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Discussions

Interactive comment on “Modeling the possible role of iodine oxides in atmospheric new particle formation” *by* S. Pechtl et al.

S. Pechtl et al.

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Response to reviewer and editor comments:

We want to thank both reviewers and the editor for their helpful comments. We separately adress them in the following.

Response to Alfonso Saiz-Lopez:

Specific comments:

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- We did not include I_xO_y (x>1; y>2) in the original manuscript because firstly reactions for these molecules are still quite uncertain and secondly the lab and model study by Burkholder et al. (2004) which we used to set up the parameterization for OIO nucleation, relies on the assumption that OIO is the only nucleating and condensing species.
  However, since there is evidence for the existence of intermediate I_xO_y between OIO and particles, we did additional sensitivity studies including formation of I_2O_3 (via IO + OIO) and I_2O_4 (via OIO + OIO) in our mechanism, assuming that both contribute to particle formation and early particle growth (scenario 14). Rate constants for the formation of I_2O_3 and I_2O_4, as well as thermal decay of I_2O_4 are taken from Saunders and Plane (2005). We added a discussion of these sensitivity studies (with respect to significance for nucleation rates as well as for OIO mixing ratios to the revised manuscript (see new paragraph in section 4.4; new scenario 14 in Table 3).

- see previous point

- According to IUPAC recommendations IO + IO gives mainly OIO + I (about 40%) and I_2O_2 (about 60%), and possible minor contributions of 2I + O_2 ($<$ 20 %). However, as explained in the mansucript (p.9912, lines 14-21), we did not include I_2O_2 into our chemical mechanism since it breaks down in less than a second to form OIO + I as the main product (J. Plane, pers. comm., see also Saunders and Plane, 2005). Hence the branching ratio of IO + IO would be OIO + I ($>$ 80 %) and 2I + O_2 ($<$ 20 %).

- (1) We do not constrain our model simulations, i.e., we do not prescribe mixing ratios. The only thing we prescribe are surface fluxes of organioiodines and I_2. Mixing ratios of these as well as any other chemical compound (e.g., IO, OIO) are caluclated by the model. (2) OIO has not beed detected above the detection limit during daytime in Mace Head, Cape Grim, and Brittany, but it has been detected in mixing ratios up to 30-40 ppt at Appledore Island (which we point out more clearly in the revised manuscript, and which will be submitted by Stutz et al. soon). (3) Sensitivity studies including I_2O_3 and I_2O_4 (see above) show that OIO mixing ratios strongly decrease compared to a model simulation which excludes those compounds (which does not fit to the observations at Appledore Island). The nucleation rates slightly increase as I_2O_3 has no other known sinks than nucleation. These findings are discussed in the revised mansucript (section 4.4).

- see previous point
- As pointed out above, I_2 mixing ratios are not prescibed. Instead, we precribe a surface flux of I_2: This flux leads at night within some minutes to mixing I_2 ratios of up to 80-100 ppt (see our Figure 10) at 15 m altitude, which is in agreement with observations. The same flux leads during daytime to very low I_2 mixing ratios of less than 1 ppt which seems to be inconsistent with measurements, but which is perfectly consistent with the short photolytic lifetime of I_2. The presence of molecular iodine during daytime despite its high photolysis frequency remains in fact an interesting issue for future research. In any case, the low mixing ratios of I_2 during daytime in our model simulations do not at all imply a small effect on formation rates of iodine oxides (see our Figure 5).
- In sensitivity studies including the formation of I_2O_3 (via IO + OIO) and I_2O_4 (via OIO + OIO) in our mechanism (see above), we find significant nucleation rates if we assume that OIO as well as I_2O_3 and I_2O_4 contribute to particle formation and early particle growth. Our conclusions regarding OIO nucleation do not substantially change if we include I_2O_3 and I_2O_4 as intermediates between OIO and particles.

Minor points:

All minor comments were addressed and respective changes were included into the manuscript.

- Typos were corrected and words/phrases were changed as suggested.
- p.9919 l.4: Numbers for maximum measured mixing ratios for the different alkyl iodides have been added.
- p.9920 l.2: The change of maximum OIO mixing ratio from 3 to 10 ppt due to data re-analyis is included and explained in the revised manuscript.
- p.9922 l.12: 'some minutes' have been specified to '5 minutes'.
- p.9923 l.17: 'some distance' has been quantified to 'several hundred meters'.

Response to referee 2:

1. thank you
2. The parameterization of apparent nucleation rates does implicitely include coagulation of clusters with background particles, which is an important sink for freshly formed particles (see our model description). As the microphysics module of MISTRA does not include coagulation, we cannot (and do not) address the further growth of particles from the lowest particle size bin (d=10 nm) to larger

sizes. We explicitly mention in the paper that the growth of particles to CCN sizes is beyond the scope of out paper (see our conclusions).

3. As our parameterization for homogeneous OIO nucleation rate is based on laboratory experiments, the shape of the particles is implicitly accounted for in our parameterization. To estimate the effect of the fractal structure of the cluster-sized particles on their further growth is beyond the scope of our paper. It is certainly an interesting point which has to be addressed in future studies.

4. We do not prescribe the source rate of condensable vapor (which is OIO in our case). We only prescribe surface fluxes of precursors (organoiodides and I_2, see our Table 4), mixing ratios of these species as well as resulting chemical products (IO, OIO, etc.) are calculated by the model. Therefore, vertical gradients of species are also not prescibed but are a consequence of the surface fluxes and the sum of processes included in the model (chemistry, vertical mixing, etc.).

5. The nucleation rates in our simulations are $< 3 \cdot 10^3$ nuclei cm^{-3}s^{-1} (marine case) and $< 10^5$ nuclei cm^{-3}s^{-1} (continental case). Model studies interpreting particle measurements at Mace Head suggest nucleation rates of 10^7 nuclei cm^{-3}s^{-1} (O'Dowd et al., 1999), or $3 \cdot 10^5 - 3 \cdot 10^6$ nuclei cm^{-3}s^{-1} (Pirjola et al., 2002). According to our studies, such large nucleation rates are very unlikely to be due to homogeneous OIO nucleation alone (as is already evident from our Figure 2), but could be due to ternary nucleation for sufficiently high H_2SO_4 and NH_3 concentrations (as was already suggested by O'Dowd et al. and Pirjola et al.). OIO could then be responsible for the early growth of the clusters. However, for clean environments with small ternary nucleation rates, OIO nucleation could be important although nucleation rates should rarely exceed 10^3 nuclei cm^{-3}s^{-1}

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(see our Figure 2). We added a sentence regarding the higher nucleation rates at Mace Head to section 4.1: ”*However, our study indicates that particle bursts observed at Mace Head, where nucleation rates of about* 10^5*-*10^7 *nuclei cm*$^{-3}$*s*$^{-1}$ *seem to be required to explain the observations (O'Dowd et al., 1999; Pirjola et al., 2002), cannot entirely be due to homogeneous OIO nucleation.*”

Response to Rolf Sander:

General comments:

- p.9912: We added a short explanation for the term 'total particle radius' to the text.
- p.9913: The nucleation rate describes the production of clusters. We corrected a typo in the text which caused this confusion.
- p.9929: We agree that HIO_3 is not unimportant for atmospheric chemistry. We deleted this statement from the text.

Technical comments:

We addressed all technical comments and included the respective corrections in the revised manuscript.

- Typos were corrected.

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- p.9913: We exchanged the symbol for the mixing ratio.

- p.9913: We keep using J as symbol for the nucleation rate as the same symbol was used, e.g., by Pruppacher and Klett (1997), Napari et al. (2002), and Kerminen and Kulmala (2002).

- p.9914 l.1: We replaced 'negligance' by 'omission'.

- Errors in the supplement were corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9907, 2005.

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