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## New particle formation from photooxidation of diiodomethane (CH<sub>2</sub>I<sub>2</sub>)

Jose L. Jimenez,<sup>1,2</sup> Roya Bahreini,<sup>3</sup> David R. Cocker III,<sup>3,4</sup> Hong Zhuang,<sup>3</sup> Varuntida Varutbangkul,<sup>5</sup> Richard C. Flagan,<sup>1</sup> John H. Seinfeld,<sup>1</sup> Colin D. O'Dowd,<sup>6,7</sup> and Thorsten Hoffmann<sup>8</sup>

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[1] Photolysis of CH<sub>2</sub>I<sub>2</sub> in the presence of O<sub>3</sub> has been proposed as a mechanism leading to intense new particle formation in coastal areas. We report here a comprehensive laboratory chamber study of this system. Rapid homogeneous nucleation was observed over three orders of magnitude in CH<sub>2</sub>I<sub>2</sub> mixing ratio, down to a level of 15 ppt ( $\sim 4 \times 10^8$  molec. cm<sup>-3</sup>) comparable to the directly measured total gas-phase iodine species concentrations in coastal areas. After the nucleation burst, the observed aerosol dynamics in the chamber was dominated by condensation of additional vapors onto existing particles and particle coagulation. Particles formed under dry conditions are fractal agglomerates with mass fractal dimension,  $D_f \sim 1.8$ – $2.5$ . Higher relative humidity (65%) does not change the nucleation or growth behavior from that under dry conditions, but results in more compact and dense particles ( $D_f \sim 2.7$ ). On the basis of the known gas-phase chemistry, OIO is the most likely gas-phase species to produce the observed nucleation and aerosol growth; however, the current understanding of this chemistry is very likely incomplete. Chemical analysis of the aerosol using an Aerodyne Aerosol Mass Spectrometer reveals that the particles are composed mainly of iodine oxides but also contain water and/or iodine oxyacids. The system studied here can produce nucleation events as intense as those observed in coastal areas. On the basis of comparison between the particle composition, hygroscopicity, and nucleation and growth rates observed in coastal nucleation and in the experiments reported here, it is likely that photooxidation of CH<sub>2</sub>I<sub>2</sub>, probably aided by other organic iodine compounds, is the mechanism leading to the observed new particle formation in the west coast of Ireland.

*INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* coastal aerosols, new particle formation, nucleation, aerosol mass spectrometer, smog chamber

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<sup>1</sup>Department of Environmental Science and Engineering and Department of Chemical Engineering, California Institute of Technology, Pasadena, California, USA.

<sup>2</sup>Now at Department of Chemistry and CIRES, University of Colorado, Boulder, Colorado, USA.

<sup>3</sup>Department of Environmental Science and Engineering, California Institute of Technology, Pasadena, California, USA.

<sup>4</sup>Now at Department of Physics, Chemical and Environmental Engineering, University of California, Riverside, California, USA.

<sup>5</sup>Department of Chemical Engineering, California Institute of Technology, Pasadena, California, USA.

<sup>6</sup>Department of Physics, University of Helsinki, Helsinki, Finland.

<sup>7</sup>Also at Department of Physics, National University of Ireland, Galway, Ireland.

<sup>8</sup>Institute of Spectrochemistry and Applied Spectroscopy, Dortmund, Germany.

### 1. Introduction

[2] Homogeneous nucleation is a source of new particles in the atmosphere. New particle formation has been observed in regions that have undergone cloud processing, forested areas, polluted air masses, the marine boundary layer, Arctic areas, and coastal regions. In some instances, observed atmospheric new particle formation is consistent with binary homogeneous nucleation of sulfuric acid and water, while in others an additional mechanism needs to be invoked, probably ternary homogeneous nucleation of sulfuric acid, ammonia, and water [Weber *et al.*, 1999; Kulmala *et al.*, 2002].

[3] Coastal zones have been known to be a locus of significant new particle formation for more than a century [Aitken, 1897], but the study of this phenomenon has

intensified only recently [O'Dowd *et al.*, 1998, 1999, 2002; Grenfell *et al.*, 1999]. Evidence points to gaseous alkyl iodides as precursors to particle production in this environment [Laturnus, 1996; Aliche *et al.*, 1999; Carpenter *et al.*, 1999; Cox *et al.*, 1999]. The 1998–99 PARFORCE campaign [O'Dowd *et al.*, 2002], conducted on the west coast of Ireland, is the most intensive field study of coastal new particle formation to date. Nucleation was observed at this location on most days, for all seasons, and all air masses. Aerosols formed by this mechanism are estimated to significantly increase both direct scattering and CCN concentrations. Observations at this location point to the possible role of diiodomethane ( $\text{CH}_2\text{I}_2$ ) in the measured new particle formation.

[4]  $\text{CH}_2\text{I}_2$  is the most abundant of the measured iodine-containing compounds released by macroalgae [Mäkelä *et al.*, 2002] and appears to be the most important compound controlling the influx of iodine atoms into the coastal boundary layer [Carpenter *et al.*, 1999].  $\text{CH}_2\text{I}_2$  is rapidly photolyzed by sunlight reaching the Earth's surface. Several studies have developed gas-phase atmospheric oxidation mechanisms for iodine species [Sander *et al.*, 1997; Vogt *et al.*, 1999; McFiggans *et al.*, 2000], but the molecular routes leading to new particle formation and particle growth have not been unequivocally established. The evidence pointing to the role of  $\text{CH}_2\text{I}_2$  in the observed nucleation included: (1)  $\text{CH}_2\text{I}_2$  and IO (the latter is produced from  $\text{CH}_2\text{I}_2$ ) showed coherence with the tidal cycle, which in turn was strongly correlated with the nucleation events; (2) Solar radiation was also needed for nucleation to occur, which is consistent with a mechanism based on  $\text{CH}_2\text{I}_2$  photolysis; (3) Iodine was always observed in the nucleation mode particles, while sulfur was detected only some of the time, and chlorine or bromine were never present; (4) Ultrafine particle hygroscopic growth factors indicated very low solubility, which rules out sulfate aerosol; (5) Neither  $\text{H}_2\text{SO}_4$ , VOCs, nor any species associated with polluted air masses can explain the observed nucleation and growth.

[5] Kulmala *et al.* [2002] conclude from a modeling study that new particle formation from ternary nucleation of  $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$  could have occurred almost continuously during PARFORCE, but there was insufficient vapor phase  $\text{H}_2\text{SO}_4$  to grow the particles to observable sizes. They suggest that while the new particle formation may be due to  $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ , another species is responsible for the growth of these particles to detectable sizes, thus decoupling the nucleation and particle growth mechanisms. If the condensing species cannot nucleate on its own, new particle formation may not occur at other coastal areas where the same condensable species are present, if the  $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$  system does not provide the initial nuclei.

[6] On the basis of laboratory experiments, Hoffmann *et al.* [2001] demonstrated that rapid particle formation occurs after photolysis of  $\text{CH}_2\text{I}_2$  in the presence of  $\text{O}_3$ . On the basis of measurements of the chemical composition of particles formed, these authors suggested that self-nucleation of iodine dioxide (OIO) may be an effective mechanism of new particle formation in coastal regions. However, their experimental setup was not well suited for a quantitative study of this system.

[7] Laboratory chamber experiments provide the ability to study aerosol nucleation and growth under well-con-

trolled conditions of temperature, humidity, preexisting particles, precursor gas-phase concentrations, and radiation [Cocker *et al.*, 2001]. Following the work of Hoffmann *et al.* [2001], we present here a comprehensive quantitative laboratory chamber investigation of particle formation from photolysis of  $\text{CH}_2\text{I}_2$  in the presence of ozone. Measurements are carried out on particle formation and growth under both dry and moderately humid conditions, as well as on the hygroscopicity and chemical composition of the aerosols produced. The goals of this work are to characterize the chemical routes leading to new particles, the rates of particle formation and growth, the properties of the aerosols formed, and to evaluate whether this mechanism could be responsible for the strong nucleation events observed in the PARFORCE campaign. In section 2 we describe the experimental system, including the laboratory chamber facility, and the instrumentation for particle number, size, composition, and hygroscopicity measurement. The experimental observations are summarized in section 3, while a detailed interpretation of the size distribution measurements is presented in section 4. Section 5 describes the results of a detailed gas-phase and aerosol uptake model for the chamber, and compares the results of the model with the experimental data. Finally, section 6 provides an integrated interpretation of the data in terms of the aerosol chemistry, and section 7 compares the results of this study with those of the PARFORCE field study.

## 2. Experimental Description

[8] Aerosol formation from the direct photolysis of  $\text{CH}_2\text{I}_2$  in the presence of  $\text{O}_3$  was investigated in the Caltech indoor chamber. This facility has been described in detail previously [Cocker *et al.*, 2001]. Briefly, the Caltech indoor facility consists of dual, 28 m<sup>3</sup> chambers illuminated by 300 1.22 m fluorescent blacklights (Sylvania 350BL), which are used to simulate the UV and near UV regions of ambient sunlight (W. Carter *et al.*, Final report to National Renewable Energy Laboratory, available at <ftp://ftp.cert.ucr.edu/pub/carter/pubs/explrept.pdf>). The UV and visible light intensity was measured with a portable spectroradiometer (LI-1800, LI-COR, Lincoln, Nebraska), which had been calibrated at the factory immediately before these measurements. The UV intensity at the peak of 354 nm was 2.9 W m<sup>-2</sup> nm<sup>-1</sup>, with the relative spectral dependence described in Cocker *et al.* [2001]. The estimated photolysis rate of  $\text{NO}_2$  was 0.6 min<sup>-1</sup>. This is in good agreement with previous measurements in this chamber for aged lights, and corresponds to about 1.2 times the maximum rate at the Earth's surface with a solar zenith angle of 0°. The reaction chamber was originally filled with clean dry air at 1 atm and 20°C. Air temperature inside the chamber and surrounding the equipment and the sample lines was maintained at 20°C ± 2°C. A dilute solution of  $\text{CH}_2\text{I}_2$  in  $\text{C}_6\text{F}_6$  was prepared and injected into a glass flask with a microliter syringe. The solution was evaporated and introduced into the bag by flowing clean particle-free dry air over the solution on the flask, and aiding the process with slight heating. For humid experiments, water vapor was injected into the chamber to reach the desired RH of 65% ± 5%. For dry experiments RH was less than 2% ± 1%, below the detection limit of the available hygrometer. Initial ozone

mixing ratios were  $100 \text{ ppb} \pm 20 \text{ ppb}$ . The UV lights were turned on after all components were well mixed in the chamber. Repetition of some experiments indicated a reproducibility of  $\pm 15\%$  or better. This level of reproducibility is not as good as that achieved for secondary organic aerosol formation experiments conducted previously in the same facility. A possible explanation may be derived from our experimental observation that  $\text{CH}_2\text{I}_2$  (and probably some of its reaction products as well) is a “sticky” substance, that is, it has a significantly larger tendency to attach to surfaces, such as injection lines and chamber walls, than the non-halogenated organics involved in secondary organic aerosol studies.

### 2.1. $\text{CH}_2\text{I}_2$ (Surrogate) Concentration Measurement

[9] An FID gas chromatograph (GC, Hewlett Packard, Model 5890, Series II) was used to check the initial concentration of  $\text{CH}_2\text{I}_2$  after injection of this species before beginning each experiment. Since  $\text{CH}_2\text{I}_2$  would not elute on the capillary column in the GC, which was optimized for analysis of nonpolar or slightly polar hydrocarbons, the GC was used to measure the concentration of  $\text{C}_6\text{F}_6$  as a surrogate of the  $\text{CH}_2\text{I}_2$  concentration. The GC was calibrated by preparing known gas-phase  $\text{C}_6\text{F}_6$  concentrations by injecting known amounts of  $\text{C}_6\text{F}_6$  into a small Teflon bag, and then sampling the small bag into the GC. The actual concentration of  $\text{CH}_2\text{I}_2$  in the chamber was deduced from monitoring the response of the GC to  $\text{C}_6\text{F}_6$  in the beginning of each experiment (before the UV lights were switched on) and using the calibration equation. The  $\text{CH}_2\text{I}_2$  concentration estimated in this manner was on average  $-8\% \pm 4\%$  of the concentration predicted from the amount of solution injected, the solution concentration, and the volume of the chamber.

### 2.2. Particle Number and Size Distribution Measurements

[10] Particle size distributions were measured by a scanning electrical mobility spectrometer (SEMS) [Wang and Flagan, 1989]. The SEMS is equipped with a TSI model 3077  $^{85}\text{Kr}$  neutralizer (TSI Inc., St. Paul, Minn.), a long column cylindrical differential mobility analyzer (TSI 3071), and a condensation particle counter (CPC, TSI 3760). The DMA was operated with sheath and excess flows of 2.5 LPM, and polydisperse and monodisperse flows of 0.25 LPM. By changing the voltage of the DMA exponentially between  $-30$  and  $-7000$  V, a mobility spectrum was obtained every 90 s over particle diameters ranging from 25 nm to 700 nm.

[11] Newly formed particles from homogeneous nucleation have diameters less than 25 nm, below the detection limit of the SEMS as operated in this study. Moreover, the number concentrations of nucleated particles may exceed the maximum concentrations and change faster than this SEMS can measure. For these reasons, independent particle number concentrations were recorded using a TSI CPC 3025 and a TSI CPC 3010. The detection efficiencies of these CPCs are 50% for particles of 3 and 10 nm, respectively [TSI, 1996; Hämeri et al., 2002]. The smallest detectable particles are about 2 nm and 6 nm for the CPC 3025 and 3010, respectively [Hämeri et al., 2002]. Particle coincidence in the CPCs was minimized by diluting the

sampled aerosol stream by a factor of 1000. This extended the measurement range up to  $10^7$  and  $10^8 \text{ cm}^{-3}$  for the CPC 3010 and CPC 3025, respectively. The detection efficiencies of the CPC 3025 as operated here are estimated at 0.17%, 8.4%, 30%, and 88% for particles of sizes 3, 6, 10, and 50 nm, respectively. The low detection efficiencies at the small size limit are due to diffusion losses in the tubing from the point of sampling, through the dilution system, to the CPC, and, to a lesser extent, to the lower efficiency of the CPC itself for small particle sizes [Hinds, 1999; Hämeri et al., 2002]. In the first moments after nucleation starts in the chamber, the CPC 3010 does not detect any particles while the CPC 3025 does. Given the size detection limits of both CPCs and the detection efficiency of the CPC 3025 at those sizes, we estimate that the concentrations reported by the CPC 3025 during this initial phase should be multiplied by a factor between 12 and 600 to determine the actual concentration. Because of the large uncertainties in the detection efficiencies, all the CPC data are presented here without correction (as recorded).

### 2.3. Aerosol Mass Spectrometer (AMS)

[12] An Aerodyne Aerosol Mass Spectrometer [Jayne et al., 2000; Jimenez et al., 2003] was used to simultaneously monitor particle vacuum aerodynamic diameter and chemical composition. The AMS uses an aerodynamic lens to focus the particles into a narrow beam that is then introduced into a high vacuum chamber while the air is differentially pumped. Volatile and semivolatile species in/on the particles are vaporized on a heated, roughened molybdenum surface under high vacuum ( $10^{-7}$  Torr) at about  $600^\circ\text{C}$ . The vaporized species are then ionized by the impact of energetic electrons (70 eV). The ions formed are analyzed by a quadrupole mass spectrometer (QMA 430, Balzers Instruments, Balzers, Liechtenstein). Particle aerodynamic size is determined via particle time-of-flight, with the starting time provided by the opening time of a rotating beam chopper and the arrival time by the chemical detection. The AMS can produce two types of data: mass spectra of the species present in/on the aerosol, without size information; and mass-weighted size distributions versus vacuum aerodynamic diameter ( $dM/d\log D_{va}$ ) of the aerosol at a series of  $m/z$  peaks of the mass spectrometer.

### 2.4. Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA)

[13] A hygroscopicity tandem differential mobility analyzer (HTDMA) was used to measure the response of the aerosol to changes in relative humidity. The HTDMA, based on the original design of Rader and McMurry [1986], consists of a  $^{85}\text{Kr}$  neutralizer, a fixed voltage long column differential mobility analyzer (DMA model 3081, TSI Inc.) used to select a narrow size range of chamber aerosol (under the humidity of the chamber), a cylindrical laminar flow chamber for aerosol humidification or dehumidification, followed by a second scanning long column DMA (TSI model 3081) and condensation particle counter (CPC model 3760A, TSI Inc.) operated as a SEMS [Cocker et al., 2001]. This SEMS performed one full particle size scan every 75 s, while the sizes selected by the first DMA and/or the final humidity were changed every  $\sim 10$  min. Flow rates of 2.5 LPM were used for both sheath and excess flows, and



**Table 1.** Summary of the Experiments Performed

Experiment	CH <sub>2</sub> I <sub>2</sub> , ppb	O <sub>3</sub> Initial, ppb	Relative Humidity, %	Radiation Intensity, Relative to Full Power <sup>a</sup>	Delay from Photolysis to Nucleation, s	Max. Number, cm <sup>-3</sup>	Max. Area, μm <sup>2</sup> cm <sup>-3</sup>	Max. Volume, μm <sup>3</sup> cm <sup>-3</sup>	Mode Diameter at 2 h, nm	Timescale of Volume, min <sup>b</sup>
E1 (base case)	5	100	<2	1	31	1.70 × 10 <sup>6</sup>	2600	85	100	45
E2	5	100	65	1	36	1.60 × 10 <sup>6</sup>	2300	50	85	50
E3	0.5	100	<2	1	80	3.50 × 10 <sup>5</sup>	640	14	65	110
E4	0.05	100	<2	1	145	9.00 × 10 <sup>4</sup>	300	4	38	220
E5	0.015	100	<2	1	720	4.00 × 10 <sup>3</sup>	70	1.2	30	470
E6	50	500	<2	1	15	8.20 × 10 <sup>6</sup>	22,000	1002	200	21 <sup>c</sup>
E7	5	100	<2	0.25	44	1.50 × 10 <sup>6</sup>	3000	100	100	120
E8 <sup>c</sup>	5, 0.5, 0.05, and 0.015	100	<2 and 65	0		No particle formation observed				
E9	5	0	<2	1		No particle formation observed <sup>d</sup>				

<sup>a</sup>Measured 2.9 W m<sup>-2</sup> nm<sup>-1</sup> at the peak of 354 nm, with the spectral dependence described by *Cocker et al.* [2001].

<sup>b</sup>Defined as the time at which the volume concentration reaches 1-1/e (~63%) of its maximum value.

<sup>c</sup>Estimated from the AMS mass signal since the SEMS is saturated for some particle sizes.

<sup>d</sup>*Hoffmann et al* [2001] report that particle formation was "drastically reduced," but not completely eliminated, when O<sub>3</sub> was not added to the chamber. We observed no particle formation at all, until O<sub>3</sub> started to build up in the chamber, an unavoidable phenomenon due to a small rate of O<sub>3</sub> formation from trace amounts of VOCs and NO<sub>x</sub> in the feed air. The presence of a small amount of O<sub>3</sub> from this source probably explains the detection of some particles by *Hoffmann et al* [2001] when no external O<sub>3</sub> was added.

0.25 LPM for both polydisperse and monodisperse aerosol flows. The classified aerosol was introduced on the center-line of the humidification chamber to minimize variations of residence time (10 s for the flow and configuration used). The data inversion algorithm used is described by *Collins et al.* [2002].

## 2.5. Summary of Experiments Performed

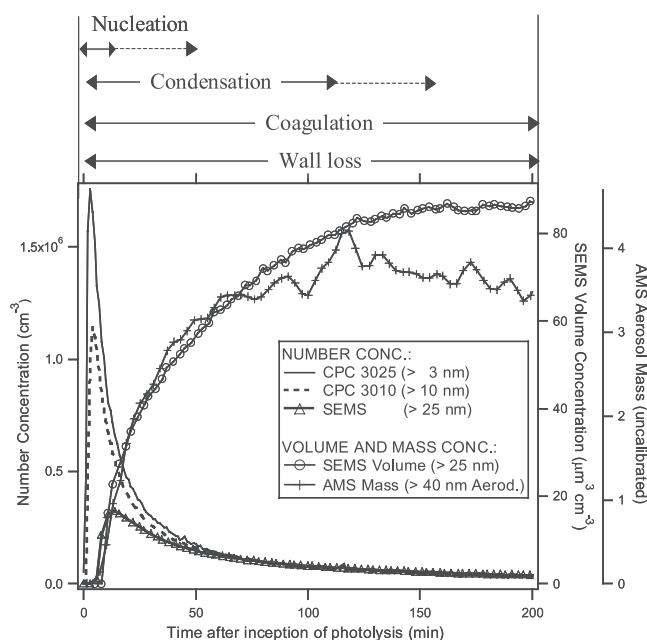
[14] Table 1 summarizes the experiments carried out. We have chosen a base case (E1) with initial conditions of 5 ppb CH<sub>2</sub>I<sub>2</sub>, 100 ppb O<sub>3</sub>, and RH < 2%. The effect of relative humidity was investigated with experiment E2, which is similar to E1 except for RH = 65%. The effect of the initial CH<sub>2</sub>I<sub>2</sub> concentration was investigated with four additional experiments at 500 ppt (E3), 50 ppt (E4), 15 ppt (E5), and 50 ppb (E6). The effect of UV radiation intensity was investigated with experiment E7. Finally, experiments E8 and E9 were conducted to investigate whether particles form in the absence of UV light or O<sub>3</sub>, respectively.

## 3. Experimental Observations

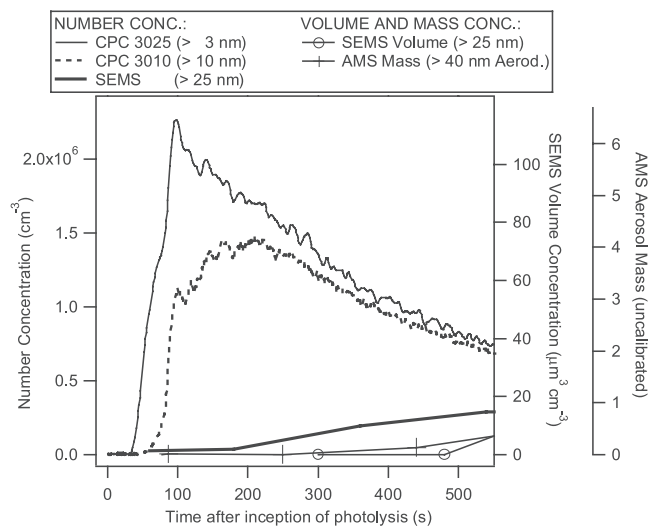
### 3.1. Particle Formation and Growth

[15] Photolysis of CH<sub>2</sub>I<sub>2</sub> in the absence of O<sub>3</sub> does not lead to particle formation; likewise, no particles form in mixtures of CH<sub>2</sub>I<sub>2</sub> and O<sub>3</sub> in the dark. Particle production requires both photolysis of CH<sub>2</sub>I<sub>2</sub> and the presence of O<sub>3</sub>. Homogeneous nucleation was observed after inception of photolysis of CH<sub>2</sub>I<sub>2</sub>/O<sub>3</sub> mixtures under both dry and humid conditions and for all CH<sub>2</sub>I<sub>2</sub> concentrations tested. Figure 1 illustrates the general behavior of aerosol number and volume concentrations over the course of the base case experiment (E1). Particle concentrations measured in the first few minutes are shown in Figure 2. A burst of new particle formation occurred ~30 s after the inception of photolysis. The newly formed particles are first detected by the CPC 3025, but not by the CPC 3010, SEMS, or AMS, which indicates that their size is at least 2 nm but less than 6 nm. As the reaction proceeded, the particle number reached a peak at about 100 s after the inception of photolysis and then rapidly decayed. Subsequent detection

of the particles by the CPC 3010, SEMS, and AMS shows that significant numbers of these particles started to grow to 10 nm or larger about after 1 min of photolysis, and to 25 nm or larger after 3 min. This growth can result from uptake of gas-phase species by the existing particles and/or from particle coagulation. Additional brief nucleation bursts were observed after the initial burst during some experiments,



**Figure 1.** Evolution of the number, volume, and mass concentrations in the chamber as a function of time after inception of photolysis for the base case experiment (E1: 5 ppb CH<sub>2</sub>I<sub>2</sub>, 100 ppb O<sub>3</sub>, <2% RH). Three measurements of the particle number concentration for instruments with different response cutoff for smaller particles are included. The processes estimated to contribute to the aerosol dynamics at each instant of time are indicated above the graph.

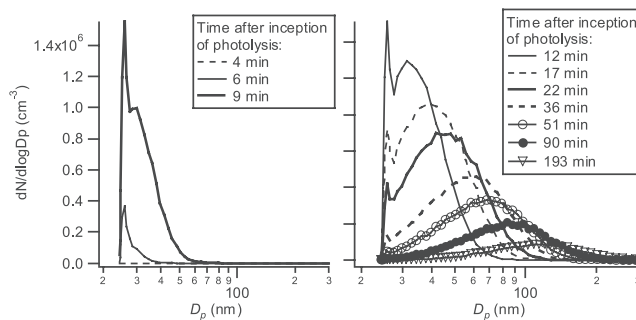


**Figure 2.** Evolution of the number, volume, and mass concentrations in the chamber during the initial minutes after inception of photolysis for the base case experiment (E1: 5 ppb CH<sub>2</sub>I<sub>2</sub>, 100 ppb O<sub>3</sub>, <2% RH).

likely as a result of a buildup of the nucleating species due to slow removal by condensation on existing particles, as described previously for other smog chamber studies of secondary aerosol formation [Flagan *et al.*, 1991].

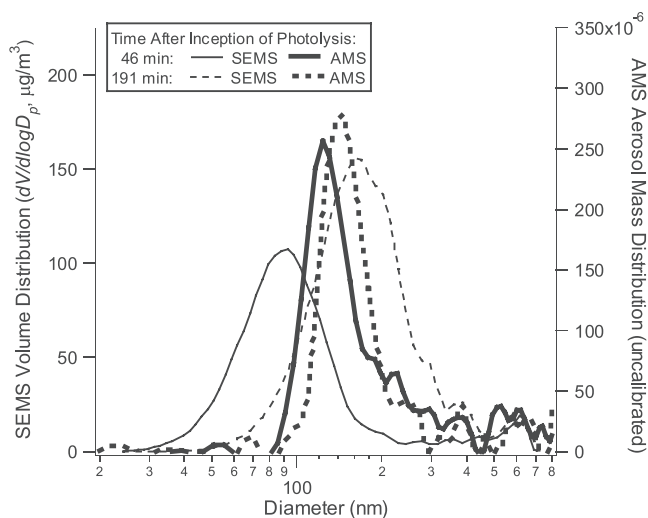
[16] A difference in measured number concentrations with the CPCs detecting a higher number than the SEMS persisted for about 50 min after inception of photolysis, indicating that significant new particle formation lasted for at most that long. The processes controlling the aerosol dynamics immediately following the number concentration peak can be estimated from the timescales of decay: e-folding time of decay  $\tau \sim 12$  min for CPC 3025 and  $\sim 19$  min. for CPC 3010. The timescales of coagulation and wall loss for 3 nm particles at that time are estimated as 39 min and 10 min, while for 10 nm particles they are 29 min and 33 min. Thus wall loss is dominant for 3 nm particles while both processes are equally important for 10 nm particles. These timescales suggest that nucleation could have ended before 50 min, and that the remaining small particles observed up to that time simply did not have enough time to grow by condensation or coagulation. However, it is not possible to determine from the available data when nucleation actually ended.

[17] SEMS size distributions of the particles produced during the photooxidation are shown in Figure 3. Particles grow into the SEMS size range in significant numbers about 5 min after the start of photolysis. These particles grow rapidly, forming a distinct large particle mode at about 8 min. after the start. Rising concentrations for the smaller particles of the size distribution reveal a second mode at sizes too small to resolve with the SEMS. The persistence of this fine particle mode for 50 min reinforces the previous observation from the CPC data that new particle formation continued for at most that time into the experiment. The population of the large SEMS mode first increases and then decreases, while its mode size increases continuously with time. The mode of the number distribution grows from the smallest detectable value of 25 nm to about 100 nm after 2 h and 170 nm after about 6 h.

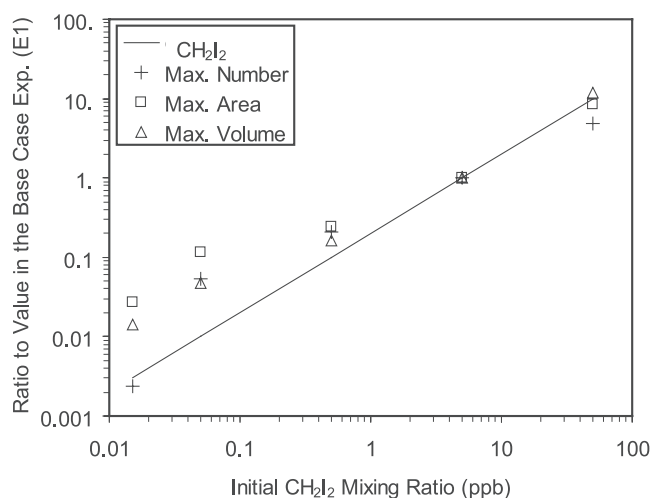


**Figure 3.** SEMS Size distributions at different times during the base case experiment (E1: 5 ppb CH<sub>2</sub>I<sub>2</sub>, 100 ppb O<sub>3</sub>, <2% RH). Particles grow into the SEMS range because of condensation/coagulation of the nucleation-mode particles. Later on, nucleation stops, and the number of particles decreases as their size increases because of the combined effects of condensation, coagulation, and wall loss. The concentrations for the smallest particles are unrealistically low during nucleation because the SEMS as configured in this study detects these particles inefficiently.

[18] The AMS provides an independent measurement of the aerosol mass distribution versus vacuum aerodynamic diameter ( $dM/d\log D_{va}$ ) at each  $m/z$  with a detectable signal. Figure 4 compares the volume and mass distributions measured for the base case by the SEMS and the AMS. The general behavior in time of the AMS mass distribution is similar to that of the volume distribution calculated from the SEMS data. However, two significant differences are observed: the size distribution measured by the AMS is narrower than that measured by the SEMS; and the growth of the mass mode as detected in the AMS slows down considerably after about 1 h, while the SEMS indicates continued growth of the mobility diameter mode. These differences between the mobility and vacuum aerodynamic diameter measurements of the SEMS and the AMS are used



**Figure 4.** Comparison of the volume size distributions measured by the SEMS with the mass distributions measured by the AMS for two times during the base case experiment (E1: 5 ppb CH<sub>2</sub>I<sub>2</sub>, 100 ppb O<sub>3</sub>, <2% RH).



**Figure 5.** Comparison of the maximum experimental particle number, area, and volume concentrations measured in the chamber as a function of initial  $\text{CH}_2\text{I}_2$  mixing ratio.

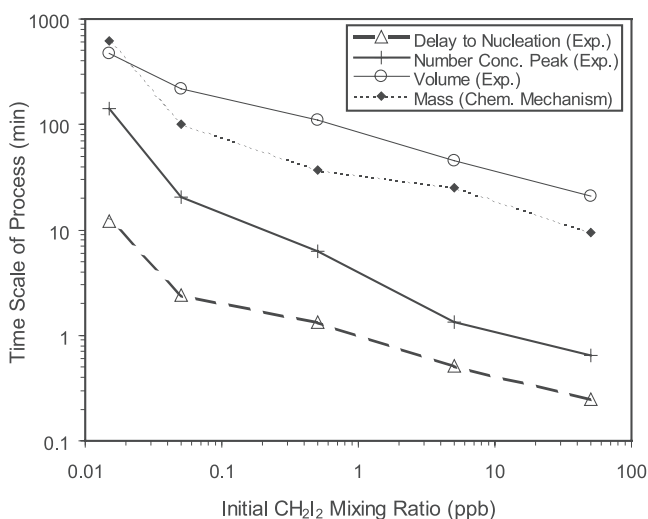
below to estimate particle effective density. The reason for the broader size distribution on the SEMs as compared to the AMS may be due to the particles being fractal agglomerates (see section 4). The particles spend a much longer time inside the SEMs column while being size-classified (seconds) than in the AMS expansion that imparts them a size-dependent velocity ( $<1$  ms). Under these circumstances, it is likely that the diffusional broadening of the distribution due to particle shape is greater in the SEMs because of the longer time available.

[19] The total aerosol volume concentration was obtained from the SEMs size distributions (assuming dense spherical particles) while a signal proportional to aerosol mass was obtained from the AMS; both are also shown in Figures 1 and 2. Since total particle volume is dominated by the largest particles, once about half of the particles have grown above the SEMs detection limit of 25 nm mobility diameter ( $t > 20$  min), the error due to the volume of particles below this limit diminishes rapidly. The particle volume increased with  $\tau \sim 45$  min, much more slowly than the particle number concentration, and reached a maximum value of about  $85 \mu\text{m}^3 \text{cm}^{-3}$  after about 150 min. The particle mass concentration measured by the AMS starts to rise a few minutes earlier than the SEMs volume, an observation that is exploited in section 4.1 to determine the effective density of the particles detected at this time. Later, the evolution of the AMS aerosol mass signal is close to that of the volume calculated from the SEMs data for about 80 min, but it levels off earlier than the SEMs volume. After nucleation ceased, the observed increase in particle volume and mass is a result of condensation of additional vapors onto the existing particles. The later discrepancy between the SEMs and AMS may indicate that while condensation has ended after about 80 min, the apparent particle volume still increases because of the production of agglomerate particles by coagulation.

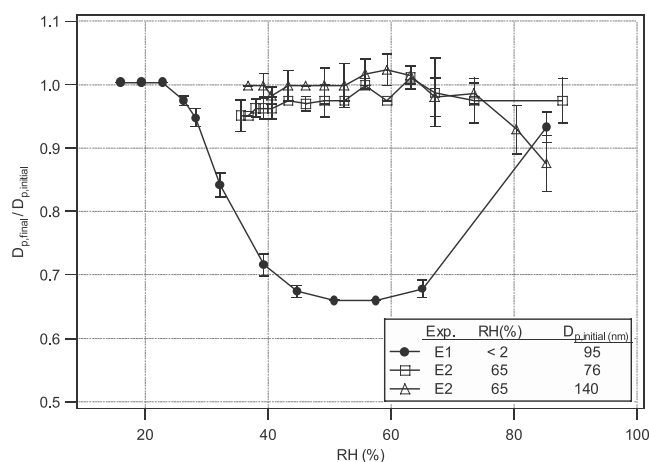
[20] The main results of the parametric experiments are summarized in Table 1. The effect of relative humidity on the particle formation process was investigated with an experiment identical to the base case except for the moder-

ately humid condition ( $\text{RH} = 65\%$ , Exp. E2). No significant difference was observed in the nucleation delay, initial particle number burst, the shape of the particle volume and mass versus time, or the shape of the SEMs and AMS size distributions compared to those of the dry case. The main difference is that the apparent particle volume (assuming dense spherical particles) calculated from the SEMs data for the humid experiment is about half of that of the dry experiment. Although the number concentrations and the shape of the size distribution are similar under both conditions, the mobility diameter of the particles is smaller under humid conditions, resulting in the observed difference in the volume. The vacuum aerodynamic diameter mode measured by the AMS, however, is larger than for the dry case. Both of these observations suggest that the particles are more dense and compact in the humid experiment than in the dry experiment, an issue that is explored further in section 4.

[21] Varying the initial concentration of  $\text{CH}_2\text{I}_2$  over more than three orders of magnitude did not qualitatively change the observed phenomena. A burst of new particle formation followed by a decrease in particle number with increasing particle size and volume was observed for all  $\text{CH}_2\text{I}_2$  levels. The maximum number, area, and volume concentrations of the aerosol formed increase with increasing  $\text{CH}_2\text{I}_2$  concentration, as shown in Figure 5, although the increase is less than linear (approximately proportional to  $[\text{CH}_2\text{I}_2]^{0.65}$  to  $[\text{CH}_2\text{I}_2]^{0.85}$ ). The most significant difference from the base case is that the timescales of all processes (delay before initial nucleation burst, particle number growth, and volume growth) increased substantially with decreasing initial  $\text{CH}_2\text{I}_2$  concentration, as shown in Figure 6. The change in timescale is well approximated by a power law dependence, with the timescale being proportional to  $[\text{CH}_2\text{I}_2]^{-0.43}$  for the nucleation delay,  $[\text{CH}_2\text{I}_2]^{-0.63}$  for the time to number peak, and



**Figure 6.** Observed timescales of gas-to-particle conversion as a function of initial  $\text{CH}_2\text{I}_2$  mixing ratio: delay to nucleation, time from nucleation to particle number peak, and particle volume increase. The e-folding timescale of iodine gas-to-particle conversion simulated by the numerical model of section 5 is also shown here.



**Figure 7.** Hygroscopic growth factor determined by the Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) as a function of relative humidity for experiments E1 and E2 (RH <2% and 65% respectively; 5 ppb  $\text{CH}_2\text{I}_2$ , 100 ppb  $\text{O}_3$ ). In this experiment particles are size selected by the first DMA at the humidity of the chamber, allowed to equilibrate at a different relative humidity, and size classified by the second DMA. The ratio of the final to initial diameters is the hygroscopic growth factor.

$[\text{CH}_2\text{I}_2]^{-0.37}$  for the volume growth. For the lowest  $\text{CH}_2\text{I}_2$  concentration (E5) the timescale of particle volume growth was about 8 h, and consequently its dynamics in the chamber are significantly affected by particle (and probably gas) loss to the chamber walls.

[22] Varying the intensity of the UV radiation (E7) to 1/4 of the base case increased the nucleation delay, the time to reach the peak of particle number concentration, and the timescale of aerosol volume by factors of 1.5, 2.4, and 2.7, respectively. The amount of aerosol formed was very similar to that of the base case.

### 3.2. Hygroscopic Properties

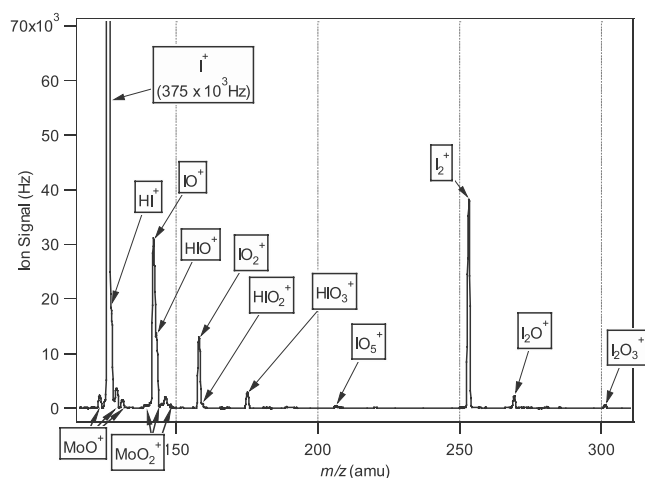
[23] The HTDMA was used to measure the hygroscopic growth factor ( $G_f$ ) of the iodine aerosol, which is defined as the ratio of the aerosol electrical mobility diameter after humidification (or drying) to that prior to humidification (or drying). Figure 7 shows  $G_f$  for the aerosol produced from the photooxidation of  $\text{CH}_2\text{I}_2$ . For the aerosol formed in the base case dry experiment (E1), increasing RH up to approximately 20% has no effect on the electrical mobility diameter. Beyond 23% RH,  $G_f$  starts to decrease, indicating that the mobility diameter of the particles is shrinking as RH increases. At ~55% RH,  $G_f$  reaches a minimum value of 0.66. For most experimental systems, aerosol growth factors for increasing RHs are equal to or exceed 1.0, that is, either the particles do not change size or they grow by water uptake. We cannot rule out that the particles lose some mass upon interaction with increasing water vapor, and, in fact, gaseous  $\text{I}_2$  has been observed to evolve from aerosol formed in dry flowtube experiments for a related chemical system after exposure to ambient air (D. Milligan, personal communication, 2002). More likely, however, the particles formed under dry conditions are not compact. The increase in water partial pressure appears to promote rearrangement

of these low-density structures, resulting in a smaller mobility equivalent diameter. Weingartner *et al.* [1997] observed similar behavior during HTDMA experiments with fractal carbon particles produced in a spark discharge between two graphite electrodes. They attributed the observed decrease in mobility diameter of their particles after exposure to water vapor to preferential water condensation in small angle cavities of the particles, due to the inverse Kelvin effect, leading to capillary forces on the aggregate branches that cause them to collapse. We speculate that a similar effect may be causing the particle diameter reduction observed here. In our system, the mobility diameter eventually rises after further increase in RH, suggesting that additional water uptake causes the particles to grow. The upward trend continues to the 85% maximum RH studied. Therefore after the initial compaction, at least one component of the aerosol is hydrophilic, leading to an increase in size with increasing RH.

[24] In contrast to the dry experiment, the aerosol formed in the humid experiment (E2) shows little tendency to change its mobility diameter when exposed to variable water vapor concentration up to RH = 75%. At higher relative humidities the larger particles shrink suggesting that the additional humidity promoted further consolidation of the particles. The reason why the particles formed under humid conditions do not show the same growth at high RH as the particles formed under dry conditions is unclear.

### 3.3. Particle Composition

[25] Figure 8 shows a total aerosol mass spectrum obtained with the AMS for the highest concentration experiment (E6). The detected  $m/z$  peaks can be assigned to  $\text{O}^+$ ,  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{I}^{2+}$ ,  $\text{I}^+$ ,  $\text{HI}^+$ ,  $\text{IO}^+$ ,  $\text{HIO}^+$ ,  $\text{IO}_2^+$ ,  $\text{HIO}_2^+$ ,  $\text{HIO}_3^+$ ,  $\text{IO}_3^+$ ,  $\text{I}_2^+$ ,  $\text{I}_2\text{O}^+$ , and  $\text{I}_2\text{O}_3^+$ .  $\text{IO}_3^+$  and  $\text{IO}_4^+$  are not observed within the detection limit of the AMS. We also observe the peaks for  $\text{MoO}^+$  and  $\text{MoO}_2^+$ , characterized by



**Figure 8.** Total aerosol mass spectrum measured with the Aerodyne AMS for experiment E6 (50 ppb  $\text{CH}_2\text{I}_2$ , 500 ppb  $\text{O}_3$ , <2% RH). In the AMS the particles are evaporated on a heated molybdenum surface (600°C) under high vacuum ( $10^{-7}$  Torr), followed by 70 eV electron ionization (see text).



the distinct isotope pattern of Mo. The Mo-containing ions must originate from the reaction of the particle material with the AMS vaporizer, which is made of molybdenum. Acid halides, which may be present in the particles, are known corrosive agents [Behrens *et al.*, 1989]. Hoffmann *et al.* [2001] report the detection of  $I^-$ ,  $IO^-$ ,  $IO_2^-$ ,  $IO_3^-$ , and  $I_2^-$  from particles produced in a similar experiment using a chemical ionization mass spectrometer after vaporization in  $N_2$ /air at 550°C. They do not report any hydrogen-containing species. The relative aerosol signals measured by the AMS at the different  $m/z$  peaks were independent of time in the experiment as well as of particle size. Since the AMS detected particles as small as about 20 nm (physical diameter), this indicates that the particle composition was homogeneous and that the species responsible for initial nucleation and growth were likely the same as those comprising most of the particles at later times (although the  $\sim 1$ –3 nm particles formed during the initial nucleation burst are too small for detection with the AMS used here). Relative humidity of 65% was found to increase the signals at  $OH^+$  and  $H_2O^+$  by a factor of five, while the signals at  $HI^+$ ,  $HIO^+$ ,  $HIO_2^+$ , and  $HIO_3^+$  were about only half as intense as in the dry case. Implications of these results are discussed below.

[26] Other minor peaks were also detected at  $m/z$  28, 30, 44, 190, and 221. The first two peaks were about 100 times less intense than the base peak ( $I^+$ ) and may correspond to  $CO^+$ ,  $CH_2O^+$ , and  $CO_2^+$ , resulting from a small amount of formaldehyde or other oxidized organics partitioning onto the aerosol. These organics must originate from reactions of the carbon-containing products of  $CH_2I_2$  photolysis. The later two peaks, which are about 1000 times less intense than the base peak, would be consistent with the ions  $HIO_3CH_2^+$  and  $IO_5CH_2^+$ .

## 4. Interpretation of Size Distribution Observations

### 4.1. Estimates of Particle Effective Density

[27] An effective particle density can be derived by comparing the particle size measurements performed by the SEMS and the AMS. In this section we first introduce the physical basis for the dependence of both size measurements on particle density and shape, and later derive particle effective densities for our chamber experiments.

[28] The SEMS measures the electrical mobility of the particle, leading to an estimation of the mobility-equivalent diameter. The electrical mobility of a particle,  $Z_p$ , is the ratio of the steady state migration velocity to the applied electric field, and it is proportional to the particle charge and inversely proportional to the drag force acting on the particle. The electrical mobility and the mobility equivalent diameter of a sphere are related by [Flagan, 2001]:

$$Z_p = \frac{neC_c(Kn)}{3\pi\eta D_p} \quad (1)$$

where  $n$  is the number of charges on the particle,  $e$  is the elementary unit of charge,  $C_c$  is the slip correction factor that accounts for noncontinuum effects,  $Kn$  is the Knudsen number,  $\eta$  is the gas viscosity, and  $D_p$  is the physical diameter of the sphere. For particles of a given charge in the

continuum regime  $Z_p \propto D_p^{-1}$ , while in the free molecular regime  $Z_p \propto D_p^{-2}$ . The Knudsen number is defined as

$$Kn = \frac{2\lambda}{D_p} \quad (2)$$

where  $\lambda$  is the mean free path of the gas molecules. Particles are considered to be in the free molecular regime for  $Kn > 10$  and in the continuum regime for  $Kn < 0.1$ . At ambient pressure and temperature  $\lambda \sim 65$  nm, so that the particles measured by the SEMS are in the transition regime between free molecular and continuum conditions.

[29] The mobility-equivalent diameter does not depend on the density of the particle material, but it does depend on particle shape. The drag force on a nonspherical particle migrating at a given velocity exceeds that of its volume-equivalent sphere by a factor  $\chi$ , known as the dynamic shape factor [Fuchs, 1964; Baron and Willeke, 2001]. The volume-equivalent diameter,  $D_v$ , is defined as the diameter of a sphere composed of the bulk particle material that has the same solid volume as the particle. It can be thought of as the diameter of the sphere that would result if the irregular particle melted to form a droplet [Hinds, 1999].  $\chi$  is equal to one for a sphere and larger than one for a nonspherical particle. The detailed relationship between particle physical shape (e.g., as determined with an electron microscope) and  $\chi$  has only been studied for a limited range of particles and pressures (mostly ambient).

[30] Using equation (1), we can relate the mobility-equivalent and volume-equivalent diameters as

$$\frac{D_v\chi}{C_c\left(\frac{2\lambda}{D_v}\right)} = \frac{D_m}{C_c\left(\frac{2\lambda}{D_m}\right)}. \quad (3)$$

In general the relationship between  $D_v$  and  $D_m$  needs to be determined numerically, because of the nonlinear dependence of  $C_c$  on  $D_v$  and  $D_m$ . However, it can be shown that the following approximate expression for  $C_c$  can be used with an error smaller than 10% for all  $Kn$  (for the values of  $\alpha$ ,  $\beta$ , and  $\gamma$  for solid or oil particles in Baron and Willeke [2001]):

$$C_c = 1 + Kn \left[ \alpha + \beta \exp\left(-\frac{\gamma}{Kn}\right) \right] \approx 1 + (\alpha + 0.73\beta)Kn = 1 + \Phi Kn, \quad (4)$$

where  $\Phi = \alpha + 0.73\beta$ . Substituting into equation (3):

$$\frac{D_v\chi}{1 + \Phi\frac{2\lambda}{D_v}} = \frac{D_m}{1 + \Phi\frac{2\lambda}{D_m}} \quad (5)$$

which is quadratic in  $D_m$ , leading to

$$D_m = \frac{D_v\chi}{2\left(1 + \Phi\frac{2\lambda}{D_v}\right)} \left[ 1 + \sqrt{1 + \frac{8\lambda\Phi\left(1 + \Phi\frac{2\lambda}{D_v}\right)}{D_v\chi}} \right] = f(D_v, \chi, \lambda). \quad (6)$$



[31] The AMS measures the particle aerodynamic diameter by determining their terminal velocity after expansion from a pressure of about 2 mbar into vacuum. The relationship between the aerodynamic diameter,  $D_a$ , and the volume-equivalent diameter is [McMurry *et al.*, 2002]:

$$D_a^2 C_c(D_a) = \frac{1}{\chi} \frac{\rho_p}{\rho_0} D_v^2 C_c(D_v), \quad (7)$$

where  $\rho_p$  is the density of the particle material, and  $\rho_0$  is the unit density ( $1 \text{ g cm}^{-3}$ ). Because the mean free path at 2 mbar is about  $33 \text{ }\mu\text{m}$ , all submicron particles are in the free-molecular regime ( $Kn > 66$ ) when acquiring a size-dependent velocity. Under these conditions we can approximate the slip correction factor as

$$C_c(D) = 1 + Kn \left[ \alpha + \beta \exp\left(-\frac{\gamma}{Kn}\right) \right] \approx (\alpha + \beta)Kn, \quad (8)$$

which leads to the following expression for the relationship between aerodynamic diameter and volume-equivalent diameter on the free-molecular regime:

$$D_{va} = \frac{\rho_p}{\rho_0} \frac{D_v}{\chi_v} = \frac{\rho_p}{\rho_0} \chi_{v,inv} D_v, \quad (9)$$

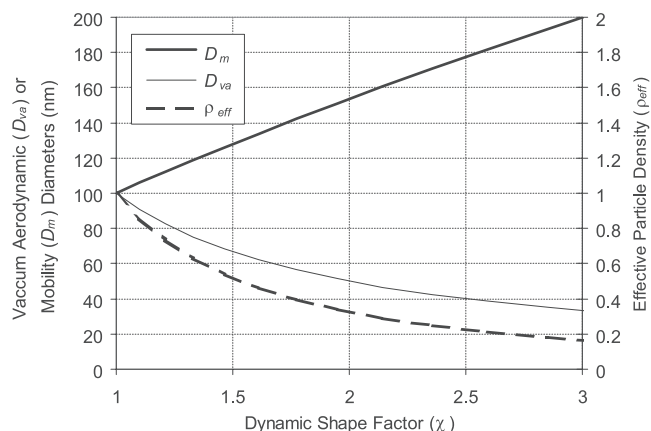
where we have introduced a new notation for the vacuum aerodynamic diameter ( $D_{va}$ ) and the dynamic shape factor in the free-molecular regime ( $\chi_v$ ), to highlight the differences with the more commonly used definitions of these parameters which apply when the particles are in the transition or continuum regimes.  $\chi_{v,inv}$  is the vacuum-aerodynamic shape factor as defined for the AMS by Jayne *et al.* [2000].  $\chi_{v,inv}$  is the reciprocal of the dynamic shape factor  $\chi_v$ .

[32] It is important to note that the vacuum aerodynamic diameter measured by the AMS is different from the classical aerodynamic diameter, which for a spherical particle equals the product of the physical diameter and the square root of the specific gravity [Hinds, 1999]. This diameter is measured when the expansion that imparts the size-dependent velocity to the particles occurs when the particles are in the continuum regime ( $C_c \sim 1$ ). For example the TSI Aerodynamic Particle Sizer operates near 1 atm and reports the sizes of particles above  $\sim 1 \text{ }\mu\text{m}$ . Under these conditions the classical aerodynamic diameter applies.

[33] The effective particle density,  $\rho_{eff}$  is defined here as the product of the unit density by the ratio of the vacuum aerodynamic and mobility diameters.  $\rho_{eff}$  would be the material density of a spherical particle with the same vacuum aerodynamic and mobility equivalent diameters as the particles in our system. Combining equations (6) and (9):

$$\rho_{eff} = \rho_0 \frac{D_{va}}{D_m} = \rho_p \frac{D_v}{\chi_{v,f}(D_v, \chi, \lambda)}. \quad (10)$$

Thus the effective particle density reported here is equal to the material density for spherical particles. For nonspherical particles, the effective density is still proportional to the material density, but also depends on the particle shape through  $\chi$  and  $\chi_v$ . Additional information besides  $D_m$  and



**Figure 9.** Calculated variation of the mobility diameter, vacuum aerodynamic diameter, and effective density ( $D_{va}/D_m$ ) for a particle with a volume equivalent diameter ( $D_v$ ) of 100 nm as a function of the dynamic shape factor  $\chi$  (assuming  $\chi = \chi_v$ ) for particles of unit material density ( $\rho_p = 1 \text{ g cm}^{-3}$ ).

$D_{va}$  would be needed to determine both the material density and the shape factors. Figure 9 illustrates the variation of  $D_m$ ,  $D_{va}$ , and  $\rho_{eff}$  with  $\chi$ , under the assumptions of unit material density,  $D_v = 100 \text{ nm}$ , and  $\chi_v = \chi$ . As the particle becomes more irregular (i.e., as  $\chi$  increases) the mobility diameter increases and the vacuum aerodynamic diameter decreases. Thus the effective density always decreases as  $\chi$  increases.

[34] The first estimate of particle effective density for our chamber experiments can be made from the observation reported above that the particle mass concentration measured by the AMS in the base case experiment (E1) starts to rise a few minutes earlier than the SEMS volume. This indicates that the AMS is detecting the mass of particles with a mobility diameter smaller than the SEMS detection limit of 25 nm (mobility). Since only particles larger than about 40 nm (vacuum aerodynamic) are efficiently transmitted by the AMS inlet, the effective density of the particles about 8 min after inception of photolysis can be estimated at about  $2 \text{ g cm}^{-3}$  or larger.

[35] Using data for later times in the experiment for the dry base case (E1), the effective particle densities at 46 and 191 min since inception of photolysis are estimated from the SEMS particle volume mode and the AMS particle mass mode to be 1.22 and  $0.86 \text{ g cm}^{-3}$ , respectively. For the humid experiment (E2) particle effective densities after 46 and 191 min are estimated to be 2.2 and  $1.6 \text{ g cm}^{-3}$ , respectively. There is a tendency for decreasing effective density as the experiment progresses under both dry and humid conditions.

[36] These effective densities are much lower than the material densities of the iodine oxides and oxyacids thought to comprise the aerosol (see below), all of which are larger than  $4 \text{ g cm}^{-3}$ . The low effective densities estimated for the particles formed in our chamber are consistent with particles being ramified structures of a solid material, most likely fractal agglomerates. The decrease in effective density with time in the experiment suggests that the particles are becoming less compact as the experiment progresses, since

the AMS indicates that the particle composition is not changing. The higher particle effective density observed under the humid experiment suggests that the structure has been made more compact by the water present in the system. This conclusion is consistent with the HTDMA results and with the decrease in the total apparent volume calculated from the SEMS data for the humid experiment as compared to the dry experiment.

#### 4.2. Estimation of Particle Fractal Dimension

[37] Both the HTDMA results and the particle effective density estimates suggest that the particles produced during chamber experiments, especially those from under dry conditions, are not dense compact structures and that they may be becoming less dense as the experiment progresses. It appears that coagulation produces agglomerates of smaller particles. The SEMS and AMS measurements reveal that the aerosol volume and mass concentrations and accompanying growth by condensation stop increasing after about 100 to 150 min of photooxidation for experiment E1. After this time, coagulation is expected to dominate particle growth, increasing the particle size and decreasing the number concentration. Particle losses to the chamber walls also contribute to the decreasing number concentration, and are estimated to become the dominant loss mechanism by 7 hours after the onset of photolysis. Hence the time between 2.5 and 5 h after the start of photolysis will be probed to examine the role of coagulation and agglomerate formation.

[38] Growth of solid particles by coagulation often leads to structures that exhibit similarities over a wide range of scales. The masses of these so-called fractal structures scale with their radius as

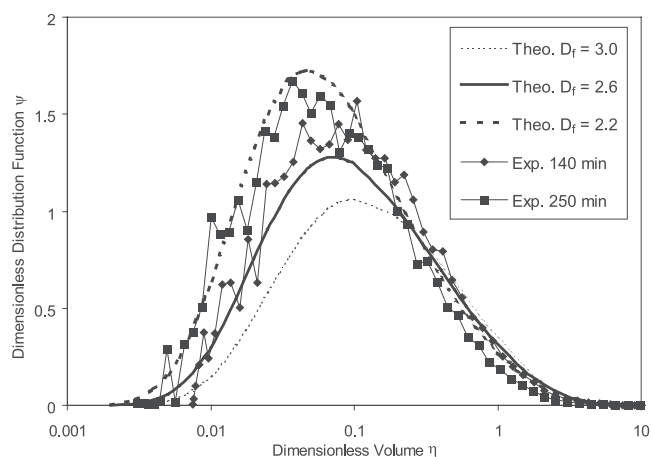
$$m \approx m_1 \kappa \left( \frac{r}{r_1} \right)^{D_f}, \quad (11)$$

where  $m_1$  and  $r_1$  are the mass and radius of the primary particles, and  $\kappa$  is an empirically derived geometry constant of order unity [Wu and Friedlander, 1993; Sorensen and Roberts, 1997]. Thus the collision radius,  $r$ , is

$$r \approx r_1 \left( \frac{m}{\kappa m_1} \right)^{\frac{1}{D_f}} \quad (12)$$

[39] Small values of  $D_f$  indicate open, ramified structures with large apparent volumes. For example, a linear chain of primary particles has a  $D_f = 1$ , while  $D_f = 3$  corresponds to a solid sphere. Growth of agglomerate aerosols by Brownian coagulation with unit sticking probability results in values of  $D_f \approx 1.75$ – $1.8$  [Friedlander, 2000; Sorensen, 2001]. This process is called diffusion-limited aggregation (DLA). Reaction limited aggregation (RLA), for Brownian coagulation with low sticking probability yields values of  $2.1$ – $2.2$ . Higher fractal dimensions likely indicate that other processes are influencing the particle structure, for example, coalescence.

[40] We employ two techniques to estimate  $D_f$  from the experimental chamber data. The first method is based on the self-similar nature of the aerosol size distribution during coagulation. Under a wide range of collision frequency



**Figure 10.** Comparison of the measured size distributions during the base case experiment (E1: 5 ppb  $\text{CH}_2\text{I}_2$ , 100 ppb  $\text{O}_3$ ,  $<2\%$  RH) with the theoretical self-preserving distributions during coagulation in the free molecular regime as a function of mass fractal dimension  $D_f$ .

functions, coagulation leads to a particle size distribution that approaches an asymptotic form known as the self-preserving particle size distribution function [Friedlander and Wang, 1966]. This distribution is expressed as  $\psi(\eta) = Vn(v, t)/N^2$ , in which  $\eta = Nv/V$ , where  $\eta$  is the dimensionless particle volume,  $\psi$  is the dimensionless particle size distribution function,  $v$  is the particle volume ( $\text{cm}^3$ ),  $V$  is the particle volume concentration ( $\text{cm}^3 \text{cm}^{-3}$ ),  $N$  is the particle number concentration ( $\text{cm}^{-3}$ ) and  $n(v, t)$  is the particle number density function at time  $t$  ( $\mu\text{m}^{-3} \text{cm}^{-3}$ ). The existence of the self-preserving particle size distribution can be tested by plotting the dimensionless particle size distribution, for example,

$$\frac{d(N/N_{tot})}{d(D_p/\overline{D}_p)}, \quad (13)$$

versus the dimensionless particle size,  $D_p/\overline{D}_p$ , where  $\overline{D}_p$  is the particle diameter with the same volume as the average volume of the size distribution. When size distributions measured at different times in the evolution of the aerosol collapse onto a single curve, that distribution is the self-preserving distribution. The shape of the self-preserving distribution depends on the transport regime, for example, free molecular or continuum regime, and on the fractal dimension of the particles. Assuming Brownian coagulation and a constant fractal dimension during the entire growth process, Vemury and Pratsinis [1995] calculated the self-preserving distributions in the free-molecular and continuum regimes for agglomerates of various mass fractal dimensions. Since the free-molecular regime is applicable to particles below about 13 nm while the continuum regime concerns particles larger than about 1.3  $\mu\text{m}$ , the chamber particles at the times of interest in this analysis are in the transition regime between the free-molecular and continuum regimes.

[41] Figure 10 compares dimensionless SEMS measurements under dry conditions (Exp. E1) and self-preserving size distributions as computed by Vemury and Pratsinis

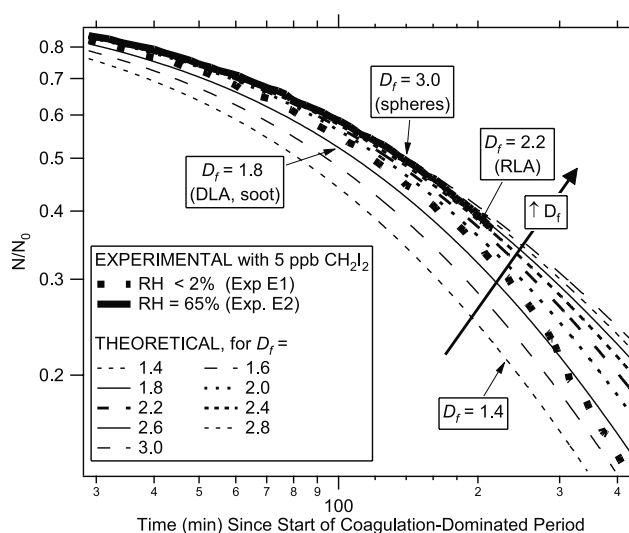
[1995]. When coagulation is dominant, the measured size distributions closely approximate the self-preserving distribution of agglomerates in the free molecular regime with a fractal dimension of  $\sim 2.5$ . Deviations from the continuum regime distribution (not shown) are large. After  $\sim 5$  hours,  $D_f$  appears to decrease to  $\sim 2.3$ , probably reflecting the development of a more open agglomerate structure as particles grow by coagulation, and consistent with the above observation of reduced effective density as the experiment progresses.

[42] The size distributions observed under humid conditions (Exp. E2, not shown) do not correspond to the self-preserving forms under either the free-molecular or continuum regimes. The difference must be due to a process other than coagulation. Wall losses are unlikely to differ significantly between dry and humid conditions. We speculate that water vapor induces structural rearrangement on a time-scale comparable to that of coagulation, changing the coagulation kinetics and affecting the particle size distribution.

[43] The second technique employed here allows estimation of the particle fractal dimension by examining the decay in the number concentration. Flagan and Lunden [1995] present an expression for the evolution of the average particle volume for an aerosol of fractal agglomerates at constant temperature in the free-molecular regime, which can be expressed as the relative number concentration decay under those conditions as

$$\frac{N(t)}{N_0} = \left[ 1 + 2^{2-\nu} \frac{6}{5} \left( \frac{3}{2} - \frac{\nu}{D_f} \right) \frac{t}{\tau_{coag}} \right]^{-\frac{1}{D_f - \frac{3}{2}}} \quad (14)$$

where  $N(t)$  is the number concentration at time  $t$ ,  $N_0$  is the initial number concentration,  $\nu = \min(D_f, 2)$ , and  $\tau_{coag}$  is the characteristic time for coagulation. Thus a plot of  $\log N/N_0$  versus  $\log t$  reveals the characteristic time for coagulation from the break in the curve and the fractal dimension from the slope at long times. For times small compared to  $\tau_{coag}$ , the number concentration is close to  $N_0$ . At much longer times, the number concentration decays as  $t^{-\frac{1}{D_f - \frac{3}{2}}}$ , so the slope in the log-log plot at long times reveals the fractal dimension. This estimate is only approximate, however, because the aerosol undergoes a transition to less dense particles as coagulation begins to dominate. Figure 11 shows the decay in the theoretical and measured number concentrations starting at  $t_0 = 150$  min after inception of photolysis. The number concentration is predicted to drop more rapidly for particles with smaller  $D_f$ , reflecting the larger coagulation rate of the looser agglomerates, due to the increase in their collision area [Matsoukas and Friedlander, 1991; Flagan and Lunden, 1995]. From Figure 11,  $D_f$  is estimated at 1.9 decreasing to 1.8 for the dry experiment (E1) and 2.8 decreasing to 2.5 for the humid experiment (E2). This result reinforces the conclusions from the HTDMA measurements, the particle effective density estimates, and the self-preserving size distribution technique that (1) the particles produced in the humid experiment are more compact than those from the dry experiment; and (2) the particles tend to become less compact (decreasing  $D_f$ ) as the experiment progresses. The values of  $D_f$  determined for the dry experiment are lower than the values (2.5 to 2.3) obtained from the self-preserving size distributions. This discrepancy may arise because of particle loss to the walls, which may



**Figure 11.** Theoretical decay of particle number concentrations as a function of the mass fractal dimension  $D_f$ , compared with the experimental decays for experiments E1 and E2 (RH  $< 2\%$  and  $65\%$  respectively; 5 ppb  $\text{CH}_2\text{I}_2$ , 100 ppb  $\text{O}_3$ ).

make decay rates steeper than with coagulation only, leading to underestimation of  $D_f$ .

[44] In summary,  $D_f$  for the dry experiment is estimated to be between 1.8 and 2.5. This is higher than the values of 1.75–1.8 for DLA, and of the same order than the values of 2.1–2.2 observed for RLA. This indicates that the particles in the dry experiment may not be undergoing significant restructuring after coagulation. The values of 2.8 to 2.5 determined for the humid experiment are larger than the values for either RLA or DLA. This indicates a modification of the primary particles after aggregation, consistent with our previous conclusion from the lack of agreement of the measured size-distribution with the self-preserving size distributions for fractal coagulation.

## 5. Gas-Phase Chemistry and Aerosol Uptake Kinetic Simulations

### 5.1. Gas Phase Mechanism

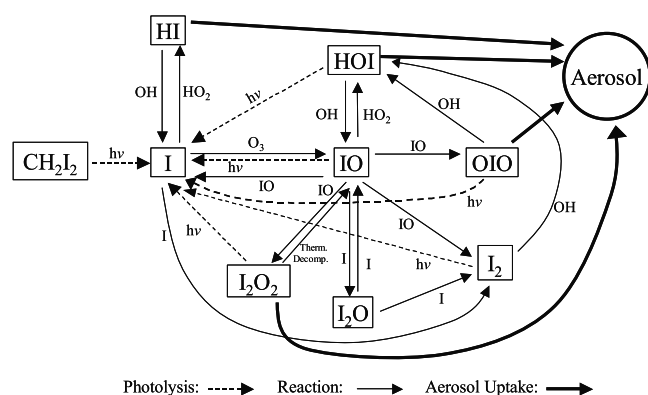
[45] A zero-dimensional photochemical box model of the photolysis of  $\text{CH}_2\text{I}_2$  in the presence of ozone is used in order to guide the interpretation of the observations. The chemical mechanism and reaction rate constants were adapted from Sander [1986], Vogt *et al.* [1999], Cox *et al.* [1999], McFiggans *et al.* [2000], Atkinson *et al.* [2000], Ashworth *et al.* [2002], and Bloss *et al.* [2001] and are given in Table 2. Photolysis rates have been modified taking into account the difference between the UV and visible light intensities and spectral distributions in the chamber and at the Earth's surface.

[46] Figure 12 shows a schematic of the gas-phase and aerosol uptake mechanism. Many of the gas-phase reactions in this diagram have been subjected to detailed laboratory studies and their rates and products are relatively well characterized. However, our knowledge of this chemistry is likely to be incomplete, and additional reactions not included in the mechanism may play a role in our chamber experi-



**Table 2.** Chemical Mechanism Used in the Gas-Phase and Aerosol Uptake Simulations

No.	Reaction	Rate Constant <sup>a</sup>	Rate at 20°C <sup>a</sup>
1 <sup>b</sup>	CH <sub>2</sub> I <sub>2</sub> + hv → CH <sub>2</sub> + 2I		1.12 × 10 <sup>-2</sup>
2 <sup>k</sup>	I + O <sub>3</sub> → IO + O <sub>2</sub>	(2.3 × 10 <sup>-11</sup> ) × exp(-870/T)	1.18 × 10 <sup>-12</sup>
3 <sup>d</sup>	I + I + M → I <sub>2</sub> + M	[M]*1.7 × 10 <sup>-32</sup>	4.17 × 10 <sup>-13</sup>
4 <sup>k</sup>	O( <sup>3</sup> P) + I <sub>2</sub> → IO + I	1.4 × 10 <sup>-10</sup>	1.4 × 10 <sup>-10</sup>
5 <sup>c</sup>	IO + IO → OIO + I (38%) → I <sub>2</sub> O <sub>2</sub> (48.5%) → 2I + O <sub>2</sub> (11%) → I <sub>2</sub> + O <sub>2</sub> (2.5%)	(4.1 × 10 <sup>-11</sup> ) × exp(220/T)	8.68 × 10 <sup>-11</sup>
6 <sup>k</sup>	I + HO <sub>2</sub> → HI + O <sub>2</sub>	(1.5 × 10 <sup>-11</sup> ) × exp(-1090/T)	3.6 × 10 <sup>-13</sup>
7 <sup>f</sup>	IO + HO <sub>2</sub> → HOI + O <sub>2</sub>	(9.0 × 10 <sup>-12</sup> ) × exp(680/T)	9.2 × 10 <sup>-11</sup>
8 <sup>f</sup>	O( <sup>3</sup> P) + IO → O <sub>2</sub> + I	1.4 × 10 <sup>-10</sup>	
9 <sup>f</sup>	OH + HI → I + H <sub>2</sub> O	(1.6 × 10 <sup>-11</sup> ) × exp(440/T)	7.2 × 10 <sup>-11</sup>
10 <sup>c</sup>	HOI + OH → IO + H <sub>2</sub> O	2 × 10 <sup>-13</sup>	2 × 10 <sup>-13</sup>
11 <sup>f</sup>	OH + I <sub>2</sub> → HOI + I	2.1 × 10 <sup>-10</sup>	2.1 × 10 <sup>-10</sup>
12 <sup>n</sup>	OH + OIO → HOI + O <sub>2</sub>		2.0 × 10 <sup>-10</sup>
13 <sup>m</sup>	I + IO + M → I <sub>2</sub> O + M	1.7 × 10 <sup>-10</sup> (at 22°C)	
14 <sup>m</sup>	I + I <sub>2</sub> O → I <sub>2</sub> + IO	2.1 × 10 <sup>-10</sup> (at 22°C)	
15 <sup>p</sup>	I <sub>2</sub> + O <sub>3</sub> → IO + I + O <sub>2</sub> (50%) → IO + OIO (50%)		3.68 × 10 <sup>-18</sup>
16 <sup>g</sup>	I <sub>2</sub> + hv → 2I		0.0036
17 <sup>h</sup>	IO + hv → I + O( <sup>3</sup> P)		0.50
18 <sup>l,m</sup>	OIO + hv → I + O <sub>2</sub>		0.0084
19 <sup>i</sup>	HOI + hv → I + OH		0.0063
20 <sup>o</sup>	I <sub>2</sub> O <sub>2</sub> + hv → 2I + O <sub>2</sub>		0.1
21 <sup>q</sup>	I <sub>2</sub> O <sub>2</sub> + M → 2IO		20
22 <sup>k</sup>	O( <sup>1</sup> D) + N <sub>2</sub> → O( <sup>3</sup> P) + N <sub>2</sub>	(1.8 × 10 <sup>-11</sup> ) × exp(110/T)	2.6 × 10 <sup>-11</sup>
23 <sup>k</sup>	O( <sup>1</sup> D) + O <sub>2</sub> → O( <sup>3</sup> P) + O <sub>2</sub>	(3.2 × 10 <sup>-11</sup> ) × exp(70/T)	4.1 × 10 <sup>-11</sup>
24 <sup>k</sup>	O( <sup>1</sup> D) + H <sub>2</sub> O → 2OH	2.2 × 10 <sup>-10</sup>	2.2 × 10 <sup>-10</sup>
25 <sup>k</sup>	OH + O( <sup>3</sup> P) → H + O <sub>2</sub>	(2.2 × 10 <sup>-11</sup> ) × exp(120/T)	3.3 × 10 <sup>-11</sup>
26 <sup>k</sup>	HO <sub>2</sub> + H → 2OH (90%) → H <sub>2</sub> O + O( <sup>1</sup> D) (2%) → H <sub>2</sub> + O <sub>2</sub> (8%)	8.1 × 10 <sup>-11</sup>	8.1 × 10 <sup>-11</sup>
27 <sup>k</sup>	2OH → H <sub>2</sub> O + O( <sup>3</sup> P)	(4.2 × 10 <sup>-12</sup> ) × exp(-240/T)	1.9 × 10 <sup>-12</sup>
28 <sup>k</sup>	H + O <sub>2</sub> + M → HO <sub>2</sub> + M	k <sub>0</sub> = (5.7 × 10 <sup>-32</sup> ) × (T/300) <sup>-1.6</sup> k <sub>∞</sub> = 7.5 × 10 <sup>-11</sup>	k <sub>0</sub> = 5.9 × 10 <sup>-32</sup> k <sub>∞</sub> = 7.5 × 10 <sup>-11</sup>
29 <sup>k</sup>	O( <sup>3</sup> P) + H <sub>2</sub> → OH + H	4.11 × 10 <sup>-18</sup>	4.11 × 10 <sup>-18</sup>
30 <sup>k</sup>	2HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	(2.3 × 10 <sup>-13</sup> ) × exp(600/T)	1.8 × 10 <sup>-12</sup>
31 <sup>k</sup>	H <sub>2</sub> O <sub>2</sub> + OH → H <sub>2</sub> O + HO <sub>2</sub>	(2.9 × 10 <sup>-12</sup> ) × exp(-160/T)	1.7 × 10 <sup>-12</sup>
32 <sup>k</sup>	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	(4.8 × 10 <sup>-11</sup> ) × exp(250/T)	1.1 × 10 <sup>-10</sup>
33 <sup>k</sup>	O( <sup>3</sup> P) + HO <sub>2</sub> → OH + O <sub>2</sub>	(3.0 × 10 <sup>-11</sup> ) × exp(200/T)	5.9 × 10 <sup>-11</sup>
34 <sup>k</sup>	H <sub>2</sub> O <sub>2</sub> + O( <sup>3</sup> P) → OH + HO <sub>2</sub>	(1.4 × 10 <sup>-12</sup> ) × exp(-2000/T)	1.5 × 10 <sup>-15</sup>
35 <sup>k</sup>	OH + H <sub>2</sub> → H <sub>2</sub> O + H	(5.5 × 10 <sup>-12</sup> ) × exp(-2000/T)	6.0 × 10 <sup>-15</sup>
36 <sup>k</sup>	OH + OH + M → H <sub>2</sub> O <sub>2</sub> + M	k <sub>0</sub> = (6.2 × 10 <sup>-31</sup> ) × (T/300) <sup>-1</sup> k <sub>∞</sub> = 2.6 × 10 <sup>-11</sup>	k <sub>0</sub> = 6.3 × 10 <sup>-31</sup> k <sub>∞</sub> = 2.6 × 10 <sup>-11</sup>
37 <sup>k</sup>	H <sub>2</sub> O <sub>2</sub> + hv → 2OH		8.6 × 10 <sup>-6</sup>
38 <sup>k</sup>	O( <sup>1</sup> D) + H <sub>2</sub> → OH + H	1.1 × 10 <sup>-10</sup>	1.1 × 10 <sup>-10</sup>
39 <sup>i,k</sup>	O <sub>3</sub> + hv → O <sub>2</sub> + O( <sup>1</sup> D)		1.0 × 10 <sup>-5</sup>
40 <sup>k</sup>	O <sub>2</sub> + O( <sup>3</sup> P) → O <sub>3</sub>	[M](6 × 10 <sup>-34</sup> )(T/300) <sup>-2.3</sup>	1.6 × 10 <sup>-14</sup>
41 <sup>k</sup>	O( <sup>1</sup> D) + O <sub>3</sub> → 2O <sub>2</sub>	1.2 × 10 <sup>-10</sup>	1.2 × 10 <sup>-10</sup>
42 <sup>k</sup>	O <sub>3</sub> + O( <sup>3</sup> P) → 2O <sub>2</sub>	(8 × 10 <sup>-12</sup> ) × exp(-2060/T)	7.1 × 10 <sup>-15</sup>
43 <sup>k</sup>	H + O <sub>3</sub> → OH + O <sub>2</sub>	(1.4 × 10 <sup>-10</sup> ) × exp(-470/T)	2.8 × 10 <sup>-11</sup>
44 <sup>k</sup>	O <sub>3</sub> + OH → HO <sub>2</sub> + O <sub>2</sub>	(1.6 × 10 <sup>-12</sup> ) × exp(-940/T)	6.5 × 10 <sup>-14</sup>
45 <sup>k</sup>	O <sub>3</sub> + HO <sub>2</sub> → OH + 2O <sub>2</sub>	(1.1 × 10 <sup>-14</sup> ) × exp(-500/T)	2.0 × 10 <sup>-15</sup>
46 <sup>r</sup>	Uptake coefficient of OIO, I <sub>2</sub> O <sub>2</sub>		1
48 <sup>c,s</sup>	Uptake coefficient of HI, HOI		0.03
49 <sup>c</sup>	Uptake coefficient of OH	(1.2 × 10 <sup>-5</sup> ) × exp(1750/T)	0.0047
50 <sup>c</sup>	Uptake coefficient of HO <sub>2</sub>	(1.4 × 10 <sup>-8</sup> ) × exp(3780/T)	0.0056

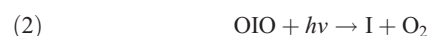


**Figure 12.** Schematic representation of the chemical mechanism used in the gas-phase and aerosol uptake simulations. For clarity, only the reactions that involve iodine species and play a significant role in any of the simulations are included in this schematic.

ments (S. P. Sander, personal communication, 2002; G. McFiggans, personal communication, 2001; J. Burkholder, personal communication, 2001). Of the reactions in Figure 12, the largest uncertainties are in the aerosol uptake coefficients of iodine oxides and the role of  $I_2O_2$  and  $I_2O$ .

[47] OIO is active in the visible region of the spectrum and its cross section is relatively well characterized. A few groups have reported OIO cross sections, some of which are only at a specific wavelength. Bloss *et al.* [2001] reported OIO cross section measurements in 514–573 nm. Cox *et al.* [1999] reported a value of  $\sigma_{549\text{nm}} = 1.09 \times 10^{-17} \text{ cm}^2$ , which agrees very well with the measurements of Bloss *et al.* [2001]. Ingham *et al.* [2000] reported value of  $\sigma_{549\text{nm}} = 3.5 \pm 1.50 \times 10^{-17} \text{ cm}^2$  which is factor of 3 larger than either of the other three reports. In our simulations we have used the cross section data reported by Bloss *et al.* [2001].

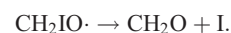
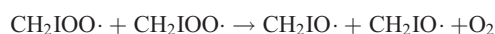
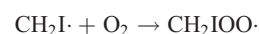
[48] Two channels for OIO photolysis have been proposed:



[49] The photodissociation threshold for OIO via channel (1) has been calculated to be  $\sim 415 \text{ nm}$  [Ashworth *et al.*, 2002]; however, there are no measurements of OIO absorption spectrum in wavelengths shorter than 514 nm. Recent laboratory work indicates that the photolysis of OIO will lead to I atom formation [Ashworth *et al.*, 2002]. Thus a unity quantum yield and a unity branching ratio have been assumed in the simulations for channel (2). On the basis of detection of I in their experiments at low laser fluences, Ingham *et al.* [2000] placed a limit on the quantum yield of channel (2) at 532 nm as  $< 0.15$ . The structural sensitivity of the model to the channel of OIO photolysis has been evaluated with model runs with 15% quantum yield of channel (2).

[50] The role of  $I_2O_2$  also introduces significant uncertainties in the mechanism.  $I_2O_2$  is a thermodynamically viable product of the IO self-reaction according to the computational chemistry calculations of Misra and Marshall [1998], and has been tentatively identified in the gas phase [Bloss *et al.*, 2001]. Its photolysis rate has been assumed to be 1/5th of the photolysis rate of IO (G. McFiggans, personal communication, 2001). However, it is likely that  $I_2O_2$  thermally decomposes rapidly on the basis of extrapolating the decreasing thermal stability of the homologous compounds  $Cl_2O_2$  and  $Br_2O_2$  (S. P. Sander, personal communication, 2002; J. Burkholder, personal communication, 2001), which would contradict the results of Misra and Marshall [1998]. Given the significant uncertainties in those computational chemistry results, due to the limitations of the available basis sets for iodine at the time (S. P. Sander, personal communication, 2002), we have assumed for our base case simulations a fast  $I_2O_2$  thermal decomposition with  $\tau_d = 50 \text{ ms}$ . A series of sensitivity cases have also been run where the thermal decomposition has been turned off.

[51] Another source of uncertainty is the fate of the  $\text{CH}_2\text{I}\cdot$  radical after photolysis. Cotter *et al.* [2001] concluded that for their experimental investigation, conducted in the absence of  $\text{O}_3$  and  $\text{H}_2\text{O}$ , the main path for  $\text{CH}_2\text{I}\cdot$  was



**Table 2.** (opposite)

<sup>a</sup>Units: unimolecular reactions,  $\text{s}^{-1}$ ; bimolecular reactions,  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; recombination reactions,  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ , calculated using the formalism in De More *et al.* [1997], where  $k = ((k_0[M]/(1+k_0[M]/k_\infty)) \times F_c^n)$ ,  $F_c = 0.6$  and  $n = \{1 + (\log_{10}(k_0[M]/k_\infty))^2\}^{-1}$ ; photolysis rate constants,  $\text{s}^{-1}$ .

<sup>b</sup>Calculated on the basis of intensity of black-lights and cross section reported by Mössinger *et al.* [1998] (quantum yield = 1).

<sup>c</sup>McFiggans *et al.* [2000].

<sup>d</sup>Sander [1986].

<sup>e</sup>Bloss *et al.* [2001].

<sup>f</sup>Atkinson *et al.* [2000].

<sup>g</sup>Calculated on the basis of intensity of black-lights and cross section reported by Finlayson-Pitts and Pitts [2000] (quantum yield = 1).

<sup>h</sup>Calculated on the basis of intensity of black-lights and cross section reported by Bloss *et al.* [2001] (quantum yield = 1).

<sup>i</sup>Calculated on the basis of intensity of black-lights and cross section reported by Rowley *et al.* [1999] (quantum yield = 1).

<sup>j</sup>Temperature and wavelength dependency of quantum yield obtained from Finlayson-Pitts and Pitts [2000].

<sup>k</sup>De More *et al.* [1997].

<sup>l</sup>OIO photolysis yields from Ashworth *et al.* [2002].

<sup>m</sup>OIO cross section from Bloss *et al.* [2001].

<sup>n</sup>G. McFiggans, personal communication, 2001.

<sup>o</sup> $J_{I_2O_2} = 0.2 \cdot J_{IO}$  (G. McFiggans, personal communication, 2001).

<sup>p</sup>Vikis and MacFarlane [1985].

<sup>q</sup>J Burkholder, personal communication, 2001; S. P. Sander, personal communication, 2002.

<sup>r</sup>Based on calculations from chamber experiments; see text.

<sup>s</sup>Percival *et al.* [1999]; Mössinger and Cox [2001]; Holmes *et al.* [2001].

[52] In the chamber, reactions with other species may compete with self-reaction of the peroxy radical. In our mechanism we have assumed that I is eventually released into the gas phase in a timescale that is short compared to that of  $\text{CH}_2\text{I}_2$  photolysis. The formaldehyde produced will either photolyze or react with OH to yield CO,  $\text{H}_2$ ,  $\text{HO}_2$ , and  $\text{H}_2\text{O}$  as final products [Seinfeld and Pandis, 1998]. A small fraction may partition onto the aerosol [Jacob, 2000].

[53] Finally, it is possible that the gas-phase  $\text{I}_2$  formed participates in the aerosol growth.  $\text{I}_2$  is a solid with high vapor pressure ( $\sim 0.2$  Torr) at  $20^\circ\text{C}$ . The mechanism predicts that most of the I atoms will form  $\text{I}_2$  when  $\text{CH}_2\text{I}_2$  is photolyzed in the absence of  $\text{O}_3$ . However, no particles were formed in the experiments under these conditions, from which we conclude that  $\text{I}_2$  is not responsible for nucleation in this system. It is possible in principle that  $\text{I}_2$  does condense on the particles after nucleation, and we have included this possibility as a mechanism variation study.

## 5.2. Aerosol Uptake Modeling

[54] For the purposes of calculating uptake of gas-phase species, the aerosol is represented in a semiempirical manner. Rather than trying to model particle nucleation and growth from first principles, we use the experimentally determined time-dependent size distribution as a basis for the calculations. Uptake of gas phase species (OIO,  $\text{I}_2\text{O}_2$ , HI, HOI, OH, and  $\text{HO}_2$ ) onto the aerosol is calculated with the transition regime mass transfer formulation of Dahneke [Seinfeld and Pandis, 1998]:

$$J = J_c \frac{1 + Kn}{1 + 2Kn(1 + Kn)/\alpha}, \quad (15)$$

where  $J$  is the molecular flux ( $\text{molec. s}^{-1}$ ) of the condensing species for a given particle,  $\alpha$  is the uptake coefficient of the species on the particle,  $Kn$  is the Knudsen number of the particle, defined in this formulation as

$$Kn = \frac{4D_g}{c_A D_p}, \quad (16)$$

where  $D_g$  is the diffusion coefficient of the condensable species in air,  $\overline{c_A}$  is its average molecular velocity, and  $J_c$  is the molecular flux in the continuum regime,

$$J_c = 4\pi R_p D_g (c_\infty - c_s), \quad (17)$$

where  $R_p$  is the particle radius, and  $c_\infty$  and  $c_s$  are the concentrations of the species in the bulk gas and at the particle surface, respectively. For the simulations in this paper,  $c_s$  is assumed to be zero, and  $D_g$  is estimated for each species on the basis of the diffusivity of molecules of similar size and molecular weight in air. Then, equation (15) is integrated over the time-varying measured particle size distribution for each experiment.

[55] No modification is needed to account for the influence of the fractal nature of the particles of the uptake of gas-phase species. Rogak *et al.* [1991] showed that spheres and agglomerates with the same mobility diameter have the same uptake rates of 1.5 nm lead clusters, which they used as a surrogate for a gas-phase species. Since the SEMS measures the mobility-equivalent diameter of the fractal particles, the uptake on the present particles will be the same as on spherical particles with the same mobility distribution. Thus

equations (15) and (17) can be applied directly to the experimentally determined mobility distribution.

[56] The key parameter for the gas-to-particle mass transfer is the uptake coefficient  $\alpha$  of each species. McFiggans *et al.* [2000] estimated uptake coefficients of the order of 0.03 for HI, HOI, OIO, and  $\text{I}_2\text{O}_2$  onto aqueous aerosol, by tuning those values in their model of iodine chemistry in the marine boundary layer to optimize the agreement of available measurements. Studies of aerosol uptake of HOI and HI on ice, sodium halide salts, or sulfuric acid indicate uptake coefficients larger than 0.01 [Percival *et al.*, 1999; Holmes *et al.*, 2001; Mössinger and Cox, 2001]. However, such low uptake coefficients are not consistent with the observed particle growth in the chamber immediately after nucleation. The molecular flux,  $J_k$  ( $\text{molec. s}^{-1}$ ) that can be supplied to a dense spherical particle in the free-molecular regime is [Seinfeld and Pandis, 1998]

$$J_k = \pi R_p^2 \overline{c_A} \alpha (c_\infty - c_s). \quad (18)$$

Applying equation (18) to the first 10 s of nucleation in the base case (E1 and S1),  $R_p = 1.5$  nm,  $\overline{c_A} = 200$   $\text{m s}^{-1}$ ,  $\alpha = 0.036$ ,  $c_\infty = 0.18$  ppb OIO (from the simulations), and  $c_s = 0$ , we obtain a flux of  $0.24$   $\text{molec. s}^{-1}$ . If we assume that the particles detected by the CPC 3025 at that time have a size of 3 nm and are composed of pure OIO with the density of  $\text{I}_2\text{O}_4$  ( $4.2$   $\text{g cm}^{-3}$ ), a flux of about  $22$   $\text{molec. s}^{-1}$  is needed to explain the rate of the observed nucleation burst. In order for both estimates to produce uptake rates of the same order-of-magnitude, the uptake coefficient needs to be of the order of 1 for whichever species is responsible for the initial nucleation burst. On the basis of this constraint, we assume in our model that uptake coefficients for OIO and  $\text{I}_2\text{O}_2$  are 1.0, that is, that every collision of a gas-phase molecule of those species with a particle results in the incorporation of the molecule into the particle, while the uptake coefficients of HOI and HI are assumed to be 0.03. Since the AMS indicates that the composition of the particles does not change during the experiment or with particle size, we assume here that the uptake coefficients for all iodine species that partition into the aerosol do not change either.

## 5.3. Kinetic Simulations: Major Paths and Timescale Analysis

[57] The mechanism predicts that none of the iodine-containing species considered in the literature as susceptible to being taken up into the aerosol (OIO,  $\text{I}_2\text{O}_2$ , HI, and HOI) is formed when either  $\text{O}_3$  or UV radiation is not present. This prediction is consistent with the lack of aerosol formation under these experimental conditions. The cases simulated and the main results are summarized in Tables 3 and 4. We have chosen a base case simulation (S1) with initial gas-phase  $\text{CH}_2\text{I}_2$  and  $\text{O}_3$  mixing ratios of 5 and 100 ppb, respectively, and 2% RH, corresponding to the base case chamber experiment (E1). The predicted concentrations of iodine-containing species for case S1 versus time are shown in Figure 13.

[58] We illustrate the importance and relative speed of the different chemical paths with a timescale analysis here. Only the photolysis reactions have a fixed timescale, while molecule-molecule reactions as well as uptake processes change in time as functions of the concentrations of the other reactant, and the particle size distribution, respec-



**Table 3.** Summary of Chemical Kinetics Simulations Performed as Direct Comparison to the Experiments and as Parametric Studies of the Base Case

Simulation	Simulation Objective	Initial CH <sub>2</sub> I <sub>2</sub> , ppb	Initial O <sub>3</sub> , ppb	RH <sub>i</sub> , %	UV Light Intensity	Timescale, <sup>b</sup> min	O <sub>3</sub> destr., ppb	Aerosol Mole Fractions <sup>a</sup>				
								OIO	I <sub>2</sub> O <sub>2</sub>	HOI	HI	HO <sub>x</sub> <sup>c</sup>
S 1	Compare to E1	5	100	2	1	25	39.9	0.993	3.91E-03	2.77E-03	1.93E-07	6.59E-06
S 2	Compare to E2	5	100	65	1	17	29.3	0.939	3.38E-03	0.058	3.91E-06	1.38E-04
S 3	Compare to E3	0.5	100	2	1	37	7.1	0.97	9.30E-04	0.028	3.07E-05	1.08E-03
S 4	Compare to E4	0.05	100	2	1	100	2.8	0.797	5.51E-04	0.152	7.20E-04	0.051
S 5	Compare to E5	0.015	100	2	1	624	11	0.596	3.17E-04	0.207	1.80E-03	0.195
S 6	Compare to E6	50	500	2	1	9.5	309	0.984	0.016	4.89E-04	3.28E-09	1.81E-07
<i>Simulations Performed As Direct Comparison to the Experiments</i>												
S 7	Low CH <sub>2</sub> I <sub>2</sub> + Marine + Chamber Lights	0.001	30	76	1	964	16.8	4.08E-03	2.96E-06	0.068	5.69E-04	0.928
S 8	Low CH <sub>2</sub> I <sub>2</sub> + Marine + Solar Light	0.001	30	76	Zenith 30	1482	29	1.99E-04	2.15E-06	0.044	8.31E-04	0.955
S 9	Effect of Humidity	50	500	65	1	9	306	0.971	1.58E-02	0.013	8.87E-08	4.97E-06
S 10	Effect of Humidity	0.5	100	65	1	35	12.2	0.705	1.04E-03	0.282	9.59E-05	0.013
S 11	Effect of Humidity	0.05	100	65	1	127	11	0.3	3.75E-04	0.474	5.32E-04	0.225
S 12	Effect of Humidity	0.015	100	65	1	820	49.9	0.12	1.09E-04	0.383	7.90E-04	0.496
S 13	Solar Light	5	500	2	Zenith 30	11.5	394	0.981	0.012	6.61E-03	1.71E-06	1.42E-05
S 14	Effect of O <sub>3</sub> Concentration	5	70	2	1	33.5	36.3	0.993	4.29E-03	2.43E-03	1.69E-07	4.86E-06
S 15	Effect of O <sub>3</sub> Concentration	5	150	2	1	19.5	49.5	0.993	3.44E-03	3.30E-03	2.29E-07	9.65E-06
S 16	Effect of Radiation Intensity	5	100	2	0.25	31	29.2	0.995	3.41E-03	1.20E-03	1.67E-08	2.08E-06
S 17	Effect of Radiation Intensity	5	100	2	2	25.5	45.6	0.991	4.44E-03	5.02E-03	1.04E-06	1.79E-05
S 18	Effect of Aerosol Surface Area	50	500	2	1	19	461.3	0.996	3.29E-03	4.72E-04	4.78E-09	5.30E-08
S 19	Effect of Aerosol Surface Area	0.05	100	2	1	23	0.5	0.709	2.46E-03	0.195	2.73E-04	0.093
S 20	Effect of Aerosol Surface Area	0.015	100	2	1	27	0.4	0.269	8.92E-04	0.234	4.15E-04	0.496
<i>Simulations Performed as Parametric Studies of the Base Case</i>												

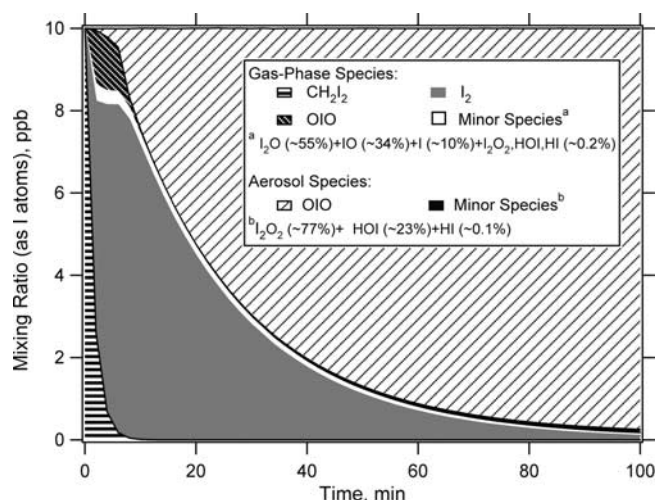
<sup>a</sup>Aerosol mole fractions when 95% of the I atoms in the system are in the aerosol phase except for S8 where 75% of I atoms are in the aerosol phase.

<sup>b</sup>Defined as the time at which I-1/e (~63%) of the initial iodine atoms are in the aerosol phase.

<sup>c</sup>The large amount of HOx predicted to be in the aerosol phase in some simulations suggests that the constant uptake coefficients assumed for these species may not be appropriate for very low aerosol concentrations.

**Table 4.** Summary of Chemical Kinetics Simulations Performed as Tests of Alternative Mechanisms for the Gas-Phase Chemical Kinetics, Different Aerosol Uptake Parameters, or With Solar Light Instead of Chamber Light (Blacklights)

Simulation	Simulation Objective	Initial CH <sub>2</sub> I <sub>2</sub> , ppb	Initial O <sub>3</sub> , ppb	RH, %	UV Light Intensity	Timescale, min	O <sub>3</sub> Destr., ppb	Aerosol Mole Fractions						
								OIO	I <sub>2</sub> O <sub>2</sub>	HOI	HI	HO <sub>x</sub>	(OIO) <sub>2</sub>	I <sub>2</sub>
<i>Simulations Performed as Tests of Alternative Gas and Aerosol Uptake Mechanisms</i>														
S 21	I <sub>2</sub> O <sub>2</sub> → 2I + O <sub>2</sub>	5	100	2	1	33	70.5	0.993	4.26E-03	2.80E-03	2.12E-07	5.19E-06		
S 22	No I <sub>2</sub> O <sub>2</sub> Thermolysis	5	100	2	1	21	46.1	0.703	2.94E-01	2.27E-03	1.63E-07	4.99E-06		
S 23	Unity Aerosol Uptake Coeff. HOI & HI	5	100	2	1	25.5	38.5	0.993	3.91E-03	2.93E-03	9.00E-08	2.61E-06		
S 24	I <sub>2</sub> taken up by aerosol (α = 1)	50	500	2	1	3.25	140	0.502	1.49E-03	1.10E-04	8.76E-09	1.01E-06	4.97E-01	
S 25	I <sub>2</sub> taken up by aerosol (α = 1)	5	100	2	1	7.25	14.5	0.273	1.34E-04	1.36E-04	7.00E-09	1.28E-06	7.26E-01	
S 26	I <sub>2</sub> taken up by aerosol (α = 1)	0.5	100	2	1	17	3.45	0.337	1.57E-04	2.98E-03	1.61E-06	1.32E-04	6.60E-01	
S 27	I <sub>2</sub> taken up by aerosol (α = 1)	0.05	100	2	1	57	1.6	0.365	2.02E-04	6.25E-02	3.56E-04	2.33E-02	5.49E-01	
S 28	I <sub>2</sub> taken up by aerosol (α = 1)	0.015	100	2	1	192	6.05	0.302	1.68E-04	1.16E-01	1.08E-03	1.28E-01	4.52E-01	
S 29	φ (OIO) = 15%	50	500	2	1	7.5	265	0.986	1.35E-02	4.84E-04	3.35E-09	2.26E-07		
S 30	φ (OIO) = 15%	5	100	2	1	18	29.9	0.995	2.60E-03	2.45E-03	1.85E-07	6.81E-06		
S 31	φ (OIO) = 15%	0.5	100	2	1	23.5	4	0.983	3.53E-04	1.60E-02	1.78E-05	7.96E-04		
S 32	φ (OIO) = 15%	0.05	100	2	1	74	1.9	0.876	2.32E-04	8.89E-02	4.64E-04	3.45E-02		
S 33	φ (OIO) = 15%	0.015	100	2	1	442	6.85	0.775	1.36E-04	1.08E-01	9.55E-04	1.16E-01		
S 34	2 OIO → (OIO) <sub>2</sub>	50	500	2	1	7.5	265	0.754	1.67E-02	5.98E-04	4.41E-09	2.80E-07	2.29E-01	
S 35	2 OIO → (OIO) <sub>2</sub>	5	100	2	1	19.5	31.05	0.793	3.51E-03	3.10E-03	2.36E-07	8.41E-06	2.01E-01	
S 36	2 OIO → (OIO) <sub>2</sub>	0.5	100	2	1	29.5	5.4	0.747	7.74E-04	2.89E-02	3.47E-05	1.27E-03	2.22E-01	
S 37	2 OIO → (OIO) <sub>2</sub>	0.05	100	2	1	94	2.6	0.721	5.05E-04	1.50E-01	7.40E-04	5.29E-02	7.53E-02	
S 38	2 OIO → (OIO) <sub>2</sub>	0.015	100	2	1	298	10.6	0.548	2.91E-04	2.04E-01	1.81E-03	2.02E-01	4.45E-02	
S 39	CH <sub>2</sub> I Rxns (1/10 Coll rate)	5	100	2	1	25.5	38.8	0.993	3.91E-03	2.78E-03	1.94E-07	6.61E-06		
S 40	CH <sub>2</sub> I Rxns (1/1000 Coll rate)	5	100	2	1	25.5	37.5	0.993	3.94E-03	2.92E-03	2.21E-07	7.79E-06		
S 41	OIO + I → I <sub>2</sub> O <sub>2</sub>	5	100	2	1	36	39.3	0.987	9.08E-03	3.63E-03	2.23E-07	7.60E-07		
S 42	OIO + I → I <sub>2</sub> + O <sub>2</sub>	5	100	2	1	46	53.9	0.988	7.75E-03	4.00E-03	2.44E-07	7.40E-06		
S 43	OIO + OH → HIO <sub>3</sub> → aerosol	5	100	2	1	25.5	38.9	0.994	3.90E-03	2.48E-03	1.80E-07	6.30E-06	2.88E-04	
S 44	OIO + OH → HIO <sub>3</sub> → aerosol	5	100	65	1	17.5	29.25	0.938	3.40E-03	5.40E-02	3.82E-06	6.84E-05	4.91E-03	



**Figure 13.** Simulated concentration profiles of the main iodine species for the simulation base case S1 (5 ppb  $\text{CH}_2\text{I}_2$ , 100 ppb  $\text{O}_3$ , 2% RH), which corresponds to the conditions of the experimental base case E1. This is a stacked plot: the vertical extent of each band represents the mixing ratio of each species (as iodine atoms) at a given time, and the total number of iodine atoms in the system remain constant. Concentrations of the species not in the legend are too small to be seen in the graph.

tively. Here we have calculated all the timescales of the base case simulation S1 for 2 min after start of the photolysis, as well as for the time in which 63% of the iodine atoms are predicted to be in the aerosol phase, written as  $\tau$  at 2 min/ $\tau$  at 25 min.

[59] The simulations indicate that  $\text{CH}_2\text{I}_2$  is photolyzed with  $\tau \sim 1.5$  min, releasing gaseous I radicals. The reaction of ozone with I to produce IO and the photolysis of IO to yield I are very fast ( $\tau \sim 0.4$  s/0.5 s, and 2.0 s, respectively). Self-reaction of IO to form I, OIO,  $\text{I}_2\text{O}_2$ , and  $\text{I}_2$  is also relatively fast ( $\tau \sim 7$ –140 s/16–300 s), while the reaction of IO with  $\text{O}(^3\text{P})$  to form I is very slow ( $\tau \sim 4$  h/9 h). Since I and IO interconvert very quickly, a local steady state is established between their concentrations.  $\text{I}_2\text{O}_2$  is assumed to thermally decompose to IO ( $\tau = 0.05$  s) in the base case.  $\text{I}_2\text{O}_2$  is also photolyzed back to I ( $\tau \sim 10$  s) and taken up by the aerosol ( $\tau \sim 30$  min/10 s). OIO is photolyzed ( $\tau \sim 2$  min) or taken up by the aerosol ( $\tau \sim 25$  min/10 s), with the first path dominating the fate of OIO at the beginning of the experiment and the second path doing so later on. Reaction with OH is about three orders of magnitude slower than photolysis as a relative loss rate for OIO.

[60]  $\text{I}_2\text{O}$  is formed from I + IO ( $\tau \sim 4$  s/9 s) and destroyed by reaction with I ( $\tau \sim 5$  s/10 s). The second reaction is the main production route for  $\text{I}_2$ , while the formation of the latter species from I + I ( $\tau \sim 40$  min/80 min) and IO + IO ( $\tau \sim 2$  min/5 min) are slower.  $\text{I}_2$  remains in the gas phase until it is photolyzed ( $\tau \sim 4.6$  min), since its reactions with  $\text{O}_3$ , or  $\text{O}(^3\text{P})$  to form HOI, IO, I, and OIO are at least two orders of magnitude slower in terms of  $\text{I}_2$  destruction.

[61] Photolysis of a small amount of  $\text{O}_3$  ( $\tau \sim 28$  h) initiates a series of reactions that result in the formation of OH and  $\text{HO}_2$  radicals, which reach concentrations of the order of  $3 \times 10^5$  and  $6 \times 10^5$  molec.  $\text{cm}^{-3}$ , respectively, at

the time of 95% gas-to-particle conversion. The main loss channel for both radicals is the formation of HOI from  $\text{I}_2$  + OH ( $\tau \sim 0.07$  s/0.1 s with respect to OH) and IO +  $\text{HO}_2$  ( $\tau \sim 3$  s/7 s with respect to  $\text{HO}_2$ ). HOI is incorporated into the aerosol ( $\tau \sim 12$  h/5 min) or photolyzed back to I ( $\tau \sim 2.6$  min), while destruction of HOI by reaction with OH is negligible ( $\tau > 9$  yr/ $>3$  yr). Conversion of I to HI is extremely slow ( $\tau > 9$  yr/ $>2$  yr) with respect to I, and thus HI is a very minor species in this case. Any amount of HI that is formed will be taken up by the aerosol ( $\tau \sim 70$  min/4 min) since its destruction by reaction with OH is very slow ( $\tau \sim 225$  h/78 h).

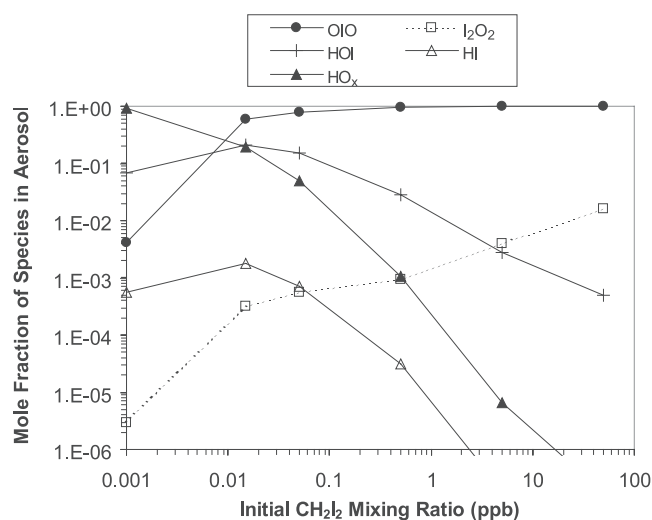
[62] The gas-phase products predicted to reach high concentration are OIO (in the early part of the experiment) and  $\text{I}_2$ , due to the high production rates (for both) and slower loss mechanism (for  $\text{I}_2$ ). Ozone remains in excess at all times, and about 8 molecules of  $\text{O}_3$  are predicted to be consumed per initial  $\text{CH}_2\text{I}_2$  molecule in the base case. More than 99% of the iodine atoms are predicted to be in the aerosol phase 108 min after the inception of  $\text{CH}_2\text{I}_2$  photolysis. The final calculated aerosol composition (mole fraction) is dominated by OIO (99.3% mole fraction), with the rest being made up by  $\text{I}_2\text{O}_2$  and HOI in similar amounts ( $\sim 0.3\%$ ).

#### 5.4. Kinetic Simulations: Parametric Studies

[63] A series of alternative cases have also been simulated using the standard mechanism, in order to evaluate the effects of relative humidity,  $\text{CH}_2\text{I}_2$  and  $\text{O}_3$  initial concentrations, and UV radiation intensity. The main results of these cases are summarized in Table 3. The effect of the initial  $\text{CH}_2\text{I}_2$  concentration is studied in cases S3 to S6. The predicted timescale of gas-to-particle conversion increases, and the  $\text{O}_3$  consumption decreases with decreasing  $\text{CH}_2\text{I}_2$  concentration. The changes in the timescale are mainly due to the slower aerosol uptake because of the smaller aerosol surface available, that is, if the simulations are rerun with the size distribution of the base case (simulations S18 to S20), gas-to-particle timescales similar to that of the base case are obtained independently of the initial  $\text{CH}_2\text{I}_2$  concentration.

[64] The changes in aerosol composition with  $\text{CH}_2\text{I}_2$  mixing ratio for the dry cases (with chamber lights) are illustrated in Figure 14. OIO is predicted to be the dominant aerosol species at all the  $\text{CH}_2\text{I}_2$  concentrations used in the chamber experiments.  $\text{HO}_x$  and HOI are predicted to take over only for 1 ppt precursor concentrations (case S7, see below). The amount of HOI relative to OIO increases as  $\text{CH}_2\text{I}_2$  decreases because the formation of HOI is first order in IO while OIO formation is second order.  $\text{I}_2\text{O}_2$  is a minor species in all cases, and it decreases as  $\text{CH}_2\text{I}_2$  is decreased because the gas-phase  $\text{I}_2\text{O}_2$  is preferentially thermalized or photolyzed as the timescale for aerosol uptake increases. The fraction of  $\text{HO}_2$  and OH in the aerosol increases with decreasing  $\text{CH}_2\text{I}_2$ , and is predicted to make up a significant fraction of the aerosol at the lowest initial  $\text{CH}_2\text{I}_2$  mixing ratios, which is somewhat surprising. The uptake coefficients of about  $5 \times 10^{-3}$  used here for both species are similar or smaller than those determined in the literature for salt and soot aerosols [Cooper and Abbatt, 1996; Ivanov et al., 1996; Saathoff et al., 2001]. However, the uptake coefficients used may not be appropriate for very small aerosol concentrations when saturation effects can be important. HI is a minor species in all cases, but its relative





**Figure 14.** Mixing ratios (i.e., mole fraction) of the aerosol species predicted by the simulation mechanism as a function of initial  $\text{CH}_2\text{I}_2$  concentration, at the time in each simulation when 95% of initial iodine is in the aerosol phase.

importance increases for low  $\text{CH}_2\text{I}_2$  for the same reason as for HOI.

[65] The effect of relative humidity is investigated with cases S2 and S9–S12, which are identical to the dry cases (S1 and S3–S6) except that RH is 65% instead of 2%. The main difference between the results of the humid cases with respect to the dry cases is that the relative importance of HOI in the predicted final aerosol increases roughly linearly with the amount of water vapor present, and becomes similar to OIO at 50 ppt  $\text{CH}_2\text{I}_2$  and dominant at 15 ppt  $\text{CH}_2\text{I}_2$ . This is due to the much higher concentrations of  $\text{HO}_2$  that are predicted to exist in the gas phase under humid conditions. The amount of  $\text{HO}_x$  in the aerosol also increases significantly, while that of  $\text{I}_2\text{O}_2$  changes very little. The predicted timescale of gas-to-particle conversion does not change significantly with humidity, while  $\text{O}_3$  consumption is enhanced at low concentrations in the humid cases as compared with the dry ones.

[66] Cases S7 and S8 have been designed to simulate ambient conditions in coastal areas, as well as the effect of solar versus chamber radiation. Marine boundary layer conditions were estimated as 1 ppt for  $\text{CH}_2\text{I}_2$  (about the maximum amount that has been directly measured) 30 ppb for ozone, 76% RH, with a typical marine aerosol size distribution [Vogt *et al.*, 1999; Seinfeld and Pandis, 1998]. The predicted gas-to-particle timescale is  $\sim 16$  h with chamber lights and 25 h with solar lights. In these cases,  $\text{HO}_2$  and OH dominate the aerosol phase, followed by HOI. OIO is one to two orders of magnitude smaller than HOI in the aerosol (lower with solar lights because of faster photolysis). Running the simulation with the solar lights (S8) rather than chamber lights (S7) increases the timescale of gas to particle conversion and depletes almost all of  $\text{O}_3$  with only 78% of iodine converted to the particle phase.

[67] The effect of the light spectrum (solar versus chamber blacklights) is further investigated in case S13. The aerosol composition does not change significantly with solar light, with OIO still making up more than 98% of the aerosol molecules. The main differences when solar

light is used in the simulation are a reduced gas-to-particle timescale and a large increase in the  $\text{O}_3$  consumption. These effects are the result of much faster photolysis of OIO and  $\text{I}_2$  with solar as compared to chamber lights. The faster photolysis of  $\text{I}_2$  speeds up the aerosol uptake of total iodine species by eliminating the role of  $\text{I}_2$  as the gas-phase reservoir species. The more rapid cycling of I to IO to OIO and  $\text{I}_2$ , and back to I from OIO and  $\text{I}_2$  photolysis causes most of the enhancement on the  $\text{O}_3$  destruction.

[68] The effect of initial ozone concentration is investigated in cases S14 and S15. The main difference from the base case (S1) is that the timescale of gas-to-particle conversion is inversely proportional to the initial  $\text{O}_3$  concentration. The reason for this trend is that increased initial  $\text{O}_3$  results in higher IO and OIO concentrations and faster aerosol uptake. The differences in the aerosol composition and  $\text{O}_3$  consumption are minor, as long as  $\text{O}_3$  is in excess at all times.

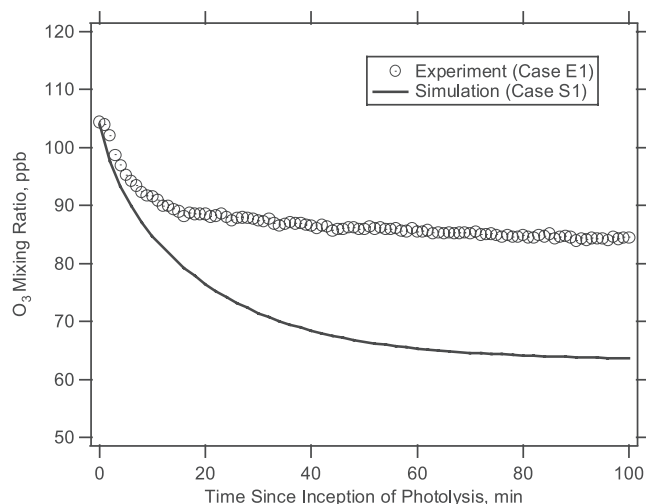
[69] Finally, the effect of UV light intensity is addressed in cases S16 and S17, which have one quarter and twice the photolysis rates of the base case for all species. The timescale of aerosol uptake in case S10 increases by only 25%, which is inconsistent with an increase by a factor of 2.7 in the experiments. The  $\text{O}_3$  consumption in case S16 is predicted to be 25% less than the base case, which again is an underestimate of the experimental observation of a 40% decrease. Both differences suggest that the chemical mechanism is incomplete in its photolysis reactions, or possibly in the reactions of the photolysis products.

## 5.5. Comparison of Experiments and Simulations

[70] We have compared several simulation results with experimental data in order to assess the degree to which the simulations reproduce the observed phenomena. First, the lack of a humidity effect on the experimental observations of particle nucleation and growth is consistent with the lack of an important humidity effect on the outcome of the gas-phase chemical mechanism. However, the simulations predict a large increase in the amount of HOI in the aerosol under humid conditions over dry conditions, which is inconsistent with the lack of increase of the  $\text{HIO}_x$  signals in the humid experiment.

[71] Second, Figure 6 compares the timescales of gas-to-particle conversion obtained from the simulations as a function of initial  $\text{CH}_2\text{I}_2$  concentration. These time constants have the same order of magnitude as the experimental ones and show the same trend with  $\text{CH}_2\text{I}_2$ . The mechanism yields faster conversion than observed experimentally by about a factor of 1.8 to 2.2 except for the case of 0.015 ppb of  $\text{CH}_2\text{I}_2$  initial concentration where the simulation predicts a slower conversion by  $\sim 30\%$ . The simulations predict that the gas-to-particle timescale is controlled almost solely by the aerosol uptake process. Thus this discrepancy could indicate that either the aerosol uptake is imperfectly modeled, or that the aerosol uptake is not the bottleneck of the gas-to-particle conversion process in the experiments.

[72] Figure 15 shows a comparison of simulated and measured  $\text{O}_3$  evolution for the base case (E1 and S1). The total  $\text{O}_3$  consumed in the chamber is only 1/2 of the predicted value. Neither the experimental or simulated  $\text{O}_3$  are fitted well with a single exponential decay, but both agree very well with a double exponential fit. The timescales of the fast and slow exponential are 3.2 and 21 min for the simulations



**Figure 15.** Comparison of the observed and predicted  $\text{O}_3$  concentrations evolutions as a function of time since inception of photolysis for the base case (cases E1 and S1).

and 5.4 and 69 min. for the experimental data. This supports the previous conclusion that the gas-phase mechanism has imperfections that make it proceed too fast as compared with the experiments. The amount of  $\text{O}_3$  destruction accounted for the fast (slow) exponential is 16 (7) ppb for the experiments and 7 (34) ppb for the simulations. Thus the mechanism underpredicts the destruction of  $\text{O}_3$  in the first few minutes by a factor of 2 but overpredicts the  $\text{O}_3$  consumed at later times by about a factor of 5.

[73]  $\text{O}_3$  is consumed mostly by the reaction with I, with a smaller amount being produced from the reaction of  $\text{O}_2$  with the  $\text{O}(^3\text{P})$  generated from IO photolysis. Since I and IO are rapidly interconverting, it seems that the mechanism underestimated the production of I in the first few minutes, but greatly overestimates it at later times. The smaller experimental consumption of  $\text{O}_3$  at longer times suggests that the predicted regeneration of I via OIO,  $\text{I}_2$ ,  $\text{I}_2\text{O}_2$ , and HOI photolysis, and IO self-reaction may be too fast in the mechanism.

[74] Finally, the mechanism also does not predict the effects of decreased UV light intensity observed in the experiments, as described above.

## 5.6. Kinetic Simulations: Results of the Alternative Mechanism Studies

[75] The simulation results show qualitative agreement with some areas of disagreement with the chamber experiments. Since the rates of a number of mechanism steps are quite uncertain, and even the structure of the mechanism is likely to be incomplete, we consider here additional simulations to evaluate whether some simple mechanism modifications, that are plausible in light of the current scientific knowledge about iodine kinetics, can bring the simulations closer to the experiments. These results are detailed in Table 4 and summarized in Table 5.

### 5.6.1. Variations of the $\text{I}_2\text{O}_2$ Thermolysis

[76] The fate of  $\text{I}_2\text{O}_2$  is one of the most uncertain steps in the mechanism. Two alternative cases are studied. Case S21 uses the same thermolysis rate and other conditions for the base case (S1) with a different product channel ( $2\text{I} + \text{O}_2$ ,

instead of  $2\text{IO}$  as assumed in the base mechanism). The predicted aerosol composition is not affected by this modification. The timescale of gas-to-particle conversion increases because of the reduction in IO concentration, which would reduce the gap with the experiments. However, the simulated  $\text{O}_3$  consumption almost doubles because of the increased release of I atoms from this thermolysis formulation, which increases the already large disagreement with the experiments.

[77] In case S22 the  $\text{I}_2\text{O}_2$  thermolysis has been turned off with respect to case S1. With this change, the amount of  $\text{I}_2\text{O}_2$  in the predicted aerosol increases by a factor of 75, up to about 30% of the final mole fraction. The timescale of gas-to-particle conversion does not change much, but again the  $\text{O}_3$  consumption increases, because of the liberation of I from the increased importance of  $\text{I}_2\text{O}_2$  photolysis.

### 5.6.2. Faster Aerosol Uptake of HOI and HI

[78] The aerosol uptake coefficients of 0.03 used here for HOI and HI are based on experimental measurement of this uptake on different surfaces than the iodine species making up the aerosol in these experiments. Thus it is possible that these uptake coefficients are larger, because of the increased affinity of HOI and HI for the iodine-containing aerosol species. Case S23 is the same as the base case S1, with the exception of unity uptake coefficients for HI and HOI. The results of this mechanism change are very minor, however.

### 5.6.3. Uptake of $\text{I}_2$ by the Aerosol After Nucleation

[79] Although we have ruled out nucleation of  $\text{I}_2$  as a new particle formation mechanism in our experiments, it is possible that some  $\text{I}_2$  partitions onto the aerosol after nucleation. To bound the importance of this route a series of cases (S24–S28) have been run with the maximum possible  $\text{I}_2$  uptake ( $\alpha = 1$ ), as a function of  $\text{CH}_2\text{I}_2$  concentration. In these cases  $\text{I}_2$  becomes the major component of the final aerosol. The timescale of gas-to-particle conversion decreases compared to the base case simulations since  $\text{I}_2$  shifts from being a reservoir gas phase species (lost only by photolysis to I with  $\tau \sim 5$  min) to being rapidly taken up by the aerosol. This increases the discrepancy with the experimental timescales. In contrast,  $\text{O}_3$  consumption decreases to a value closer to the experimental one.

### 5.6.4. Smaller Quantum Yield for OIO Photolysis

[80] As mentioned above, the work by *Ingham et al.* [2000] suggests that the quantum yield of OIO photolysis is at most 15%, in contrast with the results of *Ashworth et al.* [2002]. Since this photolysis channel is still somewhat controversial, we have tested the effect of the lower OIO photolysis rate on the mechanism in cases S29–S33. As OIO is photolyzed slower, its aerosol uptake proceeds at a higher rate and the destruction of  $\text{O}_3$  from the I released from OIO photolysis is smaller. The latter agrees better with the experimental results. However, the timescale of gas-to-particle conversion decreases, which brings the simulations even farther from the experiments.

### 5.6.5. OIO Dimerization

[81] It has been suggested that the aerosol nucleation may start as OIO dimerization [*Hoffmann et al.*, 2001]. If this were to happen, the dimers may protect OIO from photolysis. An upper bound for the OIO dimerization rate is about 1/100 of

**Table 5.** Summary of the Effects of Variations of the Rates and Structure of the Kinetic Mechanism on the Agreement Between Experiments and Simulations, and on the Major Predicted Aerosol Species<sup>a</sup>

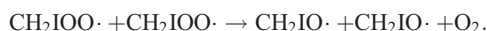
Mechanism Modification	Effect on Gas-to-Particle Timescale	Effect on O <sub>3</sub> Consumption	Effect on Aerosol OIO	Effect on Aerosol HOI	Effect on Other Aerosol Species
	Need INCREASE to Match Experiments	Need DECREASE to Match Experiments			
(a1) I <sub>2</sub> O <sub>2</sub> thermolysis to I instead of IO	INCREASE	<b>Large Increase</b>	No change	No change	No change
(a2) No I <sub>2</sub> O <sub>2</sub> thermolysis	No change	<b>Increase</b>	Decrease	No change	Large Increase of I <sub>2</sub> O <sub>2</sub>
(b) Faster aerosol uptake of HOI & HI	No change	No change	No change	No change	No change
(c) Uptake of I <sub>2</sub>	<b>Decrease</b>	DECREASE	Decrease	No change	Large Increase of I <sub>2</sub>
(d) $\phi(\text{OIO}) = 0.15$	<b>Decrease</b>	DECREASE	Increase	Decrease	
(e) OIO dimerization and dimer uptake	<b>Decrease</b>	DECREASE	No change	No change	
(f) Slower release of 2nd I atom from CH <sub>2</sub> I <sub>2</sub>	No change	No change	No change	No change	No change
(g1) OIO + I → I <sub>2</sub> O <sub>2</sub>	INCREASE	No change	No change	No change	
(g2) OIO + I → I <sub>2</sub> + O <sub>2</sub>	INCREASE	<b>Increase</b>	No change	No change	
(h) OIO + OH → HIO <sub>3</sub>	No change	No change	No change	No change	Increase of HIO <sub>3</sub>

<sup>a</sup>Bold text indicates increased discrepancy, and uppercase text indicates increased agreement, with the experiments.

the collision rate (S. P. Sander, personal communication, 2002). Cases S34–S38 incorporate that rate of OIO dimerization, followed by uptake of the OIO dimer with  $\alpha = 1$ . The effects of this mechanism change are small decreases in the gas-to-particle timescale and the ozone consumption.

### 5.6.6. Slow Release of Second I Atom After CH<sub>2</sub>I<sub>2</sub> Photolysis

[82] Finally, it is also possible that the release of the second I atom after CH<sub>2</sub>I<sub>2</sub> photolysis is slower than we have assumed in our base case. To test the effects of this possibility we have simulated two cases with the mechanism described above. The likely rate-limiting step is



[83] We have computed two cases (S39 and S40) assuming that this reaction proceeds at 1/10 and 1/1000 of the collision rate. These modifications do not affect the main results because the rate is fast enough not to act as a bottleneck in the release of I into the gas phase. As the rate constant is decreased, CH<sub>2</sub>IOO· builds up in the gas phase, resulting on a similar total rate. These results indicate that it is unlikely that the delay in release of the second I atom can result in the slower gas-to-particle conversion observed experimentally.

### 5.6.7. Fast Reaction of OIO + I

[84] Cases S41–42 are designed to study the possible reaction of OIO and I at the collision rate of  $1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$  to form an isomer of I<sub>2</sub>O<sub>2</sub> or I<sub>2</sub> + O<sub>2</sub>, respectively. Neither of these two cases affects the aerosol composition much, while both cases increase the timescale of gas-to-particle conversion by ~40–80%. S45 does not affect O<sub>3</sub> consumption, but S46 shows higher O<sub>3</sub> consumption compared to the base case, which increases the disagreement with experimental observation.

### 5.6.8. Fast Reaction of OIO + OH → HIO<sub>3</sub>

[85] The possible observation of HIO<sub>3</sub> in the aerosol by the AMS is not explained by the known gas-phase chemistry. It is possible that OIO and OH could react to form HIO<sub>3</sub> rather than HOI (G. McFiggans, personal communi-

cation, 2001), an oxyacid that if taken-up by the aerosols, might be the source of observed oxyacids in the experiments. Cases S43–S44 explore this possibility. A unity uptake coefficient has been assumed for HIO<sub>3</sub> to provide an upper bound of the contribution of this path. The results show no change in the timescale of gas-to-particle conversion or ozone consumption rate compared to the base case. The amount of HIO<sub>3</sub> formed in case S43 is one to two orders of magnitude too small to explain the signals of the HIO<sub>2</sub><sup>+</sup> and HIO<sub>3</sub><sup>+</sup> ions in the mass spectrometer. Additionally, the mechanism predicts a twenty-fold increase of the amount of HIO<sub>3</sub> in the aerosol when comparing the humid case (S44) to the dry case (S43), which is not consistent with the small decrease observed in the experiments. Thus we conclude that this gas-phase path cannot explain the presence of iodine oxyacids in the particles.

[86] The effect of all the mechanism variations is summarized in Table 5. No individual variation is able to bring the simulation results in line with the experimental data, indicating that our current understanding of gas-phase iodine chemistry is probably incomplete in several important ways.

## 6. Integrated Interpretation of the Aerosol Chemistry

[87] This section pulls together all the available evidence to address two issues: the identity of the nucleating species and the chemical composition of the aerosol at later times. The AMS data reveal that the aerosol chemical composition does not vary with time or particle size during the experiment, for particles large enough to be measured by the AMS ( $D_{va} > 40 \text{ nm}$ ,  $D_v > \sim 20 \text{ nm}$ ). This suggests that the nucleating species also comprise most of the aerosol at later times.

[88] The gas-phase and aerosol uptake simulations predict an aerosol composed mostly of OIO and HOI, the latter becoming only important at lower CH<sub>2</sub>I<sub>2</sub> concentrations. The mechanism also predicts the presence of small amounts of I<sub>2</sub>O<sub>2</sub>, HI, and the products of HO<sub>2</sub> and OH uptake in the aerosol.

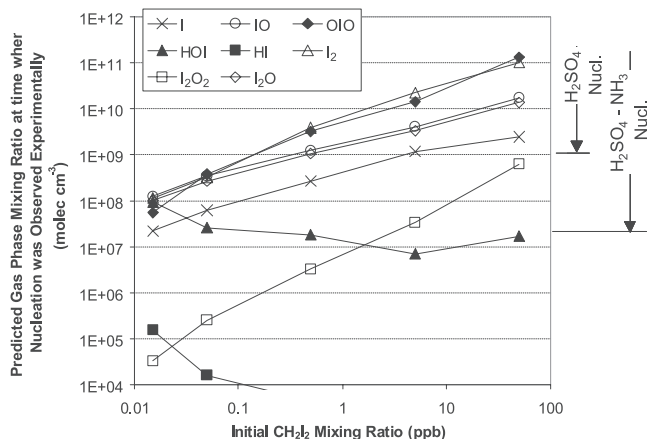
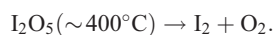
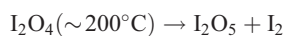
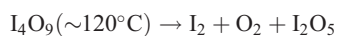
[89] The identity of the possible nucleating species can be probed by combining the results of the experiments and the gas-phase simulations. The predicted gas-phase concentra-



tions at the time at which nucleation was observed experimentally are shown in Figure 16 as a function of initial  $\text{CH}_2\text{I}_2$  mixing ratio. The orders of magnitude of the predicted gas-phase concentrations of the major species at the time of nucleation are  $10^8$ – $10^{11}$  molec.  $\text{cm}^{-3}$ . To put these levels in an atmospheric context, these concentrations are qualitatively similar to those of another atmospherically important system:  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  nucleate at ambient temperature at levels in the range  $10^9$ – $10^{11}$  molec.  $\text{cm}^{-3}$  [Viisanen *et al.*, 1997; Ball *et al.*, 1999], while  $\text{H}_2\text{SO}_4$ – $\text{NH}_3$ – $\text{H}_2\text{O}$  are estimated to nucleate when both  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  reach levels around  $2 \times 10^7$  molec.  $\text{cm}^{-3}$  [Kulmala *et al.*, 2002]. Coming back to our results, if a single species is nucleating in the chamber the nucleation rate will be a very steep function of its supersaturation [Seinfeld and Pandis, 1998], that is, its mixing ratio since all experiments were conducted at the same pressure and temperature. This should result on a “threshold” behavior, meaning that when that species reaches a critical concentration, nucleation ensues, which should appear as a nearly horizontal line for that species in Figure 16 versus  $\text{CH}_2\text{I}_2$ . However, the concentration of all major species changes by at least two orders of magnitude as the initial  $\text{CH}_2\text{I}_2$  mixing ratio changes. This result reinforces the conclusion that the current knowledge of the gas-phase mechanism is incomplete.

[90] The AMS data are consistent with the presence of iodine oxides in the particles, as well as that of water and/or iodine oxyacids. Pure iodine is a crystalline solid with a vapor pressure of  $\sim 0.2$  Torr at ambient temperature. However, the fact that no particles are formed in the chamber when  $\text{CH}_2\text{I}_2$  is photolyzed in the absence of  $\text{O}_3$ , yielding I radicals, indicates that pure iodine solid particles do not likely explain the observed nucleation behavior. Detection of  $\text{I}^+$  and  $\text{I}_2^+$  by the AMS and of the equivalent negative ions by Hoffmann *et al.* [2001] must stem from the thermal decomposition and/or fragmentation in the AMS of iodine oxides and/or hydrogen-containing iodine species in the particles.

[91] Knowledge about iodine oxides is still incomplete. The existence of a number of oxides proposed in the literature has not been confirmed, including  $\text{I}_2\text{O}_3$ ,  $\text{I}_2\text{O}_7$ ,  $\text{I}_6\text{O}_{13}$ , and  $\text{I}_{10}\text{O}_{19}$ , [Chase, 1996]. The iodine oxides known to produce a stable solid phase are  $\text{I}_2\text{O}_4$ ,  $\text{I}_2\text{O}_5$ ,  $\text{I}_2\text{O}_6$ , and  $\text{I}_4\text{O}_9$ , while  $\text{I}_2\text{O}_2$  has been tentatively identified in the gas phase [Chase, 1996; Bloss *et al.*, 2001]. Iodine oxides have a strong tendency to form polymeric networks.  $\text{I}_2\text{O}_4$  can be approximated as a one-dimensional solid with infinite  $-\text{I}-\text{O}-\text{IO}_2-\text{O}-$  chains linked by weaker interchain I-O bonds [Fjellvag and Kjekshus, 1994].  $\text{I}_2\text{O}_5$  is composed of  $\text{IO}_2-\text{O}-\text{IO}_2$  units linked by weaker I-O inter-unit bonds [Selte and Kjekshus, 1970].  $\text{I}_2\text{O}_6$  is composed of molecular subunits of composition  $\text{I}_4\text{O}_{12}$  linked by I-O bridges [Kraft and Jansen, 1995]. Little is known about the structure of  $\text{I}_4\text{O}_9$ . The chain structure of  $\text{I}_2\text{O}_4$  and the simpler molecular structure of  $\text{I}_2\text{O}_5$  seem more amenable to rapid formation via gas-phase collisions during nucleation than the more elaborate structure of  $\text{I}_2\text{O}_6$ . Three of the oxides are known to decompose upon heating [Fjellvag and Kjekshus, 1994; Kraft and Jansen, 1995; Maier and Bothur, 1997; Chase, 1996] as



**Figure 16.** Predicted gas-phase concentrations at the inception of the experimental nucleation burst, as a function of initial  $\text{CH}_2\text{I}_2$  mixing ratio. The y-axis has been limited to about six orders of magnitude below the concentration of the major species. Also shown are the minimum concentrations needed for nucleation at ambient conditions for the  $\text{H}_2\text{SO}_4$ – $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ – $\text{NH}_3$ – $\text{H}_2\text{O}$  systems (see text).

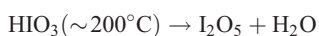
[92] During the detection process of the AMS, the particles are vaporized at  $\sim 600^\circ\text{C}$ , probably undergoing a complex thermal decomposition. Thus the  $\text{I}_2^+$  detected with the AMS is consistent with any of the iodine oxides and does not imply the presence of pure iodine in the particles.

[93] After vaporization in the AMS, the molecules are ionized by electron impact, and either the molecular ion or one of its fragments is detected by the mass spectrometer. This can explain the detection of  $\text{I}^+$ ,  $\text{IO}^+$ ,  $\text{IO}_2^+$ ,  $\text{IO}_3^+$ ,  $\text{IO}_5^+$ ,  $\text{I}_2\text{O}^+$ , and  $\text{I}_2\text{O}_3^+$  as fragments resulting from electron impact ionization of the products of vaporization of one or several iodine oxides. All of the  $m/z$  peaks detected for the chamber aerosol also appeared when sampling an  $\text{I}_2\text{O}_5$  standard that had been diluted in water, atomized, and diffusion-dried. These peaks would very likely appear for the other iodine oxides as well, none of which is available commercially. Thus the AMS data are consistent with the presence of  $\text{I}_2\text{O}_4$  in the particles as suggested by Hoffmann *et al.* [2001] or with that of any other iodine oxide.

[94] The signals at  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  could in principle arise for particle-bound water or from the decomposition of hydrogen-containing iodine species on the AMS vaporizer. The  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  signals increased by a factor of five between the dry and the humid experiments, whereas the signals at  $\text{HI}^+$ ,  $\text{HIO}^+$ ,  $\text{HIO}_2^+$ , and  $\text{HIO}_3^+$  were about half as large for the humid experiment as for the dry experiment. This indicates that the signals at  $\text{OH}^+$  and  $\text{H}_2\text{O}^+$  are likely due to particle-bound water.

[95] The signals detected at  $\text{HI}^+$ ,  $\text{HIO}^+$ ,  $\text{HIO}_2^+$ , and  $\text{HIO}_3^+$  indicate that the particles may also include hydrogen-containing iodine species, likely iodine oxyacids. Iodine acids reported in the literature include HI, HIO,  $\text{HIO}_2$ ,  $\text{HIO}_3$ , and  $\text{HIO}_4$ . Gas-phase chemical mechanisms consider only HOI and HI, while the ionic species  $\text{IO}_3^-$  detected in aerosol samples is assumed to be formed by aqueous aerosol chemistry after uptake of other iodine species [McFiggans *et al.*, 2000; Vogt *et al.*, 1999]. The detection of  $\text{HI}^+$  and  $\text{HIO}^+$  could be due to HI and HOI present as such in the

particles; however, their predicted aerosol concentrations are too low to explain the signal intensities detected in the AMS. The AMS detection of  $\text{HIO}_2^+$  and  $\text{HIO}_3^+$  indicates that either larger oxyacids are present the particles (probably  $\text{HIO}_3$ ), or that these are made on the AMS vaporizer from an iodine oxide and the particle-bound water. Both possibilities are plausible, though the former is more likely. Similar AMS signals were observed at  $\text{HI}^+$ ,  $\text{HIO}^+$ ,  $\text{HIO}_2^+$ , and  $\text{HIO}_3^+$  when sampling  $\text{I}_2\text{O}_5$  that had been dissolved in water, a process that is known to produce  $\text{HIO}_3$  [Chase, 1996]. The fact that Hoffmann *et al.* [2001] did not detect any hydrogen-containing ions is not necessarily inconsistent with the presence of  $\text{HIO}_3$  in the particles, since the aerosol undergoes a much slower vaporization in their instrument at  $550^\circ\text{C}$ , during which  $\text{HIO}_3$  can decompose by [Chase, 1996]:



Little is known about the chemical decomposition that may occur when the particles impact the AMS vaporizer. It is possible that, if the particles are composed only of  $\text{I}_2\text{O}_4$  and water, part of the  $\text{I}_2\text{O}_4$  thermally decomposes on the AMS vaporizer to  $\text{I}_2\text{O}_5$ , which in turn reacts with  $\text{H}_2\text{O}$  to yield the observed signals. However, the  $\text{HIO}_3$  formed should further decompose at the higher temperatures of the AMS vaporizer.

[96] If iodine oxyacids are present in the particles, their origin cannot be explained by the known gas-phase chemistry. Sunder and Vikis [1987] identified the solid product formed by the dark reaction of  $\text{I}_2$  with  $\text{O}_3$  under saturated water vapor conditions as  $\text{HIO}_3$ ; however, this reaction had yielded only  $\text{I}_4\text{O}_9$  when conducted under completely dry conditions [Sunder *et al.*, 1985]. The detailed gas-phase chemical mechanism is not known in either case, but is thought to involve the direct reaction of  $\text{I}_2$  and  $\text{O}_3$  to form a cyclic transition state that decomposes into either  $\text{IO}$ ,  $\text{I}$ , and  $\text{O}_2$ , or  $\text{IO}_2$  and  $\text{IO}$ , the latter path being nonnegligible [Vikis and MacFarlane, 1985]. Since the water vapor concentration was very low in our dry experiments ( $\text{RH} < 2\%$ ), the chemistry leading to iodine oxyacids may have been different in our chamber than for the experiment of Sunder and Vikis [1987]. The presence of larger oxyacids in the particles could be a result of not yet known gas-phase chemistry or of the reaction of  $\text{OH}$ ,  $\text{HO}_2$ , and/or  $\text{H}_2\text{O}$  with an iodine oxide in/on the particles. The reaction of  $\text{OH}$  and  $\text{HO}_2$  with the particles cannot explain the observed intensity of  $\text{HIO}_x^+$  signals, given the uptake coefficients that we have assumed, and that are similar to those determined in previous studies on salt aerosols, as described above. However, the much larger radical uptake coefficients that have been measured when a chemical reaction between the aerosol and the radical is involved [Bertram *et al.*, 2001] could result in the observed signals. Whichever is the actual formation path of iodine oxyacids under dry conditions, it is possible a nonaqueous path is responsible for some of the  $\text{IO}_3^-$  detected in coastal aerosol samples, contrary to the prevailing literature assumption.

[97] The HTDMA results provide another constraint on the aerosol composition.  $\text{I}_2\text{O}_5$  and  $\text{I}_4\text{O}_9$  are very hygroscopic (the former is known to yield  $\text{HIO}_3$  in solution) while  $\text{I}_2\text{O}_4$  is not. There is no information on the hygroscopicity of  $\text{I}_2\text{O}_6$  or  $\text{I}_2\text{O}_2$ . The lack of hygroscopic growth of the aerosol

**Table 6.** Synthesis of Evidence on Aerosol Composition and Identity of Nucleating Species

Source of Information	Nucleating and/or Aerosol Species
Lack of nucleation when $\text{O}_3$ not present + kinetic simulations	$\text{I}$ and $\text{I}_2$ are not the nucleating species
Chemical simulations	OIO at high concentrations HOI and OIO at low concentrations
Experimental nucleation delay	OIO, IO, and $\text{I}_2\text{O}$ could be involved in nucleation HOI is less likely to be involved $\text{I}_2\text{O}_2$ and HI are not involved $\text{I}_x\text{O}_y$ and either/both $\text{H}_2\text{O}/\text{HIO}_3$
AMS Crystalline structure and speed of nucleation	More likely $\text{I}_2\text{O}_4$ or $\text{I}_2\text{O}_5$
Lack of hygroscopic growth in HTDMA	Less likely $\text{I}_2\text{O}_6$ Most likely $\text{I}_2\text{O}_4$
Summary	Not likely $\text{I}_2\text{O}_5$ and/or $\text{I}_4\text{O}_9$ OIO most likely responsible for nucleation $\text{I}_2\text{O}_4$ most likely dominant aerosol species

formed in the humid experiment is inconsistent with an aerosol composed of either  $\text{I}_2\text{O}_5$  or  $\text{I}_4\text{O}_9$ , while it is consistent with an aerosol composed mainly of  $\text{I}_2\text{O}_4$ .

[98] Table 6 summarizes all the available evidence about nucleating and condensing species. We conclude that homogeneous nucleation of OIO is the most likely mechanism for the observed nucleation bursts. The particles formed under dry conditions are composed of iodine oxides, likely  $\text{I}_2\text{O}_4$  with some iodine oxyacids, likely  $\text{HIO}_3$ . A definitive chemical identification will necessitate the production of a larger mass of particles in a flow tube followed by an in situ analysis technique, for example, as described in Sunder and Vikis [1987].

## 7. Comparison to PARFORCE Results

[99] While the mechanism studied in this paper is capable of producing very rapid and intense nucleation bursts, it is important to determine whether it is a good model for the mechanism that produced the observed nucleation bursts during the PARFORCE campaign described in the introduction [O'Dowd *et al.*, 2002], from whose results the mechanism tested in this paper was hypothesized. In this section we evaluate this point by comparing the results of the chamber experiments presented in this paper with those of the PARFORCE campaign.

[100] First, the chamber experiments indicate a lack of hygroscopic growth (growth factor  $\sim 1.0$ ) in the HTDMA for particles formed under humid conditions. This is similar to the growth factors of 1.05 or less observed during nucleation events at Mace Head under low  $\text{H}_2\text{SO}_4$  concentrations for 8–10 nm particles using a nano-HTDMA [Väkevä *et al.*, 2002; O'Dowd *et al.*, 2002]. These particles were found to contain either only iodine, or iodine and sulfate, while larger particles had a significantly larger sulfate to iodine ratio [Mäkelä *et al.*, 2002]. This suggests that the chemical composition of the newly formed particles may be the same in both cases. The low hygroscopicity points toward  $\text{I}_2\text{O}_4$  as the major iodine oxide produced in both cases.

[101] Second, we can also compare the nucleation and particle growth rates observed in the chamber with those

observed during PARFORCE. During PARFORCE the source rates of detectable sub-10 nm particles measured with a CPC array were  $1-7 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$ . The particle growth rates were estimated at  $0.1-0.36 \text{ nm s}^{-1}$  from the CPC data and at  $0.005-0.5 \text{ nm s}^{-1}$  with a model based on the observations [Hämeri *et al.*, 2002; O'Dowd *et al.*, 2002]. Since  $\text{O}_3$  and UV radiation will always be present at Mace Head during the daytime periods when nucleation was observed, we only need to determine the order of magnitude of  $\text{CH}_2\text{I}_2$  (and other photolabile organic iodine species) during nucleation at PARFORCE to be able to compare field and chamber observations. The condensable vapor concentrations needed to explain the observed growth were estimated by two different models at 4–40 ppt and 240–440 ppt [O'Dowd *et al.*, 2002]. In measurements performed in coastal areas, mixing ratios of up to 6 ppt IO, 3 ppt OIO, and 0.45 ppt  $\text{CH}_2\text{I}_2$  have been reported [Alicke *et al.*, 1999; Allan *et al.*, 2001; Carpenter *et al.*, 1999]. IO and OIO were detected with a long-path DOAS technique and may have been one to two orders of magnitude higher over the shore areas [O'Dowd *et al.*, 2002], up to  $\sim 60-600$  and  $\sim 30-300$  ppt, respectively. Since  $\text{CH}_2\text{I}_2$  photolyzes with a timescale of a few minutes and was measured with a slow instrument (1 h), while the nucleation bursts at PARFORCE changed with a timescale of seconds, it is possible that the flux of iodine atoms from its photolysis at PARFORCE was significantly larger than the reported concentration of 0.45 ppt. From all the available data we estimate that the amount of iodine present in gas-phase species that originate from  $\text{CH}_2\text{I}_2$  is in the range 4–600 ppt. Thus we will use the results of the chamber experiments with 15, 50, and 500 ppt  $\text{CH}_2\text{I}_2$  (Exp. E3, E4 and E5) to provide order-of-magnitude estimates of the nucleation and growth rates. The source rates of sub-10 nm particles in the chamber during those experiments are  $10^3-10^6 \text{ cm}^{-3} \text{ s}^{-1}$ , while the growth rates of the nucleated particles are  $0.005-0.08 \text{ nm s}^{-1}$ . Thus the source and growth rates observed in the chamber are reasonably consistent with those observed in the field experiments, given the large uncertainties present in both sets of ultrafine particle measurements, and on the estimated precursor concentration at PARFORCE.

[102] Kulmala *et al.* [2002] propose that the nucleation and particle growth steps could have been decoupled during PARFORCE, with  $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$  providing the nuclei for another species to condense on. Our laboratory results indicate that photooxidation of  $\text{CH}_2\text{I}_2$  can result in nucleation and particle growth rates similar to those observed in coastal areas, and thus that ternary nucleation of  $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$  need not be invoked.

[103] Finally, the results in this paper provide an explanation of the lack of correlation between  $\text{O}_3$  and particle formation during PARFORCE, with the exception of one strong nucleation event in which  $\text{O}_3$  was noticeably reduced [O'Dowd *et al.*, 2002]. The total  $\text{O}_3$  consumption predicted by the chemical mechanism for the chamber experiments between 15 and 500 ppt  $\text{CH}_2\text{I}_2$  is  $\sim 2-7$  ppb over a time-scale of 20 min. These estimates can be used as an upper bound of  $\text{O}_3$  destruction since the simulations overpredict the measured  $\text{O}_3$  destruction for the 5 ppb experiments by a factor of 2 (Figure 15). From these results, we estimate an  $\text{O}_3$  destruction rate of at most  $0.1-0.35 \text{ ppb min}^{-1}$ , which

would be difficult to detect on top of fluctuations on a natural background of the order of 30 ppb and the noise of the  $\text{O}_3$  analyzer itself. Also, since this chemical system consumes little  $\text{O}_3$  and is insensitive to the  $\text{O}_3$  concentration (as long as there is excess  $\text{O}_3$ ), it is unlikely that ozone will ever be the limiting reactant. If  $\text{CH}_2\text{I}_2$  (or other photolabile organic iodine species) is available at concentrations of tens of ppt together with UV light, new particle formation will proceed.

## 8. Conclusions

[104] We have studied the photooxidation of  $\text{CH}_2\text{I}_2$  in the presence of  $\text{O}_3$  experimentally in the Caltech indoor chamber and by means of gas-phase chemical simulations. We can summarize the observed aerosol dynamics in the base case experiment (Exp. E1, 5 ppb  $\text{CH}_2\text{I}_2$ , 100 ppb  $\text{O}_3$ , RH < 2%) as (1) a nucleation burst immediately after the inception of photolysis with its highest intensity for about 1 min, (2) condensation of additional vapors onto the nucleated particles for a period of 1.5–2.5 h, (3) particle coagulation, which occurs after the nucleation burst and controls the dynamics from the point when condensation ceases, and (4) a size-dependent wall loss of particles, which is important for the freshly nucleated particles and later has a characteristic time of about 5 h. Particles formed under dry conditions are fractal agglomerates with mass fractal dimensions,  $D_f \sim 1.8-2.5$ . Higher relative humidity does not alter the nucleation or growth behavior but results in more compact and dense particles ( $D_f \sim 2.5-2.8$ ). The main features of this process do not change with decreasing initial  $\text{CH}_2\text{I}_2$  concentration; however, the gas-to-particle conversion is slower, likely due to reduced aerosol surface for uptake.

[105] On the basis of all the available information, the most likely species that could be responsible for the observed nucleation bursts and condensation growth is OIO. Chemical analysis of the particles is consistent with the presence of iodine oxides, although the available evidence is inconclusive for any one of them. Water and/or iodine oxyacids, likely  $\text{HIO}_3$ , are also present in the particles. The acid may be formed in the gas phase or by reactions in/on the aerosol. Comparison between particle hygroscopicity, composition, and nucleation and growth rates observed in coastal measurements and in the present experiments suggest that photooxidation of  $\text{CH}_2\text{I}_2$ , possibly coupled with other photolabile organic iodine species, is the mechanism leading to the observed new particle formation on the west coast of Ireland. For  $\text{CH}_2\text{I}_2$  concentrations of tens of ppt during daylight hours, new particle formation can occur without the need for preexisting clusters from species outside the iodine system.

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- R. Bahreini, R. C. Flagan, J. H. Seinfeld, and H. Zhuang, Department of Environmental Science and Engineering, California Institute of Technology, Mail Code 210-41, 1200 East California Boulevard, Pasadena, CA 91125, USA.
- D. R. Cocker III, Department of Chemical and Environmental Engineering, University of California, Riverside, CA 92521, USA.
- T. Hoffmann, Institute of Spectrochemistry and Applied Spectroscopy, P. O. Box 10 13 52, D-44013 Dortmund, Germany.
- J. L. Jimenez, Department of Chemistry and Biochemistry and CIRES, UCB 216, University of Colorado, Boulder, CO 80309-0216, USA. (jllj@alum.mit.edu)
- C. D. O'Dowd, Department of Physics, University of Helsinki, P. O. Box 9 (Siltavuorenpenger 20D), FIN-00014, Helsinki, Finland.
- V. Varutbangkul, Department of Chemical Engineering, California Institute of Technology, Mail Code 210-41, 1200 East California Boulevard, Pasadena, CA 91125, USA.