

## ***Interactive comment on “Characterization of iodine particles with Volatilization-Humidification Tandem Differential Mobility Analyser (VH-TDMA), Raman and SEM techniques” by Z. D. Ristovski et al.***

### **Anonymous Referee #1**

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### **Review of Ristovski et al., ACPD 6: 1481-1508, 2006.**

This paper presents results from three analytical techniques to address the question of the chemical composition of the particles formed in the photooxidation of CH<sub>2</sub>I<sub>2</sub> with O<sub>3</sub>. This chemical system has received intense attention in recent years from the atmospheric chemistry community, due to its implication in new particle formation in coastal areas. The composition of the particles formed is still not well characterized, so this study is timely. This is a difficult experimental system due to the instability of

several of the species involved, as described in this paper.

The present study used CH<sub>2</sub>I<sub>2</sub> instead of I<sub>2</sub> as the gas-phase precursor. I<sub>2</sub> is the more relevant precursor to coastal areas, based on recent DOAS results that have detected this species at much higher concentrations than what has been reported for CH<sub>2</sub>I<sub>2</sub> (Saiz-Lopez and Plane, 2004; Saiz-Lopez et al., 2006). The gas-phase chemistry in both systems is thought to be the same following the release of I radicals to the gas-phase (Burkholder et al., 2004). Also the composition of particles formed in both systems is identical as far as it can be discriminated with AMS analysis (McFiggans et al., 2004). However it would be useful if future studies analyzed particles generated from the photooxidation of both I<sub>2</sub> and CH<sub>2</sub>I<sub>2</sub> (the later for comparison with previous studies).

The results in the paper are interesting and provocative, however they are not thoroughly elaborated, or tied together by a consistent interpretation. The VHTDMA data are new and unique, but do not yield a conclusive identification of the photooxidation product. The Raman data and their interpretation are somewhat confusing, in part because the particles may have changed upon exposure to ambient air. The description of both the VHTDMA and Raman data are too short. A table comparing the observed / not observed Raman peaks in every system and those in the literature references would be useful.

Most importantly, the identification of the photooxidation product as I<sub>2</sub>O<sub>4</sub> is based on the SEM EDX spectrum, which is described in a total of 7 lines at the end of the paper. The uncertainty analysis of the I/O ratio presented should be thoroughly described. An important omission is the lack of reference to the recent paper of Saunders and Plane (2005) in this topic, recently published in an Australian journal (the country of three of the authors here). In that study it is found using EDX that particles formed from photooxidation of I<sub>2</sub> in the presence of O<sub>3</sub> are composed of I<sub>2</sub>O<sub>5</sub>, in contrast with the results presented here. R. Saunders has already submitted an online comment to this discussion on the details of the EDX results. These results should be discussed in

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more detail, and the questions from R.S. should be thoroughly addressed.

Overall this paper presents some new information on this system and can eventually be published in ACP after addressing the points in this and the previous reviews. It is important to remember that we did not know the composition of the photooxidation particles because of the difficulties of working with these compounds. The analyses presented here add to our knowledge of the system, but a tighter interpretation and integration with other literature results is needed.

If the composition of the particles formed here (20 ppm CH<sub>2</sub>I<sub>2</sub>, 230 ppb O<sub>3</sub>, dry (?), 3 min.) and in the Saunders study (1 ppm I<sub>2</sub>, 10 ppm O<sub>3</sub>, 12 s) are indeed different beyond doubt, this would imply that this general photochemical system can produce different particle compositions depending on the exact conditions, and a parametric study using EDX would be warranted. Saunders and Plane speculate that heterogeneous reactions may change the particle composition. These reactions may play a more important role under the conditions in their system, in which O<sub>3</sub> is in great excess, than on the Ristovski et al. experiment, where O<sub>3</sub> may be rapidly depleted and may not be available to react with the particles.

### Detailed Comments

- p. 1487, section 2.2.2: what is the RH inside the photochemical reactor? Previous studies have shown an influence of humidity on the morphology and composition of the particles formed, so this detail is important.

- On the discussion of Fig. 3 and 4, it would be useful if the relative particle number concentrations of the hygroscopic and non-hygroscopic peaks (observed at T > 200 C) were given in graphical or text form.

- p. 1490, discussion of Fig. 3: it appears that the hygroscopic growth factor is 0.92 for all T < 200 C. This would mean that the particles are shrinking upon exposure to elevated humidity, as observed by Jimenez et al. (2003) for particles produced from

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photooxidation of CH<sub>2</sub>I<sub>2</sub> under dry conditions. If this shrinkage is real, it should be briefly discussed in the paper. Similarly, also in Fig. 4 it appears that  $G_f$  at the lower temperatures is  $< 1$ .

- p. 1490, lines 1-13: the appearance of a double peak in the hygroscopic growth distribution, even though all particles were produced in the same way, is indicative of the effect of phase transitions in this system. A hygroscopic phase seems to nucleate in some particles and not in others. This possibility should be mentioned in the paper.

### Minor Issues

- p. 1483, line 14: the acronym for the Aerodyne instrument is AMS, not AAMS

- The citation info for the Burkholder et al. reference is incorrect. The volume and page range given correspond to the ACPD version, not the ACP one.

- p. 1486, line 8: the 'Collison' (not 'Collision') nebulizer is named after its inventor

- p. 1493, line 17: it is stated here that certain bands in NaNO<sub>3</sub> spectra are due to iodate ions. I assume this is an error and the authors meant to refer to a compound other than NaNO<sub>3</sub>.

### Grammar and Spelling Issues

- p. 1482, line 7: should be 'gases' instead of 'gasses'

- p. 1482, line 21: remove 'the' before 'aerosols'

- p. 1483, line 29: 'particles' should be 'particle'

- p. 1496, line 2 and Eq. A1: different Greek letters are used in the text and the equation for the osmotic coefficient.

### References

Burkholder et al. Laboratory studies of the homogeneous nucleation of iodine oxides, *Atmos. Chem. Phys.*, 4, 19-34, 2004.

Jimenez et al. New Particle Formation from Photooxidation of Diiodomethane (CH<sub>2</sub>I<sub>2</sub>). Journal of Geophysical Research-Atm., 108, 4318, 2003.

McFiggans et al. Direct evidence for coastal iodine particles from Laminaria macroalgae - linkage to emissions of molecular iodine, Atmos. Chem. Phys., 4, 701-713, 2004.

Saiz-Lopez, A. and Plane, J. M. C.: Novel iodine chemistry in the marine boundary layer, Geophys. Res. Lett., 31, L04112, doi:04110.01029/02003GL019215, 2004.

A. Saiz-Lopez et al. Modelling molecular iodine emissions in a coastal marine environment: the link to new particle formation. Atmos. Chem. Phys., 6, 883-895, 2006.

R.S. Saunders and J.M.C. Plane. Formation Pathways and Composition of Iodine Oxide Ultrafine Particles. Environmental Chemistry 2005, 2, 299-303.

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 1481, 2006.

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