reaction rates of SO$_2$ with sCI and OH radical could compete with the scavengers considering their concentrations in the system.
Finally, at the step 6, NO was injected to the system to check whether peroxo radical could be causing the majority production of (HIO₃). (3.19) illustrates the reaction between CH₂IOO peroxo radical and NO. We observed a factor of a hundred deduction in the (HIO₃) signal with the injection of NO. This is suggesting that the CH₂IOO might be one of the components that is producing (HIO₃). However, with this set of experiments, we could not exclude the possibility that the iodine radical might be the main iodine precursor for producing (HIO₃). As the iodine radical could also react with NO radical and thereby NO to scavenge iodine radical in parallel with scavenging CH₂IOO. The second possibility is that the iodine radical reacts with ozone to produce iodine oxides first which further reacts with NO to produce nitrogenated iodine compounds. Further detailed experiments investigating whether CH₂IOO or iodine radical is the main iodine precursor for producing (HIO₃) are needed to understand this issue.

\[
\text{CH₂IOO + NO \rightarrow CH₂O + NO₂}
\]  

(3.19)

3.2.3 The formation of HIO₃ from CH₂IOO without OH, NO₃, O₃, sCI

Though Figure 3.2 qualitatively illustrates a pathway forming (HIO₃) might start from CH₂IOO as an iodine precursor, the experiments are not dedicated enough. First the steps in fig. 3.2 are not well controlled. For example, the acetic acid which is a sCI scavenger was not the dominant reactant reacting with sCI. This made the SO₂ compete with acetic acid in reacting with sCI. Ideally, a scavenger should be effective enough that it becomes the major remover of a compound that is supposed to be scavenged. Second, UVC was used as a light source to photolyse H₂O, CH₂I₂ and O₂ to initial photochemical reactions. UVC is a strong light source that contains light with wavelength below 200 nm. A light sources with so strong energy will produce iodine radical with different energy states (IUPAC, 2017). We could not be certain whether the chemical reaction of iodine radical with a higher energy is similar and representative to the iodine radical with lower energy state which is often produced in troposphere. Thus, dedicated experiments with well-controlled precursor concentrations and more tropospheric relevant light sources are needed to study whether the pathway forming (HIO₃) is realistic in real tropospheric condition.

Seven sets of more dedicated experiments aiming to repeat and deepen the understanding in fig. 3.2 were carried out to investigate the main iodine precursor that is forming (HIO₃) following the photolysis of CH₂I₂ in absence of ozone. From previous discussion in section 3.2.2, the CH₂IOO peroxo radical is speculated to be the iodine precursor of the formed (HIO₃). However, whether other oxidants (sCI, OH, ozone, NO₃) are involved in the process is currently not known. The experimental conditions in these experiments are listed in Table 3.1.
The experiments are numbered the same order as shown in the legend of Figure 3.3. In all the experiments, ozone was excluded from the system. Only nitrogen, synthetic air, humidified nitrogen and synthesized CH$_2$I$_2$ from bottle were injected into the flow tube system. In principle, the main oxidants under these conditions should be sCl, which is a product following the photolysis of CH$_2$I$_2$, and OH radical, which could be a product from sCl (Novelli et al., 2014). There should not be notable ozone and NO$_3$ radical sources. However, as the purity of the gases we were using was 99.99999%, which means there are maximum 10 ppm impurities in the system. Thus, we use scavengers for scavenging different oxidants to determine whether OH, ozone, NO$_3$ and sCl are involved in the formation of (HIO$_3$), following the photolysis of CH$_2$I$_2$. The 7th experiments were done without the presence of any scavengers. This serves as a reference for the other experiments.

Table 3.1: Experimental conditions in Figure 3.3. There is no ozone injection in any of the 7 sets of experiments. Scavengers indicated in the scavenger column were injected into the system. Experimental number corresponds to the numbers in the legend of Figure 3.3. The temperature was measured by placing a temperature sensor on the the outer surface of the flow tube.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>T(°C)</th>
<th>CH$_2$I$_2$, ppb</th>
<th>O$_2$, ppm</th>
<th>H$_2$O, ppm</th>
<th>Ozone, ppb</th>
<th>Scavenger, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26</td>
<td>1.15-2.88</td>
<td>10500</td>
<td>3138</td>
<td>0</td>
<td>CH$_4$ 5000</td>
</tr>
<tr>
<td>2</td>
<td>36</td>
<td>0.58-2.88</td>
<td>10500</td>
<td>3138</td>
<td>0</td>
<td>SO$_2$ 12.5</td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>1.15-2.88</td>
<td>10500</td>
<td>3138</td>
<td>0</td>
<td>Cyclohexene 29.62</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>1.15-2.88</td>
<td>10500</td>
<td>3138</td>
<td>0</td>
<td>Acetic acid 3.17</td>
</tr>
<tr>
<td>5</td>
<td>37</td>
<td>1.15-2.88</td>
<td>10500</td>
<td>3138</td>
<td>0</td>
<td>SO$_2$ 12.5 and CH$_4$ 5000</td>
</tr>
<tr>
<td>6</td>
<td>37.5</td>
<td>0.86-2.88</td>
<td>10500</td>
<td>3138</td>
<td>0</td>
<td>NO 0.25</td>
</tr>
<tr>
<td>7</td>
<td>26</td>
<td>1.15-2.30</td>
<td>10500</td>
<td>3138</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The first set of experiments used CH$_4$ as an OH scavenger. 5000 ppm of CH$_4$ was injected into the flow tube with experimental conditions identical to the 7th experiments. The temperature in both system was roughly 26°C. Both experiments produced identical amount of (HIO$_3$) at every applied concentration of CH$_2$I$_2$. This indicates that the OH radical is not the main oxidant that is involved in the formation of (HIO$_3$) in this condition. At the meantime, the HO$_2$ should not be responsible for the (HIO$_3$) production neither. This is because if both OH and HO$_2$ are present in the system, the injection of CH$_4$ should increase the amount of HO$_2$ in the system, with subsequently higher (HIO$_3$), which was not observed in the comparison between the 7th experiments and the first experiments.

The second experiments used SO$_2$ as both OH and sCl scavengers, as SO$_2$ could also be oxidized by sCl as suggested by (Mauldin III et al., 2012). The fifth experiments utilized both SO$_2$ and CH$_4$ to scavenge OH radical and sCl. These two sets of experiments were done
Figure 3.3: Production of HIO$_3$ without ozone in the presence of different oxidants scavengers. 1. CH$_4$ as a OH scavenger. 2. SO$_2$ as an OH and sCI scavenger. 3. Cyclohexene as an ozone and OH scavenger. 4. Acetic acid as a sCI scavenger; A green lamp is on at the same experiments which could eliminates NO$_3$ radical. 5. SO$_2$ and CH$_4$ as OH and sCI scavengers. 6. NO as a peroxy radical, I radical and IO radical scavenger at similar temperature, 36°C and 37°C respectively. They yield similar amount of (HIO$_3$) as illustrated by the blue circled line and yellow circled line in Figure 3.3. The other phenomenon we could observe is that the yield of (HIO$_3$) is higher than in the 7th experiments which are background values without any scavenger. This could result from distribute to the difference in experimental temperature, as the temperature in the second and the 5th experiments is roughly 10°C higher than in the 7th. If the OH radical or sCI would be the dominant oxidant for the formed (HIO$_3$), the (HIO$_3$) should be scavenged regardless of the small temperature change. This phenomenon suggests that neither OH radical or sCI is the oxidant for the formed (HIO$_3$).

The fourth experiments used acetic acid as a sCI scavenger as in Novelli et al. (2014). The temperature in these experiments was around 30°C, which is in between of the second and 7th experiments. We could observe the yield of (HIO$_3$) (orange stared line) is as well between the yields of the second (blue circled line) and 7th (green stared line in Figure 3.3). Again, if the sCI would be the dominant oxidant forming (HIO$_3$), the (HIO$_3$) would decrease. And the yield difference could be explained by the temperature difference between the experiments.
The sixth experiments adopt NO for scavenging I, IO and CH₂IOO peroxy radicals. An abrupt deduction of (HIO₃) signal could be observed by comparing the sixth experiments with all the other experiments. It is obvious that high concentration of NO prohibits the formation of (HIO₃). From previous understanding, the formation of (HIO₃) from I radical or IO radical needs the participation of either HO₂ radical or OH radical. Thus, it suggests that the CH₂IOO peroxy radical might be the iodine precursor for (HIO₃). The non-linear dependence of HIO₃ on CH₂I₂ indicates there might be a bimolecular reaction from two CH₂IOO radicals forming (HIO₃) as shown by reaction:

\[
\text{CH}_2\text{IOO} + \text{CH}_2\text{IOO} \rightarrow \text{(HIO}_3\text{)} + \text{products}
\]  (3.20)

However, it is worth noting that the powers of the power fittings of the seven experiments are within the range 2.6 – 3.1. Whether it is an experimental uncertainty, or the formation of (HIO₃) could not be explained by (3.20) remains a question.

The third experiments used cyclohexene as a ozone and OH scavenger. Though cyclohexene is not a sufficient ozone scavenger, the concentration of cyclohexene is at least 5 order of magnitudes higher than iodine radical in these experiments, while the reaction rate of iodine radical with ozone is roughly $1 \times 10^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$ and that of cyclohexene is roughly $8.1 \times 10^{-17}$ cm$^3$ molecules$^{-1}$ s$^{-1}$. This makes the rate of cyclohexene in reacting with ozone roughly 10 times faster than iodine radical. Thus, if there would be some unknown sources of ozone existing in the flow tube system, it should be reacting with cyclohexene faster than iodine radical. Furthermore, if the production of (HIO₃) relies on ozone, a clear deduction of (HIO₃) would be observed. At the mean time, a green fluorescence lamp which is efficient for NO₃ photo-dissociation was turned on to eliminate NO₃ if it was present in the chemical system. Interestingly, a higher production of (HIO₃) was observed compared to the second experiments, which used SO₂ as an OH and sCI scavenger. This phenomenon could not be explained by temperature effects as in both the second and the third experiments as the temperatures are roughly the same. A proposed mechanism is that OH radical produced by sCl is reacting with cyclohexene to produce peroxy radicals. And he peroxy radical could react with CH₂IOO to produce (HIO₃), as shown by reaction:

\[
\text{CH}_2\text{IOO} + \text{ROO} \rightarrow \text{HIO}_3 + \text{products}
\]  (3.21)

However, currently there is not enough experimental data to confirm this pathway.

### 3.2.4 Formation of HIO₃ from O₃

Experiments were performed to investigate the formation mechanism of (HIO₃) from the photo-oxidation of I₂ with in presence of ozone. Humidified nitrogen together with synthetic air were
used as carrier gases in a flow tube. Approximately 25 ppb ozone was injected into the flow tube and the concentration of molecular iodine varying roughly from 0.3 ppb to 1 ppb. The flow tube is directly illuminated by a green fluorescent lamp, which could photolyse molecular iodine efficiently. Significant amount of (HIO\textsubscript{3}) (ppt level) was observed by from nitrate CI-API-TOF (NCI) without active input of HO\textsubscript{x} radicals in the system which poses a question that how could the (HIO\textsubscript{3}) be formed from reactive iodine species without HO\textsubscript{x} radicals. Although two green fluorescent lamps were applied to photolyse molecular iodine, these lamps were not sufficient for photolyzing ozone to produce the OH radical due to the long wavelength of the lamps. Thus, if there are HO\textsubscript{x} radicals in the chemical system, they are produced by reactions between impurities from the nitrogen gas with ozone. If this is the case, then the injection of OH scavengers should eliminate (HIO\textsubscript{3}) from the system. On the other hand, if HO\textsubscript{x} radicals are not necessary in producing (HIO\textsubscript{3}), the introduction of OH scavengers should not affect the yield of (HIO\textsubscript{3}).

Four sets of experiments were carried out to investigate whether the observed (HIO\textsubscript{3}) from the photo-oxidation of molecular iodine needs the participation of HO\textsubscript{x} radicals. The (HIO\textsubscript{3}) normalized signal from NCI versus the ratio between I\textsubscript{2}Br\textsuperscript{-} to Br\textsuperscript{-} in bromide CI-API-TOF (BrCI) are plotted in Figure 3.4, with the experimental conditions listed in Table 3.2. The ratio in X-axis is used as a proxy for indicating the amount of molecular iodine input in the system. Note the Br\textsuperscript{-} anion is the reagent ion of the BrCI. Normally it is required to operate the system so, that the dominant ion peak is the reagent ion peak. However, in some parts of the experiments, I\textsubscript{2}Br\textsuperscript{-} anion has higher signal than the Br\textsuperscript{-} anion, which could cause non-linear response of the chemical ionization system. Nevertheless, qualitatively, higher ratio still represents higher concentration of molecular iodine in the system. Temperature in all the four sets of experiments was roughly 27\textdegree C. The first experiments were reference experiments without an additional scavenger. While the second set of experiments utilized SO\textsubscript{2} as OH scavenger, the third experiments used CH\textsubscript{4} as OH scavenger; and the last set of experiments employed NO as an I and IO radicals scavenger.
Table 3.2: Experimental conditions in Figure 3.4. The system is illuminated by green fluorescence lamps with stable input of ca. 25 ppb ozone and humidified nitrogen and synthetic air gases. The first experiments were reference experiments. The second experiments utilized SO\(_2\) as an OH scavenger to check if the OH radical is a necessary oxidant in the formation of (HIO\(_3\)) from the photo-oxidation of I\(_2\). The third experiments use CH\(_4\) as the other choice of OH scavenger to double check if OH radical has an effect on the formation of (HIO\(_3\)) in this circumstance, and to compare whether SO\(_2\) has an effect on the chemical system other than scavenging OH radical.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>I(_2), ppb</th>
<th>O(_2), ppm</th>
<th>H(_2)O, ppm</th>
<th>Ozone, ppb</th>
<th>Scavenger, ppm</th>
</tr>
</thead>
<tbody>
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<td>3138</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>~0.28-1</td>
<td>10500</td>
<td>3138</td>
<td>25</td>
<td>SO(_2) 12.5</td>
</tr>
<tr>
<td>3</td>
<td>~0.28-1</td>
<td>10500</td>
<td>3138</td>
<td>25</td>
<td>CH(_4) 5000</td>
</tr>
<tr>
<td>4</td>
<td>~0.28-1</td>
<td>10500</td>
<td>3138</td>
<td>5</td>
<td>NO 0.25</td>
</tr>
</tbody>
</table>

Figure 3.4: Production of (HIO\(_3\)) from the photo-oxidation of molecular iodine. X-axis is the ratio between I\(_2\)Br\(^-\) to Br\(^-\) in BrCl. Y-axis is the normalized signal of (HIO\(_3\)) from NCI. The first experiments are background experiments without any scavengers. The second experiments deploy SO\(_2\) as an OH radical scavenger. The third experiments utilize CH\(_4\) as an OH scavenger. The 4th experiments use NO to scavenge iodine radical and iodine oxides.

When the ratio of I\(_2\)Br\(^-\) to Br\(^-\) was over 1, Br\(^-\) is not the dominant peak, the charging in
the chemical ionization inlet is random and it causes problems to quantitatively compare the
signals of different peaks in the BrCl. Thus, the focus should be put into the data with X-axis
below 1.

When the ratio is below 1, we could observe that the first and the third sets of experiments
show similar productions of \((\text{HIO}_3)\). This indicates that the OH radical is not playing an
important role in the formation of \((\text{HIO}_3)\) in the chemical system. However, when applying
\(\text{SO}_2\) as an OH scavenger, the yield of \((\text{HIO}_3)\) decreased compared to the first and third sets of
experiments. This phenomenon will be discussed in the following section further. When using
\(\text{NO}\) as an I and IO radical scavenger, the production of \((\text{HIO}_3)\) is shut down immediately.
This phenomenon is directly suggesting that either the I radical or iodine oxides should be the
precursor of the formed \((\text{HIO}_3)\). Based on the assumption that the formation of higher iodine
oxides first involve a self-reaction of IO radical ( (4.3)), iodine radical and iodine monoxide are
the likely iodine precursors of the formed \((\text{HIO}_3)\). This is because if the higher iodine oxides
would be the main precursors of the formed \((\text{HIO}_3)\), the correlation of the observed \((\text{HIO}_3)\)
signal in NCI and the molecular iodine observed by BrCl should be non-linear, while it behaves
linear in Figure 3.4.

Thus, up to now, the proposed formation mechanism/s to support this observation would
be

\[
\text{I/IO} + \text{O}_3 + \text{H}_2\text{O} \rightarrow (\text{HIO}_3) + \text{products} \tag{3.22}
\]

Either one or both iodine radical and/or iodine monoxide, are participating in the reactions
to produce \((\text{HIO}_3)\), which also involves ozone and water. The exact formation pathway is not
known yet.

### 3.3 Reactive iodine as a \(\text{SO}_2\) oxidant

Sulfuric acid is an important species that participates in atmospheric nucleation and the for-
mation of cloud condensation nuclei (Kirkby et al., 2011). OH radical is known to be the main
gas-phase oxidant of \(\text{SO}_2\) as illustrated in

\[
\text{SO}_2 + \text{OH} \rightarrow \text{H}_2\text{SO}_4 \tag{3.23}
\]

However, the oxidant budget of \(\text{SO}_2\) is not fully constrained yet. Observations in Hyytiälä, a
boreal forest site in southern Finland, suggested that new oxidant/s, possibly stabilized Criegee
intermediates (sCI), are needed to explain the discrepancy between the measured sulfurous acid
concentration and the theoretical sulfurous acid concentration calculated from measured OH
radical (Mauldin III et al., 2012). Another example is that evidence from a coastal site in Mace
Head, Ireland, showed that one or more oxidants were needed to explain the observed sulfurous
acid concentration. As again the observed OH radical concentration could not explain the sulfuric acid presenting there. A factor of $4.7(\pm 2.7)$ higher concentrations of sulfuric acid was observed compared to the calculated values, if the SO$_2$ was only oxidized by OH radical. sCI was suggested not important in the marine boundary layer in Mace Head (Berresheim et al., 2014). These observations urge more studies need to be performed to complete the understanding of the oxidation processes leading to the formation of sulfuric acid under ambient conditions.

Iodine monoxide has been speculated a potential oxidant for oxidizing SO$_2$ by

$$\text{IO} + \text{SO}_2 \rightarrow \text{SO}_3 + \text{I}$$

Larin et al. (2000) measured that the rate of IO reaction with SO$_2$ should be lower than $\leq 5.6 \times 10^{-15}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ at 343K condition. Berresheim et al. (2014) used an ab initio method to calculate the rate of the same reaction as $1.610^{-15}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ at 343K, resulted a reaction rate of $8.510^{-16}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ at 293K. The ratio between the reaction rate of SO$_2$ with IO radical to the rate with OH radical is $1/1050$ in their study. Considering a typical IO to OH ratio of 30, the OH pathway is 35 times faster than the IO pathway to produce sulfuric acid (Berresheim et al., 2014). This would suggest an insignificant contribution of IO in the production of sulfuric acid in Mace Head.

However, no direct measurement of sulfuric acid was performed by Larin et al. (2000), which is the final product of the reaction between SO$_3$ and water in the experiments. Also elevated temperature was used in the same study which was much higher than in the ambient. A direct measurement of sulfuric acid would needed to further investigate reactions between iodinated species and SO$_2$ as there might be other iodine species than IO that could react with SO$_2$ to produce sulfuric acid.

In order to compensate for the missing knowledge in whether reactive iodine could accelerate the oxidation processes of SO$_2$ which further leads to the production of sulfuric acid, dedicated flow tube experiments were carried out to measure directly the sulfuric acid production from the photo-oxidation of the SO$_2$ and iodine mixture. Beside from the sulfuric acid, reactive iodine species, higher iodine oxides, iodine and nitrogen containing species as well as iodine acids were measured simultaneously using the above mentioned BrCI (chapter 2). This technique enables us to measure most of the species that could be participating in the photo-oxidation of iodine species and the oxidation processes of SO$_2$.

Three sets of experiments were performed as listed in Table 3.3. The first experiments investigated the effect of varying ozone concentration in the mixture of iodine species and SO$_2$. The second experiments investigated whether changing iodine precursor could affect the production of sulfuric acid. The third experiments examined the role of changing SO$_2$ in the production of sulfuric acid. Each of these experiments are described in their own subsections.
Table 3.3: Experiments investigating the sulfuric acid production from interaction with iodinated species. The first experiments explore the effect of ozone in the production of sulfuric acid with the presence of reactive iodine species. The second experiments investigate the effect of the amount of reactive iodine species in the production of sulfuric acid. The third experiments vary the amount of \( \text{SO}_2 \) in the system to insect whether sulfuric acid production depends on it. All of the three experiments were performed under the illumination of a green fluorescent lamp which is effective in photolysing molecular iodine.

<table>
<thead>
<tr>
<th>Number</th>
<th>( I_2 ), ppb</th>
<th>( O_2 ), ppm</th>
<th>( H_2O ), ppm</th>
<th>Ozone, ppb</th>
<th>( \text{SO}_2 ), ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.674</td>
<td>15000</td>
<td>224.2</td>
<td>0.9-175</td>
<td>35.7</td>
</tr>
<tr>
<td>2</td>
<td>≥ 0.2</td>
<td>10500</td>
<td>3138</td>
<td>32</td>
<td>1.25</td>
</tr>
<tr>
<td>3</td>
<td>0.674</td>
<td>15000</td>
<td>224.2</td>
<td>1.3</td>
<td>1.07-35.7</td>
</tr>
</tbody>
</table>

### 3.3.1 Ozone dependence of the production of sulfuric acid

The results of the first experiments are shown in Figure 3.5. The green circled line shows the results from experiments with the conditions shown on Table 3.3, experiment number 1. The blue circled line illustrates the reference experiments without molecular iodine injection. It is worth noting that in the reference experiments, there was molecular iodine re-evaporating from the flow tube surface due to the deposition of molecular iodine from previous experiments. However, the concentration of the residual iodine is much less than the injected amount. From the figure, we could observe notable sulfuric acid production under the reference conditions with low iodine concentrations in the system. Nevertheless, the experiments with iodine injection produced significantly more sulfuric acid, at least an order of magnitude, compared to the reference experiments. This indicates the photo-oxidation products of molecular iodine are participating in the oxidation processes of \( \text{SO}_2 \). We could also observe there is a saturation point for the ozone in the production of sulfuric acid. When the ozone concentration was between 0 to 40 ppb, the production of sulfuric acid sharply increased, while when the ozone concentration was over 40 ppb, the increase of ozone did not affect the production of sulfuric acid significantly. This is likely due to the fact that the relevant chemical processes are limited by other factors, for example, the amount of iodine radical produced from photo-oxidation of molecular iodine.

### 3.3.2 \( \text{SO}_2 \) dependence of the production of sulfuric acid

The third experiments were carried out to examine the effect of different \( \text{SO}_2 \) concentrations on the production of sulfuric acid. The results are shown on Figure 3.6. Beside from sulfuric acid, different measurable iodine compounds are plotted as well.
Figure 3.5: Normalized sulfuric acid signal from BrCI versus different ozone concentrations in the experiments. The experimental condition is described in Table 3.3, experimental number 1. The first green circled line is the experiments with the presence of a fixed concentration of roughly 0.67 ppb molecular iodine. The blue circled line is the condition identical to the first experiments, except no active input of molecular iodine.

Figure 3.6: Normalized signals for different species from BrCI versus different SO$_2$ concentrations in the experiments. The experimental conditions are described in Table 3.3, experiment number 3. A fixed amount of molecular iodine input of about 0.67 ppb is applied in the experiments.
The sulfuric acid has a positive correlation with the amount of SO$_2$ input to the flow tube, which is as expected. Interestingly, even with the lowest amount of SO$_2$ input at around 1.07 ppm, all the products of iodine oxidation processes, including iodine radical, are either completed scavenged or largely eliminated, without significant increase in molecular iodine signal. According to the previous assumption that IO could oxidize SO$_2$ as described by (5.4), it is understandable that with a large SO$_2$ input to the system reduces the amount of oxidation products formed through IO. This is because normally IO is the necessary precursor for higher iodine oxides, iodine acids and other iodine-nitrogen containing compounds. However, a negative correlation of the amount of SO$_2$ and iodine radical was also observed. If the reaction (5.4) was the major pathway that is producing sulfuric acid at this experimental condition, the amount of iodine radical should increase rather than decrease with the increasing SO$_2$ input. Moreover, the total amount of major iodine species observed as shown on the plots are also decreasing with the increasing SO$_2$. The reason for this behavior is not known. The first possibility is that the oxidant for SO$_2$ is not IO solely, there is another pathway that is oxidizing SO$_2$ and producing an iodine species that is not measurable by our technique. The second possibility is that the produced iodine species is measurable by our instruments, but is decomposing inside the vacuum parts of our instruments which is not detected afterwards. The third possibility is that the SO$_2$ increases the wall loss of IO at laboratory temperature as mentioned by Larin et al. (2000).

### 3.3.3 I$_2$, Green light and SO$_2$ dependences of the production of sulfuric acid

The second experiments shown in Table 3.3 are investigating the effect of molecular iodine concentrations on sulfuric acid production. Four different subsets were carried out to investigate whether the green fluorescent lamps, and SO$_2$ were necessary in the production of sulfuric acid in the mixture of iodine and SO$_2$.

An order of magnitude more sulfuric acid was produced with green lamp on and stable input of SO$_2$, compared to the three references experiments having one or both the conditions missing. This implies that the photolysis products of I$_2$ and SO$_2$ are required in the production of sulfuric acid. Although there is clearly some sulfuric acid production without green light on at the third experiments, it was possibly due to the sulfuric acid evaporating from the surface of the flow tube. Or potentially the ozonolysis processes happen with the contaminant organic matter in the carrier gas flow which produces OH radical which then oxidizes SO$_2$. 

45
Figure 3.7: Measured sulfuric acid normalized signal versus molecular iodine input concentrations under four different conditions. The first experiments have green fluorescent lamps turned on with fixed amount of SO$_2$ input (1.25 ppm). The second experiments turned off green lamps but with the same SO$_2$ input. The third experiments turned off green lamp and shut down SO$_2$ input. The fourth experiments turned off the SO$_2$ flow into the system but with green lamp on.

3.4 OH initiated iodine oxide formation

Beside from photolytical production of the iodine radical discussed in the previous chapters, OH radical could also initiate the formation of iodine radical, and further iodine oxides, from molecular iodine through reaction

\[ \text{I}_2 + \text{OH} \rightarrow \text{HOI} + \text{I} \]  \hspace{1cm} (3.25)

From the reaction of molecular iodine and OH radical, one iodine atom and a hypoiodous acid is produced.

After the production of HOI, HOI also goes photo-dissociation processes under the illumination of different light sources. The four pathways that could happen under a pen mercury lamp radiation are shown in reaction (IUPAC, 2017)
\[
\text{HOI} + \text{hv} \rightarrow \text{OH} + \text{I} \quad \lambda_{\text{threshold}} = 507\text{nm} \tag{3.26a}
\]
\[
\rightarrow \text{HI} + \text{O}^\text{(3P)} \quad \lambda_{\text{threshold}} = 327\text{nm} \tag{3.26b}
\]
\[
\rightarrow \text{IO} + \text{H} \quad \lambda_{\text{threshold}} = 288\text{nm} \tag{3.26c}
\]
\[
\rightarrow \text{HI} + \text{O}^\text{(1D)} \quad \lambda_{\text{threshold}} = 216\text{nm} \tag{3.26d}
\]

The photo-dissociation of HOI will produce more reactive iodine either by direct production of I or IO, or indirectly by producing oxygen atoms, which could further react with molecular iodine to produce an iodine atom and an iodine monoxide. Thus, the yield of iodine radical and iodine oxides from the reaction of OH and I\textsubscript{2} should be over unity, as one molecule of molecular iodine could produce two iodine radicals or oxides.

The panel A and B on Figure 3.8 show the IO and OIO normalized counts with respect to normalized I\textsubscript{2} respectively. The experimental set three has significantly higher IO and OIO counts than set 4. The experimental set 4 has active CH\textsubscript{4} injection in addition to the experimental condition in experimental set 3. This difference in the IO and OIO signals suggests that the OH radical should be participating in the process producing iodine oxides. This phenomenon could be explained by the OH initiation to form reactive iodine species in the system as shown by reaction (3.25).

Another direct indication that the OH participates in the formation of iodine oxides comes from the normalized signal of HOI, as shown by Figure 3.9. The experimental set 3 has notably larger HOI than all the other experiments. This could be caused by the large amount of HO\textsubscript{x} radical produced by the pen mercury lamp. Beside from the production of HOI from reaction (3.25), another pathway producing HOI could be as described by reaction
\[
\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2 \tag{3.27}
\]

However, the production of HOI in the 3rd experiments should mainly be from OH pathway, as when adding CH\textsubscript{4} into the system, as shown by the 4th experiments, the HOI signal dropped a magnitude. This indicates that the OH radical is the main reason of the HOI production. However, if comparing the HOI yield from the 4th experiments with first, second and 5th experiments, HO\textsubscript{2} pathway still plays a role in the production of HOI. As the 4th experiments have significantly higher HO\textsubscript{2} radicals compared to the other three experiments, and the HOI normalized signal in the 4th experiments is slightly higher than the other three experiments.
Figure 3.8: \( I_2 \) normalized counts versus iodine oxides normalized counts. A) \( I_2 \) normalized versus IO normalized. B) \( I_2 \) normalized versus OIO normalized counts. C) \( I_2 \) normalized versus \( I_2O_2 \) normalized counts. D) \( I_2 \) normalized versus \( I_2O_3 \) normalized counts. The experimental conditions are the same as Table 2.2. The whole experiments were under dark conditions except for some indication lights on different instruments and short time illumination of computer screen at changing steps. Legends indicate the different experimental conditions of different sets of experiments. Ozone means the existence of ozone at similar level. The input of the ozone at different experiments was kept unchanged. However, the illumination of UVC2 will increase the ozone concentration by roughly 3ppb. The UVC1 means only filtered mercury lamp was turned on. The UVC2 means both the filtered and the bare mercury lamps were turned on. CH\(_4\) means CH\(_4\) was injected to the system with known concentration as written on Table 2.2.
Figure 3.9: The comparison of I$_2$ and HOI in the selected experiments. The experimental condition is described in Table 2.2.
4. Iodine particle formation

Previously, sulfuric acid was proposed to account for the particle formation process over oceans, and Antarctica (O’Dowd et al., 1997). The source of sulfuric acid has been related to the oxidation of DMS(dimethyl sulfide). However, nucleation rate from sulfuric acid alone has failed to explain the vast amount (300,000cm⁻³) of particles formed in Mace Head during low tide condition. This implied an unknown compound 'X' to be involved in this nucleation process (O’Dowd et al., 1999). Investigations later showed that the tidal cycles of organoiodide (Carpenter et al., 1999) and iodine compounds (Alicke et al., 1999) indicated that iodine might be involved in the nucleation process in coastal areas (Saiz-Lopez et al., 2012). In the sea water, the concentration of iodide ion(I⁻) is generally very low, while the bromide(Br⁻) and chloride(Cl⁻) ions are present in substantial quantities. However, particle composition analysis showed that marine particles are concentrated in iodine, but depleted in chlorine and bromine, which is in contrast to their relative abundance in sea water (Simpson et al., 2015). This phenomenon indicates a more important role of iodine containing species than chlorine and bromine containing species in marine new particle formation processes.

4.1 Iodine particle formation

A comprehensive and dedicated campaign was carried out on the western coast of Ireland (O’Dowd et al., 2002). 90% days in a two year long campaign observed new particle formation. Aerosol concentration exceeding 10⁶ cm⁻³ was often observed. Nucleation rates were estimated, to be at least 10⁵ to 10⁶ cm⁻³s⁻¹ (O’Dowd et al., 2002). However, modeling results showed that the sulfuric acid concentration (10⁶ cm⁻³) during the campaign could not explain the fast growth of particles from 1nm to 3nm in size. Furthermore, hygroscopic analysis showed that these particles likely comprised also some other compounds, which were less soluble to water than sulfate aerosols (O’Dowd et al., 2002). Considering the strong biogenic emission of halocarbons from the biota in the coastal areas, iodine oxide could explain the rapid particle formations in coastal areas (O’Dowd et al., 2002). This was already proved by pioneering laboratory studies by Aitken in 1911.
However, whether the nucleation was triggered by iodine oxide alone, or the first stable cluster is formed by either halocarbons or sulfuric clusters, remained a question at the time. North Atlantic Marine Boundary Layer Experiments (NAMBLEX) (Heard et al., 2006) aimed to solve the question between the relationship between iodine and the nucleation process was carried out in 2002. Modeling results, which were based on the assumption that the homogeneous nucleation of OIO forms particles, were applied to explain the particle formation in NAMBLEX campaign. However, this approach failed to explain the observed NPF as the IO and OIO were found to be 1 to 2 orders of magnitude too low (Burkholder et al., 2004).

After studying coastal new particle formation in Mace Head for a while, one question arose: does the same mechanism exist elsewhere than Mace Head? In the Reactive Halogens in the Marine Boundary Layer (RHaMBLe) experiments conducted on the northwest coast of France, this question was answered with a ’yes’ (McFiggans et al., 2010). The LP-DOAS even measured higher in-situ IO concentrations than had been measured in Mace Head. A similar low tide with high particle formation during the daytime was observed, which agrees with the phenomenon observed in Mace Head (Saiz-Lopez et al., 2012). This suggests that the coastal new particle formation process observed in Mace Head might be more universal than previously thought.

Photooxidation experiments using CH$_2$I$_2$ as a precursor were performed in the presence of O$_3$ in Caltech indoor chamber (Jimenez, 2003). Surprising amount of particles were formed after the exposure of CH$_2$I$_2$ and O$_3$ mixture to the UV light, while no particles were formed under dark conditions, or without the presence of O$_3$. Thus, photooxidation of CH$_2$I$_2$, resulting in the formation of OIO, was proposed to be the dominant mechanism to form particles over coastal areas (Jimenez, 2003). However, the authors also admitted that the this nucleation process is likely not complete, as if the OIO is the only compound that is nucleating, the mass accommodation factor for the gas to particle conversion would be nearly unity (Jimenez, 2003; Saiz-Lopez et al., 2012).

Further, probable solid particle compositions resulting from oxidation of reactive gas-phase iodine were proposed to be I$_2$O$_4$ and I$_2$O$_5$ (Saiz-Lopez et al., 2012; Saunders and Plane, 2005; Saunders et al., 2010). Transmission electron microscope analysis of particles generated from molecular I$_2$ and O$_3$ showed that the IOPs(iodine oxide particles) were I$_2$O$_5$ (Saunders and Plane, 2005). The formation of I$_2$O$_5$ was speculated by Saunders and Plane (2005) to be the reaction between I$_2$O$_4$ and O$_3$. However, a study carried out with the photolysis of N$_2$O showed that even without the presence of O$_3$, the IOP could also be produced. These experiments were done with photolysis of N$_2$O to produce O atom, which further reacts with iodine molecule to produce one iodine atom and one iodine monoxide as shown by reactions

\[ \text{N}_2\text{O} + \text{hv} \rightarrow \text{N}_2 + \text{O} \quad (4.1) \]
\[ \text{I}_2 + \text{O} \rightarrow \text{IO} + \text{I} \quad (4.2) \]

Though, the authors cannot exclude that particles could form from \( \text{I}_2\text{O}_5 \) from this piece of clue, they could conclude that at least there is another mechanism producing IOPs from iodine oxides than this mechanism alone. Saunders et al. (2010) then proposed that the \( \text{I}_2\text{O}_3 \) and \( \text{I}_2\text{O}_4 \) should account for the particle formation observed in the \( \text{N}_2\text{O}_5 \) system, as those two iodine oxides can be produced by reaction (4.4) and (4.5).

\[
\begin{align*}
\text{IO} + \text{IO} & \rightarrow \text{OIO} + \text{I} \\ 
\text{IO} + \text{OIO} & \rightarrow \text{I}_2\text{O}_3 \\ 
\text{OIO} + \text{OIO} & \rightarrow \text{I}_2\text{O}_4 \\ 
\text{I}_2\text{O}_4 + \text{O}_3 & \rightarrow \text{I}_2\text{O}_5
\end{align*}
\] (4.3) (4.4) (4.5) (4.6)

To explain the observed \( \text{I}_2\text{O}_5 \) in the particles, Saunders et al. (2010) proposed the \( \text{I}_2\text{O}_3 \) and \( \text{I}_2\text{O}_4 \) should further polymerize to form \( \text{I}_4\text{O}_7 \) and \( \text{I}_4\text{O}_8 \) through reactions

\[
\begin{align*}
\text{I}_2\text{O}_3 + \text{I}_2\text{O}_4 & \rightarrow \text{I}_4\text{O}_7 \\ 
\text{I}_2\text{O}_4 + \text{I}_2\text{O}_4 & \rightarrow \text{I}_4\text{O}_8
\end{align*}
\] (4.7) (4.8)

which then restructure to \( \text{I}_2\text{O}_5 \) and \( \text{I}_2 \) in the solid phase (Saiz-Lopez et al., 2012). Though kinetic study showed the IOP particles can form fractal-like structures (Saunders and Plane, 2006), they were suggested to collapse under humid environment (Saunders et al., 2010). This seems not able to explain the coastal area nucleation process, as the MBL is a place where the humidity is normally very high. Thus, an assumption was proposed that the IOPs should form from liquid droplet which contains \( \text{HIO}_3 \) or \( \text{I}_2\text{O}_5\text{HIO}_3 \) (Saiz-Lopez et al., 2012).

Only recently, the homogeneous nucleation process from \( \text{HIO}_3 \) was observed in Mace Head, and was proposed to be the mechanism behind the particle formation process (Sipilä et al., 2016). This happens as shown by reactions

\[
\begin{align*}
\text{HIO}_3 + \text{HIO}_3 & \rightarrow \text{I}_2\text{O}_5 + \text{H}_2\text{O} \\ 
\text{I}_2\text{O}_5 + \text{HIO}_3 & \rightarrow \text{I}_2\text{O}_5\text{HIO}_3 \\ 
\text{I}_2\text{O}_5\text{HIO}_3 + \text{HIO}_3 & \rightarrow \text{I}_4\text{O}_{10}
\end{align*}
\] (4.9) (4.10) (4.11)

The process is initiated by the reaction of two (\( \text{HIO}_3 \)), which leads to the formation of a \( \text{HIO}_3\text{HIO}_3 \) cluster. The cluster will then dehydrate to form \( \text{I}_2\text{O}_5 \). The formed \( \text{I}_2\text{O}_5 \) can stick with another (\( \text{HIO}_3 \)) to form a \( \text{I}_2\text{O}_5\text{HIO}_3 \) cluster, which can add another \( \text{HIO}_3 \) and can go dehydrate process. This process was observed by mass spectrometer until the formation of \( (\text{I}_2\text{O}_5)_2(\text{HIO}_3)_2 \). This mechanism finally explained the proposed \( \text{I}_2\text{O}_5 \) as the major particle composition and too little OIO to explain the total particle mass formed.
Though, iodine-containing particles were suggested to be formed through sequential addition of \((\text{HIO}_3)\), the particle composition information as well as the exact process leading to the sequential addition of \(\text{HIO}_3\), which further forms iodine oxides containing particles are missing. In order to understand the molecular level details of this process, a well-controlled chamber experiments are needed.

In the upcoming CLOUD12 project in CERN, we are going to investigate the particle formation from \((\text{HIO}_3)\) in the sophisticated CLOUD chamber to achieve a better understanding of the nucleation process, as well as the particle composition information. In order to estimate the impact of iodine driven particles in CCN formation and global climate, nucleation rates of iodine driven nucleation processes are to be obtained in the experiments.

### 4.2 Particle formation from macroalgal incubation experiments

Baker et al. (2000) used an enrichment factor which could be represented as equation

\[
\text{EF} = \frac{(\text{I}/\text{Na})_{\text{aerosol}}}{(\text{I}/\text{Na})_{\text{seawater}}} 
\]

(4.12)

where EF is the enrichment factor which represents the extent to which the iodine atom is enriched. \((\text{I}/\text{Na})_{\text{seawater}}\) is the molar ratio between iodine and sodium in the sea water and \((\text{I}/\text{Na})_{\text{aerosol}}\) is the molar ratio in the aerosol. Thus, the higher the EF factor, the more the particle is enriched in iodine. They found that marine aerosols are generally enriched with iodine compounds. This implies that the iodine containing compounds might be more important for NPF than other halogens. However, the processes how the iodine species in the sea water convert into particles in the ambient air remain questions. Part of the processes might be explained by biological processes.

Laminaria digitata (a large brown alga) can accumulate iodine 10000 times higher than seawater, and the iodine weight can be as high as 1% of the dry weight, depending on the environmental conditions (Küpper et al., 1998). McFiggans et al. (2004), for the first time, examined the particle formation from exposing the macroalgal fronds from Laminaria digitata to the ambient light and \(\text{O}_3\). The authors also applied the new photolysis rate of molecular iodine (Saiz-Lopez et al., 2004) in their study and suggested that molecular iodine is more likely the source of atomic iodine than diiodomethane, if the atomic iodine is involved in the particle formation process. Moreover, the observed particle composition was similar as what was observed previously in the Caltech chamber (Jimenez, 2003), which resulted in a conclusion from (McFiggans et al., 2004) that the exposure of macroalgae to the ambient condition while the tide is low, is connected to the \(\text{I}_2\) emission and IOP formation.
In order to quantify the relationship of Laminaria digitata and the emission of iodine species, Sellegri et al. (2005) delivered experiments with multiple macroalgae in near-ambient condition. This study also tried to quantify the particle growth rates in relation to macroalgal emission of \( I_2 \) per unit mass of algae. Later, Dixneuf et al. (2009) for the first time did in situ measurement of the release of molecular iodine from Laminaria digitata under ambient condition. Short and strong bursts of molecular iodine were observed with complex time signature. This study further confirmed that the molecular iodine can be released by Laminaria digitata. However, Palmer et al. (2005) found that the \( \text{CH}_2\text{I}_2 \) release from Laminaria digitata is much larger than molecular iodine. This indicates that both inorganic and organic form iodine species might be both participating in the oxidation and nucleation processes.

4.3 Challenges in studying iodine particle formation

Direct measurement of the rates of polymerization of iodine species remain an open question. The understanding of the iodine particle formation mechanism is still way off (Saiz-Lopez et al., 2012). Any new mechanism should be able to reproduce the results of both laboratory and field measurement before it can be trusted. Although more studies have been done to understand the coastal iodine particle formation processes, extrapolation of the same mechanism to remote marine boundary layer is still risky, considering the different environmental conditions. Saiz-Lopez et al. (2012).

Giordano et al. (2017) suggested that in the late austral winter to early spring, an unknown secondary aerosol mode with unknown composition comprises the majority of the aerosol number population in Antarctica. The author speculated either the halogen species or the mercury is responding for the population of aerosols.

However, in the model applied by (Sherwen et al., 2016b), the iodine particle tracers were assumed to have the same physical properties with the iodine containing particles. Also the nucleation processes of iodine species were also missing. While, on the other hand, homogeneous nucleation from \( \text{HIO}_3 \) was suggested to be an important process in coastal areas (Sipilä et al., 2016). Moreover, in this study, we found that the \( \text{HIO}_3 \) might be more widely spread than previously expected. The existence of \( \text{HIO}_3 \) over a wide variety of locations in the world, from Greenland to Antarctica, from coastal areas to a boreal forest, are identified. This result implies that the potential involvement of iodine-containing species in particle formation processes in places other than coastal areas, should also be included into consideration in the future.
4.4 HIO\textsubscript{3} distribution over different environments

Although, Sipilä et al. (2016) revealed the active role of (HIO\textsubscript{3}) in homogeneous nucleation processes in Mace Head, a coast in western Ireland, the existence of (HIO\textsubscript{3}) in other locations than coastal areas has never been reported. In our study, we investigated the existence of (HIO\textsubscript{3}) over different landscapes than coastal areas. The results are shown in Figure 4.1. ABOA is a Finnish Antarctica site. Mace Head is a coast site in west of Ireland. HYDE tower is a tower with height over the canopy in Hyytiälä boreal forest site, Finland and Siikaneva is a wet land near the Hyytiälä forest site. All the data are from boreal summer months if the sites are in the Northern hemisphere and from austral summer if the site is in the south hemisphere (only ABOA site in this figure).

![Figure 4.1: (HIO\textsubscript{3}) median concentrations over different landscapes in the world. The x-axis is the local time in a specific location. Y-axis is the (HIO\textsubscript{3}) estimated from the ratio of IO\textsubscript{3}\textsuperscript{−} and HNO\textsubscript{3}IO\textsubscript{3}\textsuperscript{−} anions divided by nitrate monomer, dimer and trimer, multiplied by $5 \times 10^9$ cm\textsuperscript{−3}. Each line represents the median value of all the valid data in a month as marked by the legend.](image)

Surprisingly, the existence of (HIO\textsubscript{3}) is confirmed in the measurements of all the above mentioned sites. Each line of the data set is the median data from the valid data in a month in the specific campaign. The calibration factor $5 \times 10^9$ cm\textsuperscript{−3} used here is the same for all the campaigns. This calibration factor would potentially increase the errors in the data showing here. This is because different instruments deployed in the campaigns had various calibration
factors. Further analysis could be done to correct the discrepancy in the calibration factors in the campaigns.

In all of the measurements, the diurnal maximum values of (HIO₃) are above 10⁵ # cm⁻³, while the instrumental LOD is about 10⁴ # cm⁻³. In Greenland and ABOA station, (HIO₃) show vague diurnal pattern. This is potentially because of the polar day phenomenon which happens in local summers in polar regions. In locations other than polar regions, a clear daytime maximums of (HIO₃) could be observed. This clearly implies photochemical reactions are involved in the chemical pathways to produce (HIO₃).

Sulfuric acids from two campaigns were also plotted as a comparison to (HIO₃). The dashed lines in Figure 4.1 are sulfuric acid data from specific campaigns. We could see that in both HYDE tower and the Siikaneva, (HIO₃) has comparable values to that of sulfuric acid, which is believed actively participate in atmospheric nucleation. These results indicate that (HIO₃) might be more widely distributed over a wide range of landscapes and the role of (HIO₃) in the nucleation processes in the globe might be more important than previously thought.
5. Conclusion and future work

New mass spectrometric methods have been developed to measure inorganic halogenated species which can detect over 20 different inorganic halogenated species. The measurable species cover halogen oxides, halogen acids, nitrogenated halogenated species, halogen radicals and molecular halogens. These categories consist the majority of the inorganic halogenated species that could be present in the ambient atmosphere. These techniques are powerful compared to known techniques which could measure one or a few inorganic halogenated species at a time. However, not all the known inorganic form halogenated species that could be present in the ambient atmosphere were measured. There are potentially two reasons for the absence of the missing species in our measurements. First, the missing species were produced in the in the flow tube, but the concentrations of the species were too low to exceed the LOD of our techniques. Second, the missing species were not measurable by our techniques at all. For completing the knowledge on whether the developed technique could measure the missing compounds, qualitative experiments could be carried out with a chemical system that could produce enough missing species. The second way is to deploy the instruments to field studies where halogen activities are intense. The ambient conditions would supply efficient long reaction time for halogen species that need more steps to be produced.

The second problem that inhibits the direct deployment of the current techniques is that the techniques are sensitive to humidity. Although the result of the humidity effect on the measurement is not shown in this work, the following work will focus in details of this topic. In brief, we observed that higher humidity could decrease the sensitivity of ICI and BrCI. In most of our experiments presented above, the humidity in the flow tube is normally below 1% at 25°C. At this relative humidities, the sensitivity of the techniques were high enough. However, if the humidity increases to atmospheric level at 25°C, the sensitivity of the techniques dropped by roughly a factor of 10 or even higher for specific species. For solving this problem, a dilution system or other system that could decrease the absolute water content in the sample would be needed. It is worth noting that if a dilution system is applied, the targets of the measurement will be diluted at the same time as water vapor. Thus, this requires detailed laboratory experiments and analysis to find a suitable ratio for the dilution system.
Following the preceding work by Sipilä et al. (2016) which has revealed homogeneous nucleation processes by (HIO$_3$) in a coast area, we further investigated the formation mechanism of (HIO$_3$). One pathway suggested by our laboratory experiments were in align with a quantum mechanism study by Plane et al. (2006), through

$$\text{OIO} + \text{OH} \rightarrow \text{(HIO}_3\text{)}$$  \hspace{1cm} (5.1)

Two novel (HIO$_3$) formation pathways from photo-oxidation of CH$_2$I$_2$ and molecular iodine were revealed. One pathway suggested that the homogeneous bimolecular reaction of CH$_2$IOO could form (HIO$_3$) as shown by

$$\text{CHIOO} + \text{CHIOO} \rightarrow \text{(HIO}_3\text{)} + \text{products}$$  \hspace{1cm} (5.2)

The other reaction

$$\text{I/IO} + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{(HIO}_3\text{)} + \text{products}$$  \hspace{1cm} (5.3)

indicated that either iodine radical or iodine monoxide could react with ozone and water vapor to form (HIO$_3$) These findings might be able to explain the large amount of (HIO$_3$) observed in Mace Head. Even though only qualitative results were derived from laboratory experiments revealing the formation mechanism of (HIO$_3$), the exact reaction rates of the above mentioned three pathways have not been obtained. Further work needs to be done to check the experimental data carefully to get representative reaction rates for the pathways so that conclusions on their atmospheric relevance could be obtained.

As for the role of (HIO$_3$) in a global scale, we presented (HIO$_3$) concentrations from different landscapes over the world. These places include a boreal forest site, a wet land site, Greenland and Antarctica. These results imply that iodine species might be presenting over a wider range of landscapes than previously thought. This is because iodine species are normally associated with marine and polar atmospheric chemistry. In addition, the presence of (HIO$_3$) in the locations other than coastal areas indicates that (HIO$_3$) might be participating in the nucleation and/or particle growth processes in these areas. For achieving the understanding on whether (HIO$_3$) is also participating in the secondary aerosol formation in these areas, particle composition measurements and analysis in these areas would be required. Moreover, although the presence of (HIO$_3$) in these locations were revealed, the sources of (HIO$_3$) in these places are unknown. Future work is required to analysis the back trajectories of (HIO$_3$) in these locations when (HIO$_3$) was present to understand its sources.

Experiments indicate that iodine species might be participating in the oxidation processes of SO$_2$. However, the exact mechanism causing this phenomenon is not known. From a previous laboratory study, the reaction rate of IO and SO$_2$ was measured below $5.6 \times 10^{-15}$ (Larin et al., 2000). This would be too slow for IO to cause significant influence on the sulfuric acid concentration in Mace Head (Berresheim et al., 2014). On the the other hand, if
\[ IO + SO_2 \rightarrow SO_3 + I \]  \hspace{1cm} (5.4)

is the mechanism that is oxidizing SO₂, we would expect more iodine radicals if we inject SO₂ into a flow tube with molecular iodine, ozone and green light on. However, in our experiments, we observed both of IO and iodine radical were scavenged or eliminated with the presence of SO₂. One possible explanation for this phenomenon is that the oxidation process in (5.4) is not a complete view of the story. Rather, SO₂ could also be oxidized in a yet unknown mechanism with iodine species. Future work needs to be done in order to figure out the exact processes that are governing this oxidation of SO₂ and producing sulfuric acid.
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