Iodine oxide homogeneous nucleation: An explanation for coastal new particle production

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Abstract. A series of laboratory experiments on the chemical composition of aerosol particles formed after photodissociation of CH_2I_2, a major volatile alkyl halide released from macroalgae, have been performed in a laboratory scale reaction chamber using on-line atmospheric pressure chemical ionization mass spectrometry (APCI/MS). Based on the mass spectrometric results and the molecular properties of iodine oxides, we suggest that the self-nucleation of iodine oxides provides an efficient source of natural condensable material in coastal environments and discuss this concept focusing on OIO as one potential key species for new particle formation. The presented hypothesis not only fits the measured enrichment of iodine species in submicrometer particles, but also can explain the frequently observed nucleation bursts in the coastal boundary layer.

Introduction

The study of the sources and formation pathways of new particles in the troposphere is presently a subject of considerable interest. Recent field studies point to two environments as regions of significant natural new particle production, remote forested areas (e.g. [*Kavouras et al.*, 1998]) and coastal sites [*O'Dowd et al.*, 1999, 1998]. While new particle formation events in forested areas are speculated to be connected with homogeneous or heterogeneous nucleation of low volatility oxidation products of naturally released VOCs, the observed nucleation bursts in the coastal boundary layer are less well understood. Nevertheless, observational evidence of the underlying processes at coastal sites do exist. For example, particle measurements at 'Mace Head', located at the West coast of Ireland, showed that the occurrence of nucleation events coincides with low tide and solar radiation, suggesting a tidal-biological source of the aerosol precursors. *Grenfell et al.* [1999] focused their analysis of the rapid increase in condensation nuclei concentrations at Mace Head on the role of DMS, however no convincing mechanism for the burst phenomenon could be

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identified. Similarly, *O'Dowd et al.* [1999] analyzed the field data from Mace Head and performed a series of model simulations, which suggested a ternary nucleation processes involving H_2SO_4, H_2O and NH_3, but the authors could only explain the bursts when an additional unknown species X, emitted directly from the shore biota or produced from a released parent species, was assumed to be present. Motivated by existing knowledge about release of alkyl iodides by seaweed [*Laturnus*, 1996; *Carpenter et al.*, 1999] and their rapid photodissociation during daytime [*Roehl et al.*, 1997; *Mössinger et al.*, 1998], we report the results of laboratory experiments on the particle composition following photolysis of CH_2I_2.

Experimental Measurements

Ground cuvette measurements on two prevailing seaweed species at Mace Head showed that CH_2I_2 is the most abundant single iodine-containing compound released by macroalgaes [*O'Dowd and Hämeri*, 2000]. Therefore, we have studied particle formation and composition after photolysis of CH_2I_2. Experiments were performed in a 100 L cylindrical reaction chamber, equipped with a tubular low-pressure mercury lamp in the center of the chamber (Philips, CLEO PL-L 36W, sunlight simulation lamp between 300-400 nm, λ_{max} 350 nm, mean actinic flux (300-400 nm) 4.6×10^{15} photons cm^{-2} s^{-1}). CH_2I_2 was added to the reaction vessel from a dynamic test gas generator, which was based on an open tube diffusion technique. The resulting CH_2I_2 concentrations were adjusted between 4 and 17 ppb(v/v). Additionally, ozone could be introduced into the chamber, produced by UV irradiation of another synthetic air supply. Ozone concentrations were adjusted in the range of < 2 and 50 ppb(v/v). The humidity in the chamber was controlled by adjusting the ratio of humidified to dry synthetic air in the inlet region of the chamber. The overall flow through the chamber was adjusted to 8.4 L min^{-1}. A small ventilator was installed inside the chamber to enable rapid mixing of all components. Particle number concentration was measured with a condensation nucleus counter (TSI 8020, 50% cut-off size 20 nm). After constant mixing ratios of all reactants were achieved, the light source was switched on and resulting particle number concentration and particle composition were recorded.

The chamber air was introduced directly into the ion source of a Finnigan LCQ ion trap mass spectrometer. De-
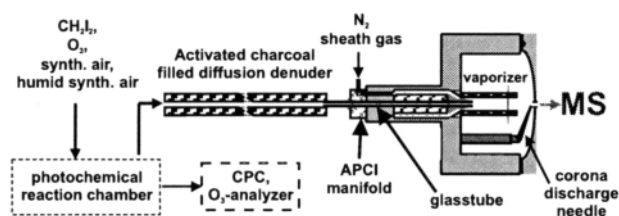
Figure 1. Sketch of the experimental setup to investigate the particle composition after CH_2I_2 photolysis.

tails of the on-line mass spectrometric technique are given by *Kückelmann et al.* [2000] and are therefore only briefly described here. Using an activated charcoal filled denuder in front of the ion source, only the particle phase was allowed to enter the MS (see Fig. 1). The particle phase products formed after CH_2I_2 photolysis were introduced into the ion source using a small glass tube extending into the vaporizer of the ion source. The temperature of the vaporizer was set at 550°C to allow evaporation and hence ionization of the components.
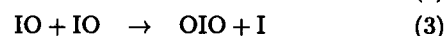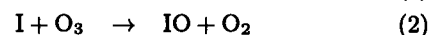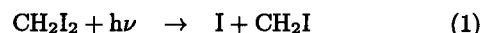
Results and discussion

Figure 2 shows the signal intensity of the total ion current (TIC), the relative abundance of m/z 175 (Fig. 2a) and the particle number concentration (Fig. 2b) during a photolysis experiment ([O_3]= 50 (ppb(v/v)). Immediately after the light source was switched on at $t = 2\text{min}$, particles were produced in the chamber by homogeneous nucleation (Fig. 2b). It should be noted that the maximum particle number concentration recorded by the CPC seriously exceeds the measurement range of the instrument and, as a result, CPC saturation effects have to be taken into account [*O'Dowd and Hämeri*, 2000]. Therefore, the numbers shown in Figure 2b certainly underestimate the actual particle number concentration in the reaction chamber.

At the same time when the particle number concentration increased, the total ion current of the MS increased (Fig. 2a). Figure 3 shows the background corrected mass spectrum in the negative ion mode of the aerosol reaching the ion source. The dominant ion is m/z 175, indicating the $[IO_3]^-$ ion. Also the relative abundances of m/z 143 and m/z 159, presumably $[IO]^-$ and $[IO_2]^-$ respectively, as well as, to a lesser extent, m/z 127 ($[I]^-$) and m/z 254 ($[I_2]^-$) increased. Although to our knowledge no APCI reference spectra of iodine oxides are available, the on-line mass spectrum shown in Fig. 3 indicates that the particles formed are composed purely of oxides of iodine. These either undergo molecular fragmentation in the ion source to yield mainly $[IO_3]^-$-ions or thermally decompose in the vaporizer region to compounds that subsequently give rise to the observed iodate-ion. Changes in the relative humidity of the chamber air between < 1 and 20% significantly altered neither the resulting mass spectra nor the development of the particle number concentration. In contrast, particle number concentration was drastically reduced when no ozone was added to the chamber.
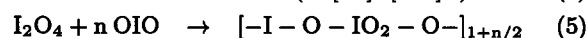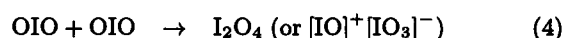
In the positive ion mode, the dominant ion observed was m/z 177, which could be characterized by MS/MS-experiments as a water adduct of $[IO_2]^+$, most likely formed in the APCI-source following the ionization step. No indi-

cations for organic ions were found when only the particle phase was allowed to enter the ion source.

Based on these results and available literature data, we suggest the following reaction sequence:

$$CH_2I_2 + h\nu \quad \rightarrow \quad I + CH_2I \qquad (1)$$

$$I + O_3 \quad \rightarrow \quad IO + O_2 \qquad (2)$$

$$IO + IO \quad \rightarrow \quad OIO + I \qquad (3)$$

Reactions (1) and (2), the photodissociation of alkyl iodides to produce I atoms followed by the rapid reaction of I with O_3 to form IO radicals, have been described previously [*Vogt et al.*, 1999; *Davis et al.*, 1996]. Direct observation of IO in the boundary layer at remote coastal locations by DOAS supports the occurrence of reactions (1) and (2) under ambient conditions [*Alicke et al.*, 1999]. Recent investigations on the IO self-reaction (3) showed that iodine dioxide (OIO) is produced in these reactions. Based on ab initio methods *Misra and Marshall* [1998] assessed certain thermodynamic constants of OIO and reported its formation from the IO self-reaction to be exothermic by 48.3 kJ mol^{-1}. *Cox et al.* [1999] studied the kinetics and mechanisms of the reactions of IO with itself and with BrO and found that OIO is a product of these reactions. Together with the results of the studies of *Misra and Marshall* [1998], Cox and coworkers conclude that, due to its photochemical stability, OIO is a significant gas-phase iodine reservoir. Nevertheless, the authors also suggested that OIO is lost to particles, a process that might explain the high enrichment of iodine in the small size fraction of marine aerosol [*Sturges and Barrie*, 1988; *Wimschneider and Heumann*, 1995]. However, based on the results presented above, we suggest that OIO is not only removed from the gas-phase by heterogeneous uptake on existing particles, but also might be the source of observed nucleation events in coastal areas by self-reaction of OIO,

$$OIO + OIO \quad \rightarrow \quad I_2O_4 \text{ (or } [IO]^+[IO_3]^-) \qquad (4)$$

$$I_2O_4 + n\,OIO \quad \rightarrow \quad [-I - O - IO_2 - O-]_{1+n/2} \qquad (5)$$

Although knowledge about the oxides of iodine is incomplete, a series of investigations do exist that form the basis of speculation on the fate of OIO and support the occurrence
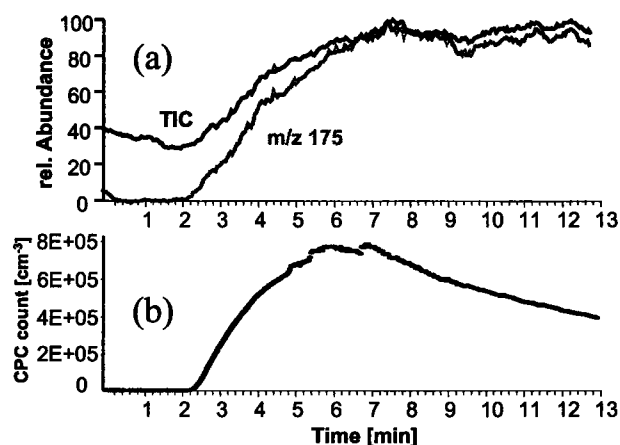

Figure 2. Temporal behavior of the total ion current, the relative abundance of m/z 175 (a) and the CPC readout (b), [CH_2I_2] 17ppb(v/v), r.H. 10%, T = 298 K.
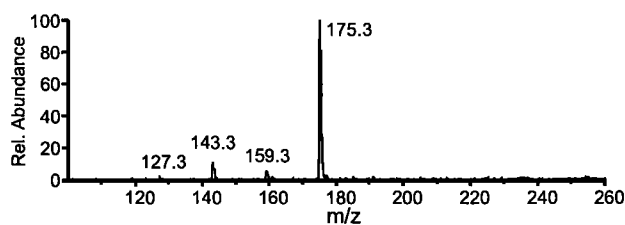
Figure 3. Background corrected APCI mass spectrum (negative ion mode) of aerosol reaching the ion source.

of reactions (4) and (5). In contrast to the halogen (IV) oxides of chlorine and bromine, which rapidly decompose at sub-ambient temperature [Bailar et al., 1973], OIO forms a stable iodine oxide at room temperature that can be isolated as yellow crystals [Fjellvag and Kjkshus, 1994]. There exist no data on the vapor pressure of solid OIO nor on its melting point, since the compound decomposes to I_2O_5 and I_2 at temperatures higher than about 130°C [Chase, 1996]. However, iodine (IV) oxide exhibits some remarkable properties that are related to its potential to form new particles. The investigation of the crystal structure of OIO shows that the compound is better described as I_2O_4, since the crystalline solid is considered to be $[IO]^+[IO_3]^-$ (iodosyl iodate)(disproportionation of iodine (IV)). Beside this interaction of two OIO entities, recent investigations on the I_2O_4 structure suggest that the I_2O_4 units are strongly interacting with the formation of one-dimensional ...-I-O-IO_2-O-...chains, which are bonded together by weaker interchain interactions [Fjellvag and Kjkshus, 1994]. This polymeric structure was suggested responsible for the low solubility of I_2O_4 in many solvents including water [Ellestad et al., 1981].

There are few other laboratory studies that report the formation of aerosol in iodine/O_3 reaction systems. For example, Cox and Coker [1983] observed an aerosol in the photolysis of CH_3I in the presence of O_3. Without chemical analysis of the yellow deposit at their cell walls, the authors proposed a molecular formula of I_4O_9, based on literature data of product studies of the dark reaction of I_2 with O_3 (see e.g. [Vikis and MacFarlane, 1985]) and on the stoichiometry of the ozone removal for each I atom produced in their CH_3I photolysis ($\Delta O_3 = 2.1 \pm 0.2\ \Delta I$). Obviously, also a molecular composition of $(IO_2)_n$, as suggested above, would meet these observations. More recently, Harwood et al. [1997] observed aerosol formation when mixtures of I_2 and O_3 were photolyzed whereas no aerosol was observed when the photolysis of N_2O/I_2 mixtures was used as a IO source. The latter observation might be used to argue that the products of the IO self reaction, such as OIO, are not directly involved in the formation of condensable species. However, due to the high I atom concentration present when N_2O/I_2 systems are photolyzed, Harwood et al. [1997] assumed that reactions like $OIO + I \rightarrow 2IO$ might prevent a significant built-up of this species in the gas phase, a reaction that can be expected to be less important when ozone is present.

Based on the discussion above, we suggest that OIO molecules, which are formed in the gas-phase by reaction sequence (1)-(3), not only attach to pre-exiting particles, but, driven by strong intermolecular interactions, readily form OIO dimers (I_2O_4) as a first step. This dimer

might also be described as a mixed iodine (III/V) oxide ($[IO]^+[IO_3]^-$)(reaction (4)). Collisions with further OIO molecules can lead to the formation of chain-like structures in which the loss of single OIO units from the clusters is hindered by the strong association between the -I-O-IO_2-O-units (reaction (5)). Such intermolecular associations can explain not only the spectroscopic behavior of solid OIO and the stability of the condensed phase but also the high particle formation potential observed in the chamber after photolysis of CH_2I_2.

Conclusions

We have carried out laboratory experiments focusing on the particle formation after photolysis of CH_2I_2 in the presence of O_3 and unequivocal rapid new particle formation was observed in the lower ppb-range of CH_2I_2. Chemical characterization of the newly formed particle phase by on-line MS indicates that the particles are composed purely of oxides of iodine. One plausible explanation of the experimental results is the self-reaction of iodine oxides, such as OIO + OIO, to form inorganic polymeric structures as proposed for I_2O_4. Although other reactions of iodine species might be also involved in the particle formation process (e.g. IO + OIO or reactions which involve HOI or I_2O_2), the hypothesis presented above is consistent with the most prominent signals observed in the mass spectra of the aerosol, since both undecomposed I_2O_4 ($[IO]^+[IO_3]^-$) and its thermal decomposition product (I_2O_5) are expected to result in the formation of iodate ions.

The laboratory results presented here are highly significant in light of field investigations at Mace Head. The concentration data of alkyl iodides (CH_2IBr, CH_2ICl, CH_2I_2) measured in air samples at the site, which reached their highest concentrations in air masses influenced by the local shoreline and were rapidly destroyed in sunlit hours [Carpenter et al., 1999], together with the temporal behavior of nucleation bursts [O'Dowd et al., 1999], and the occurrence of iodine in submicrometer particles [O'Dowd and Hämeri, 2000] support the proposed nucleation mechanism. Likewise, if simple photochemical box model calculations are performed, based on the measured IO concentrations at Mace Head (up to 6ppt) [Carpenter et al., 1999], an OIO yield from IO self-reaction ($k = 8.2 \times 10^{-11}$ molecules^{-1}cm^{3}s^{-1}) of 0.38, a photolysis rate of OIO of $J = 1.2 \times 10^{-5}$ s^{-1}, and OIO is assumed to react with NO and OH [Cox et al., 1999], production rates of OIO of the order of 1-6 $\times10^5$ molecules cm^{-3}s^{-1} result, a range that fits well the expected source rate of condensable species during nucleation events at the site [O'Dowd and Hämeri, 2000]. Whether the nucleation events observed at Mace Head are a result primarily of homomolecular homogeneous nucleation of compounds like OIO or if iodine oxides simply lead to rapid growth of already existing thermodynamically stable sulfate clusters [Kulmala et al., 2000] remains an open question. Certainly, more work is necessary on the chemistry of iodine species (e.g. kinetics of the OIO self reaction) to thoroughly understand the overall processes in the marine boundary layer.

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