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

R. Saunders
r.saunders@uea.ac.uk

Received and published: 28 November 2003

The authors present some very interesting results from the generation and detection of ultra-fine particles from the photo-oxidation reactions of iodine containing precursor species with ozone. Building on previous studies of similar chemical systems, this work addresses for the first time the dependence of particle production (particle number and nucleation induction time) on the ozone concentration and reaction temperature - parameters of direct relevance to the environment of the lower troposphere where rapid coastal particle production has been observed.

The formation of the pivotal iodine dioxide (OIO) species has previously been thought to result primarily from the IO self reaction. The assertion that an additional route (IO + O₃) could be involved which would explain the ozone dependence of the particle nucleation mechanism is certainly deserving of attention in future laboratory studies. As
stated in the paper, accurate determination of the rate coefficient for this reaction would be important in order to estimate the relative contribution of this channel to formation of OIO and subsequent aerosol production.

Observations of background particle production prior to lamp photolysis of CH$_3$I and CH$_2$I$_2$ were assigned to the presence of I$_2$ impurities in the reactant gases. Previous studies and unpublished data from our laboratory show that the I$_2$ + O$_3$ reaction, under both dark and irradiated conditions, does indeed rapidly produce large numbers of particles (>$10^5$ cm$^{-3}$s$^{-1}$, d > 3 nm). Our studies have shown that particle nucleation in the I$_2$ / O$_3$ system is extremely light sensitive with room light levels alone causing significant variation in particle concentration, total number and size distribution. This observation along with recent detection of molecular iodine in the MBL at Mace Head on the west coast of Ireland (Saiz-Lopez and Plane, University of East Anglia, personal communication) suggests that photolysis of I$_2$ is also likely to play an important role in the nucleation of iodine oxide aerosol in addition to the iodocarbon species which to date have received much closer attention. Appreciable levels of I$_2$ produced biogenically or otherwise and transported into the MBL, would necessarily lead to rapid photolysis across the visible wavelength range, providing an additional input of reactive iodine.

The paper concludes from model calculations that for published concentrations of IO and OIO detected in the MBL, homogeneous nucleation of OIO could not account for the observed particle bursts observed at Mace Head. Rather, inhomogeneous hot-spots of elevated iodine emissions would be necessary. Obviously, measurements of these species at more and varied locations (remote MBL) along with detection of additional particle formation events would be crucial for establishing the validity of this conclusion. However, the potential for I$_2$ photolysis as an additional source of reactive iodine atoms in coastal locations would certainly lend weight to the scenario suggested in this paper.