Atmos. Chem. Phys. Discuss., 3, S2005–S2007, 2003
www.atmos-chem-phys.org/acpd/3/S2005/

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 #2

Received and published: 26 November 2003

Review of MS-NR: 2003-090: Atmos. Chem. Phys. Discuss., 3, 4943-4988, 2003. Laboratory studies of the homogeneous nucleation of iodine oxides, by J.B. Burkholder, J. Curtius, A.R. Ravishankara, and E.R. Lovejoy.

General Comments

This manuscript presents a laboratory study on the particle formation induced by the UV photolysis of CF3I or CH2I2 in the presence of O3. Hereby I atoms are produced that react with O3, and produce IO, which upon self reaction lead to oxides of iodine, such as OIO, IOI, I2O2, etc,. New particles with diameter $>$ 3 nm were detected using an ultrafine condensation particle counter. The results were interpreted using a coupled gas phase chemical reaction scheme and a kinetic homogeneous nucleation model. The authors assume that solely OIO is responsible for the observed nucleation,

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

and that (OIO)-clusters grow due to coagulation/evaporation processes. Particle production curves were simulated for different experimental conditions, such as initial concentration of the iodine precursors and ozone, photolysis rate and duration, and temperature. New kinetic information was deduced for the reaction IO + O3 –> OIO +O2, representing an additional source for OIO. The modeled profiles show good agreement with the experimental data, and model parameters, such as the bond enthalpy of the OIO dimer, were optimized. The model was applied to recent field measurements in the marine boundary layer, where iodine oxides (IO ands OIO) were reported. However the model predicted insignificant aerosol production. Only when inhomogeneous (elevated) sources of iodine oxides were considered (hot spots), then the model could account for the observed large aerosol production.

1This study seems to have been performed with extreme care. This work represents a useful model describing the homogeneous nucleation of iodine oxides species under atmospheric conditions. The combination of a chemical mechanism with a model representing the nucleation rate is currently of great interest in the field of atmospheric chemistry. I strongly recommend this paper to be published in ACP after taking into account the comments addresses below.

Specific comments 1. 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.

2. It is interesting to note that the derived rate constant for the reaction IO + O3 –> OIO + O2 (5 x 10-15 cm3 molecule-1 s-1) is approximately 3000 times faster than the analogous reactions ClO and BrO with O3. 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.

ACPD

3, S2005–S2007, 2003

3. 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?

4. 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.

Technical corrections

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

Page 4951, line 2: O2 and N2. correct to O2 and N2 (subscripts)

Page 4953, line 2: correct oversimplified (one word).

Page 4954: check careful subscripts and symbols of equations 10 and 11

Page 4955: line 8: correct particle 1 into particle i

Page 4956: Equation 16: correct Kp (not kp)

Page 4964: line 16: Jimenez et al, 2002: Error year, should be: 2003

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