

Interactive comment on “Toward a general parameterization of N₂O₅ reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride” by T. H. Bertram and J. A. Thornton

Anonymous Referee #2

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The article describes a laboratory study of the heterogeneous kinetics of N₂O₅. N₂O₅ is a night-time reservoir for NO_x and heterogeneous uptake has been shown in modelling studies to have an impact on ozone levels in the troposphere. The study provides additional data on the uptake onto sulfate and nitrate aerosols, and shows an important new facet of reaction: heterogeneous uptake onto relatively unreactive nitrate aerosol is shown to be significantly enhanced by trace amounts of chloride ion. The experimental results will be of interest to the researchers in the field of atmospheric chemistry and air quality modelling.

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An aerosol flow tube coupled to a chemical ionisation mass spectrometer was used to measure the kinetics and differential mobility analysis provided the particle size distributions. The setup was used in two modes: first uses a conventional determination of kinetics, measuring the decay in concentration with increasing contact time; the second a single-point determination of uptake, from which uptake coefficients are determined. CIMS detection of N₂O₅, HNO₃ and ClNO₂ was achieved.

The experimental methods are adequately described and clearly presented, being partly an extension of the authors' previous work. As such, there are few issues arising from the experimental design and execution. I would ask if the size distribution consists entirely of particles with $D \leq 800$ nm, so that the authors are confident that the measured size distribution is an accurate reflection of the PSD within the AFT?

The study presents three sets of data regarding the reactivity of N₂O₅ on laboratory generated aerosol, each of high quality. The first set of data describes uptake to ammonium bisulfate aerosol as a function of RH; a second set describes uptake to aerosol as a function of [NO₃⁻] and a third as a function of [Cl⁻]. The increase in reactivity of aerosols containing chloride is striking and rationalized on the basis of competition between the two Cl⁻ and NO₃⁻ nucleophiles for the H₂O.NO₂⁺ intermediate.

The kinetic dataset is then analysed. The mechanism for uptake proposed is similar to that already described by Wahner et al. and by Thornton et al. The data, together with the AIM of Clegg and co-workers, shows that [H₂O] is able to account for the reactivity of aerosol below 50% RH. Here, it might help to state how the molarity was calculated from the molality. Above this RH, the reactivity is constant, a measurement that lays to rest a long-standing issue arising from the measurements of Kane et al. As the authors note, parameterisations such as that presented in the work of Evans and Jacob need to be reviewed. The data are then used to constrain relative rate coefficients for reaction of the intermediate with H₂O/NO₃⁻ and Cl⁻/NO₃⁻. Is it possible to compare the ratio k_3/k_{2b} with previous determinations?

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The layout of the figures is generally good, but the grey symbols are difficult to pick out and the figures should be re-done to improve this. Overall I felt this was a very high quality study.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15181, 2009.

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