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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Laboratory studies of the homogeneous nucleation of iodine oxides" *by* J. B. Burkholder et al.

J. B. Burkholder et al.

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Our ACPD paper, Laboratory studies of the homogeneous nucleation of iodine oxides by J. B. Burkholder, J. Curtius, A. R. Ravishankara, and E. R. Lovejoy, received three referee reports and one comment during the Open Comment period. We thank the referees for their constructive comments on the paper. We have responded to the reviews and comment separately below. To improve comprehension, we have included the Referee Comments (paraphrased) followed by our response and the actions taken in revising the manuscript.

Anonymous Referee 1

$\mathrm{RefereeComment}$: The only major issue in my opinion is the modeling assumption of the aerosol density as 1 g cm^{-3}. This presents two separate problems.

First, for the bulk density of I_2O_4, the authors cite a value of 2.57 g cm^{-3} from Fjellvag and Kjekshus (1994). The density of the related oxide I_2O_5 is reported as 5.08 g cm^{-3} by the same group (Selte and Kjekshus, 1970) and as 4.8 by Sigma-Aldrich. The structures of I_2O_4 and I_2O_5 are similar (Fjellvag and Kjekshus). It seems odd that there could be as large of a difference as from 4.8 g cm^{-3} for I_2O_5 to 2.6 g cm^{-3} for I_2O_4 when the compounds are so close in composition and crystalline structure. Thus I recommend using a bulk density of 5 g cm^{-3} for I_2O_4.

The second issue for the value of the density used here is the assumption that the effective density of the nucleated particles is lower than that of the bulk material, due to the fractal structure determined by Jimenez et al. (2003) for particles formed in the same chemical system. However the lower densities determined in that study correspond to much larger particles (100-200 nm) compared to the ones measured here (tens of nm). A fractal structure would be likely be composed (by analogy to soot and other such particles formed by similar dynamics) of monomer particles 20-60 nm that coagulate together into larger agglomerates. Thus the assumption of a lower effective density for the particles is appropriate for simulating particles 50 nm and higher, but not for smaller particles.

In summary, if the particle density has an important effect on the model I recommend using a size-dependent value of 5 g cm^{-3} for particles smaller than 50 nm, gradually decreasing to a value of 1 g cm^{-3} at 1 micron. If such a change would not impact the results presented here, the authors should state that in the paper.

AuthorResponse: The referee has raised an interesting question related to the micro-physical properties (density and effective radius) of the newly formed OIO clusters and particles. The referee has suggested that the experimentally determined OIO particle density reported in the Jimenez et al. (2003) work, determined using primarily 100 to 200 nm diameter particles, may not be appropriate for our experiments in which the particle diameters are less than 20 nm. At present the geometry of the OIO particles, < 100 nm diameter, is unknown. Hoffmann et al. (2001) have suggested, based on theoretical considerations, that the initial formation of OIO clusters is via the nearly straight chain addition of OIO monomers to form polymeric structures. The physical properties of these small fractal particles may therefore differ from those of the bulk (contrary to the referee comment, i.e. a larger density for the smaller particles). In the absence of particle geometry data as a function of size, the model calculations presented in our ACPD paper assumed a spherical geometry with a density of 1.0 g cm^{-3} as reported by Jimenez et al. (2003) for all particles.

In reviewing the issue of particle density, we have discovered an error in reporting the density used in our model calculations. The model results presented in the ACPD paper were obtained using an OIO particle density of 2.5 g cm^{-3} rather than a value of 1.0 g cm^{-3} as reported. The revised paper that includes additional model results (described below) will correct this error.

To best address the influence of the OIO particle density used in the model, we have performed additional modeling calculations using different OIO particle densities as input. Model calculations were performed using densities of 1.0, 2.5, and 5 g cm^{-3}. A density of 1.0 g cm^{-3} is consistent with the experimental data from Jimenez et al. (2003). A density of 2.5 g cm^{-3} was used to represent the bulk value reported by Fjelvag and Kjekshus (1994) as referenced in our ACPD paper. We assume this value supercedes the previously reported higher value from this group (not referenced in our paper) and other earlier reported values. This bulk density therefore represents an upper limit to the new particle density while OIO particles with fractal structures would have even lower densities. However, the referee has questioned the accuracy of the Fjelvag and Kjekshus density value and suggests that a higher density (4.8 g cm^{-3}) that has been measured for a different but similar iodine oxide, I_2O_5 might be more appropriate. Therefore, model calculations with a density of 5.0 g cm^{-3} have also been included.

In the process of evaluating the model dependence on the OIO particle density, we have also re-evaluated our assumptions for the OIO uptake coefficient. In our ACPD paper, an uptake coefficient value of 1.0 (i.e. every collision results in uptake) was used. In the revised model calculations, the uptake coefficient was also allowed to vary (values less than 1.0) to achieve the best agreement with the experimental data.

Action: Table 3 and the text of the paper have been revised to reflect the changes in the modeling approach and results. The conclusions drawn from these additional model calculations are: (1) The optimized thermodynamic parameters were independent of the particle density used, (2) A density of 5.0 g cm^{-3} does not reproduce the experimental data very well. These calculations fail to capture the correct induction time for particle detection (too late), the rate of rise in the particle concentration (too fast), and the particle concentration at the end of the observation time (too high). Using an uptake coefficient less than 1.0 yielded even worse fits to the experimental data. (3) A density of 2.5 g cm^{-3} with an uptake coefficient of 1.0 reproduces the experimental data very well and is identical to that given in our ACPD paper. (4) A density of 1.0 g cm^{-3} also reproduces the experimental data very well with an uptake coefficient value of $\sim$0.3. This would be consistent with a fractal particle geometry for small particles, < 50 nm diameter, and a physically realistic uptake coefficient.

MinorRefereeIssues:

Referee: Page 4947, lines 6-10: The description of Figure 1 should mention the nano-DMA, since this instrument is shown in the figure.

Author: OK, text changed.

Referee: Page 4947, line 19: The use of a Teflon line for sampling aerosols may cause concern for of aerosol experimentalist, due to the large particle losses typically associated with charged particles when using tubing of this material. This is probably not an issue here because the charging probabilities of nanoparticles are very small and the system does not appear to have a source of charge. The authors may want to mention these points when describing their sampling system.

Author: We agree with the referee comment that charging issues and therefore the material of the sampling line are not an issue in these experiments. We have added the following sentence to the clarify this point: The use of a Teflon sampling line did not influence the measurement of the uncharged iodine oxide particles.

Referee: Page 4949, line 5: It is stated that particle loss was determined to be negligible, < 5%. However no details are given about how this determination was made. Was this done theoretically, or experimentally, and if the later with 3 nm particles or with e.g.100 nm particles? A little more detail should be given since diffusion losses are such a steep function of particle size.

Author: This was determined experimentally during an iodine oxide nucleation experiment by changing the sampling flow rate of the UCPC from 1500 to 500 cm^3 min.$^{-1}$. The following sentence has been added: Particle loss was determined experimentally by comparing particle concentrations for the high, 1500 cm^3 min.$^{-1}$, and low, 500 cm^3 min.$^{-1}$, sample flows of the UCPC during an iodine oxide nucleation experiment.

Referee: Page 4953, lines 1-4. It is stated that the mechanism used here does not treat explicitly the release of the second I atom. The authors should provide an estimate of the time scale of this release based on current knowledge, so as to bound the uncertainty due to this assumption.

Author: The time scale for the release of the second iodine atom is dependent on the radical concentrations (which vary from experiment to experiment) and the kinetics of the CH_2IOO radical. The kinetics of the CH_2IOO radical is unknown at present. As presented in the paper, this is one of the reasons we preferred using CF_3I as our iodine atom source standard.; To clarify this issue we have deleted the following text: but we expect k_7 to be similar to that of the CH_3OO radical self-reaction, 4.7 x10^{-13} cm^3 molecule^{-1} s^{-1} (Sander et al., 2002). from this section so as to avoid too much speculation about the kinetics. Second, we have added a statement to the results and discussion section to indicate that the model results are consistent with the assumption of an immediate release of the iodine atom, page 4963, line 6: Also, the experimental

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data is most consistent with the model assumption of prompt iodine release from the CH_2IOO radial.

Referee: Page 4964, line 16: A Jimenez et al (2002) reference is cited here, but none is given in the author list. Perhaps this should be the Jimenez et al (2003) reference cited elsewhere.

Author: Yes, date of reference changed.

Referee: Page 4968, line 12: the first and third questions addressed by the modeling effort are phrased as questions, which makes them easier to follow. Perhaps the second question that is introduced in this line could also be phrased as a question.

Author: We have changed the introductory sentence to: In the second model calculation, we address the question: Using the field measured IO radical concentrations, what are the expected iodine oxide particle concentrations?

Referee: The modeling study of ODowd et al. (2002) should be briefly discussed in the modeling section and compared to the results obtained here.

Author: The ODowd et al. paper addresses the impact of iodine on aerosol nucleation and growth under a range of conditions expected to be representative of the open ocean. Our ACPD paper failed to cite and properly discuss this paper. We thank the referee for bringing this work to our attention. We only briefly mention open ocean conditions in our paper. On page 4968 we mention the impact of our aerosol model results for open ocean conditions and on page 4971 we summarize these results in the conclusions. The ODowd et al. paper concludes that iodine oxides can make a significant impact to the formation and growth of particles under open ocean conditions. Our model results conclude that based on the currently available OIO concentration measurements by Plane and co-workers that OIO would not lead to new particle, > 3 nm diameter, formation (i.e. no significant homogeneous nucleation of iodine oxides) under open ocean conditions, see our Fig. 10a. However, OIO could still make a significant contribution to the growth of small sulfuric acid particles as shown in the ODowd modeling study.

Action: To clarify this issue we have changed the wording in our paper to clearly state that we are referring to new particle formation and not particle growth. On page 4968 we have changed: The lone field measurement of OIO, < 0.5 ppt, at Cape Grim, Tasmania may therefore be more representative of the open ocean conditions. Our aerosol model calculations would lead us to conclude that OIO homogeneous nucleation in the open ocean would not be a significant source of MBL aerosol. To: The lone reported field measurement of OIO, < 0.5 ppt, at Cape Grim, Tasmania (Allan et al., 2001) includes coastal influences but may represent an upper limit for the OIO concentration in the open ocean. Our aerosol model calculations would lead us to conclude that OIO homogeneous nucleation in the open ocean would not be a significant source of new particles in the MBL at these concentrations. A recent modeling study by ODowd et al. (2002) however has shown that iodine oxides could contribute to the growth of small, ∼1 nm diameter, sulfuric acid particles into detectable sizes, > 3 nm diameter. Further open ocean modeling studies using the iodine oxide nucleation parameters determined in this study and direct measurements of the OIO concentration in the open ocean could aid the refinement of this analysis.

We have also added the ODowd et al. (2002) reference to the paper.

Referee: Page 4955, line 8: 1 should read i. **Author**: Corrected.

Referee: Page 4956, line 6: Kp should be capitalized in equation 16. **Author**: Corrected.

Referee: Page 4956, line 9: Dahnekes.**Author**: Corrected.

Referee: Page 4964, line 22: atmosphericly should read atmospherically. **Author**: Corrected.

Referee: Page 4966, lines 23-27: the word calculation is repeated 4 times in 5 lines.

Author: True, but used properly. No changes made in the text.

Referee: Page 4970, line 17: 100 s to 1000 s ppt can be confusing to readings since s could be interpreted as the symbol for seconds. I recommend replacing by hundreds to thousands of ppt. **Author**: Changes made to text.

Referee: Page 4978, Figure 2. It is not possible to distinguish the spectra of the two lamps on the right part of the graph. I recommend making one of them dashed, while maintaining the extra thickness. **Author**: Figure has been modified to clarify the two lamp spectra.

Referee: Page 4982, Figure 6: This figure may be easier to read if it was replaced by a single, much bigger, graph and the model lines represented as dashed lines (such as it was done in Figure 4). **Author**: We have found that plotting the six experimental curves and five model curves in the same frame was too difficult to read (the overlap between the experimental and model curves is not perfect). Therefore, we presented the experimental and model data in separate frames. No changes have been made.

Anonymous Referee 2

Referee: It is mentioned on page 4959, line 15, that the data showed clearly a highly non-linear dependence of the nucleation on the initial I-atoms concentration. The authors claim that this is characteristic for homogeneous aerosol nucleation when a nuclear barrier exist. It is not clear what is meant by this nuclear barrier, so the authors might specify this in more detail. **Author**: What is meant here is that there exists a barrier in the free energy in the formation of small OIO clusters. We have re-worded this to read: This highly non-linear dependence is characteristic for homogeneous nucleation with a free energy barrier.

Referee: It is interesting to note that the derived rate constant for the reaction IO + O_3 $\rightarrow$ OIO + O_2 (5 x 10^{-15} cm^3 $molecule^{-1}$ s^{-1}) is approximately 3000 times faster than the analogous reactions ClO and BrO with O_3. This rate constant was derived from a global data analysis. It would be of interest to mention how sensitive this analysis procedure was, and how large the error limits might be for this reaction. **Author**: It is difficult to assign error limits to this parameter. In addition, the most recent IUPAC summary of kinetic data has included a reference to Larin et al. (Kinet. Katal. 1999) in which an upper limit for this reaction, 2 x10^{-16} cm^3 $molecule^{-1}$ s^{-1}, was reported. We overlooked this work in our ACPD paper. This would contradict our assignment of the OIO nucleation ozone dependence under certain conditions to the IO + O_3 gas phase reaction. As stated in our paper the assignment of the ozone dependence does not change any of our conclusions. The ozone dependence remains an open scientific question. We have revised the text to acknowledge the discrepancy between the rate coefficient for IO + O_3 used in this work with the work published by Larin et al. (1999). We have added the more readily available IUPAC summary (Atkinson et al., 2003) to the references.

Referee: A strong temperature dependence of the particle yield was demonstrated in Figure 10, showing a factor 1000 increase in yield for a decrease in temperature from 300 to 270 K. In section 4.2 the authors claim that particle formation are expected to demonstrate strong temperature dependence due to cluster evaporation. Are other additional factors causing this strong temperature dependence?

Author: The main factor is as given in the text, the free energy barrier to nucleation that establishes the temperature dependence of the nucleation process. No changes have been made to the text.

Referee: What photolysis rates for OIO were used in the box model for the first box model calculations (p.4967), shown in Fig.10? Do the box model calculations take into account the data from Ingham et al., who claim that OIO is stable against photolysis between 480 and 660 nm? The steady state concentrations of OIO will definite depend on its photolysis rate.

Author: In these model calculations the OIO concentration is held constant (i.e. at

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steady state) and is therefore independent of the specific formation and loss processes. These calculations are performed to determine the magnitude of the OIO concentrations needed to achieve the observed particle concentrations and formation rates at Mace Head Station. The subsequent box-model calculations presented in the paper are then used to evaluate what conditions are required to achieve such OIO concentrations. In these calculations the OIO loss processes play an important role and are discussed in the text. No changes have been made to the text with regards to this comment.

Referee: Page 4945, line 8: Carpenter et al, 1999: Error year, should be: 2001. **Author**: Corrected.

Referee: Page 4951, line 2: O2 and N2. correct to O_2 and N_2 (subscripts). **Author**: Corrected.

Referee: Page 4953, line 2: correct oversimplified (one word). **Author**: Text as been revised.

Referee: Page 4955: line 8: correct particle 1 into particle i. **Author**: Corrected.

Referee: Page 4956: Equation 16: correct Kp (not kp). **Author**: Corrected.

Referee: Page 4964: line 16: Jimenez et al, 2002: Error year, should be: 2003. **Author**: Corrected.

Third Review: Referee: T. Hoffmann

Referee: Table 1 gives the calculated photolysis rate coefficients for I_2, IO and OIO. Are theses values also calculated for the lamp used in the experiments ? **Author**: Yes, the column headings identify the lamps. No changes made to the text.

Referee: Figure 8 shows the results from photolysis pulse experiments. I dont understand where the peaks in particle number concentration are coming from. Any speculations? **Author**: We assume that this may be an issue related to the inhomogeneous

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nature of the sample but we do not have any further speculation. No changes made to the text.

Referee: In the abstract and conclusion part the authors summarize their results based on the measured IO and OIO concentrations, stating .... that IO and OIO concentrations reported in the field measurements .... are not sufficient to account for significant aerosol production.... Although this statement is correct, in my opinion it is the wrong way of argumentation, since it is based on the intrinsic feature of the underlying measurement technique (DOAS) to average concentrations. Therefore, the line of argumentation is - in principle - based on a measurement artefact. However, I do agree with the main conclusion that locally high concentrations are a likely source for new particle formation in Mace Head.

Author: In the papers of Plane and co-workers and Platt and co-workers (DOAS measurements of IO and OIO) the issue of a measurement artifact and its possible implications are not discussed. Therefore, we have addressed the issue of a measurement artifact in our paper and have not assumed this to be general knowledge. To help clarify, we have changed the text to include that the field measurements of IO and OIO were obtained using long path absorption.

Referee: A final remark. Certainly, one of the most important aspects of iodine oxide nucleation is the question if it might also happen in the open ocean marine boundary layer. As discussed by the authors, this would be strongly dependent on the emission rate and photolysis lifetimes of the precursor compounds as well as the photolysis of the iodine oxides. In my opinion there are still too many open questions (including uncertainties about emission of iodine compounds from oceans) to conclude that the particle formation mechanism is restricted to the hot spot areas discussed in the paper. Therefore, I would conclude that several hypothesises ... await confirmation by future field and laboratory studies.

Author: This question has been addressed above in response to a comment by Ref-

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eree 1 with regards to ODowd et al. (2001). The box-model calculations presented in our paper describe the range of OIO concentrations required for homogeneous nucleation to occur. The thermodynamic parameters derived in this work can be used for a more comprehensive modeling evaluation in future studies. Changes described above.

Open Comment: R. Saunders

In his comment, Saunders discussed, as yet, unpublished results from studies that indicate I2 in the MBL coastal regions is a significant source of I atoms. These observations would be consistent with enhanced iodine oxide nucleation in the MBL coastal regions and the conclusions drawn from our laboratory nucleation studies and box-model calculations.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4943, 2003.

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