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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.

Anonymous Referee #1

Received and published: 25 November 2003

Peer Review for Atm. Chem. Phys. Discussions Paper: Burkholder et al., Laboratory Studies of the Homogeneous Nucleation of Iodine Oxides

This paper presents laboratory and modeling results on the homogeneous nucleation of iodine oxides arising from the photolysis of a iodocarbons followed by the reaction of the liberated I atom with O3. This topic is of great current interest in the atmospheric chemistry area, thus the paper is very appropriate for ACP.

This is an impressive and very complete study that focuses on the nucleation and early particle growth kinetics in this system, the creation of a predictive model, and the application of the model to atmospherically relevant conditions. The nucleation kinetics aspects have not been addressed by previous studies, which prevented them from directly modeling the nucleation rate under atmospheric conditions. As such this study

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fills a critical gap in our knowledge in this area and is very complementary to previously published work. The use of CF3I rather than CH2I2 as I atom precursor is very clever and has allowed the authors to overcome some important limitations encountered in previous studies.

I recommend that this paper be published in ACP after one major issue and a few minor issues are addressed.

Major Issue

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 I2O4, the authors cite a value of 2.57 g cm-3 from Fjellvag and Kjekshus (1994). However a previous reference from the same group (Daehlie and Kjekshus,1964) reports a density of 4.97 g cm-3, and cites an earlier measurement of 4.2 g cm-3 by Muir. The same synthesis method for I2O4 was used in both studies (the 1994 paper cites the 1964 paper on this point). On the other hand the density of the related oxide I2O5 is reported as 5.08 g cm-3 by the same group (Selte and Kjekshus, 1970) and as 4.8 by Sigma-Aldrich (I2O5 is available commercially from this company). The structures of I2O4 and I2O5 are similar (Fjellvag and Kjekshus) and in fact I2O4 decomposes into I2O5 and I2 (density ˜4.9 g cm-3) upon heating. It seems odd that there could be as large of a difference as from ˜4.8 g cm-3 for I2O5 to ˜2.6 g cm-3 for I2O4 when the compounds are so close in composition and crystalline structure. Thus I recommend using a bulk density of ˜5 g cm-3 for I2O4. Perhaps the authors could contact Dr. Kjekshus who may be able to provide additional insight on this issue.

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

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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.

Minor Issues

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

- 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.

- 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.

- 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

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due to this assumption.

- 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.

- 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.

- The modeling study of O'Dowd et al. (2002) should be briefly discussed in the modeling section and compared to the results obtained here.

Grammar and Formatting Issues

- Page 4955, line 8: '1' should read 'i'.

- Page 4956, line 6: Kp should be capitalized in equation 16.

- Page 4956, line 9: 'Dahnekes' should read 'Dahneke's'

- Page 4964, line 22: 'atmosphericly' should read 'atmospherically'

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

- 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.'

- 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.

- 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).

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Interactive Comment

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Selte, K., and A. Kjekshus, Iodine oxides: part III, The crystal structure of I2O5, Acta Chem. Scandinavica, 24, 1912Ű1924, 1970.

Daehlie, G., and Kjekshus, Iodine Oxides: Part I. On I2O3-SO3, I2O3-4SO3, I2O3-SeO3, and I2O4. Acta Chem. Scandinavica, 18, 144-156, 1964.

O'Dowd, Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Kulmala, M., Pirjola, L., and Hoffmann, T. Particle Formation in the Marine Atmosphere Controlled by Biogenic Iodine Emissions. Nature 417: 632-636 (2002).

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

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