UNCOVERING A NEW CLASS OF REACTIONS IN THE ATMOSPHERE: SN2-TYPE SUBSTITUTION REACTIONS OF NITROGEN OXIDES AND SEAWATER

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Recent studies indicate that nitrogen oxide species in the atmosphere, including N_2O_5 and $ONONO_2$, undergo a new class of S_N2-type substitution reactions when in contact with seawater and sea spray aerosols.[a,b,c] The reactions of atmospheric nitrogen oxides with seawater play many integral roles in regulating levels of O_3, OH, NO_x, and CH_4, thus directly affecting radiative forcing and global climate. However, the effect of the number of water molecules on the mechanisms for this new group of S_N2-type reactions of nitrogen oxides and the competition of these processes with hydrolysis have not yet been characterized. Here we present the mechanisms and timescales of S_N2-type substitution and hydrolysis reactions of N_2O_5 with seawater in the cluster series $N_2O_5 + Cl^- + nH_2O$ (n=1-5). Previous studies of the cluster $N_2O_5 + Cl^- + H_2O$ provide deep insights into the local behavior of these systems.[c] The presented studies of this cluster with water molecules added one-by-one allows for a detailed understanding of the effects of a solvation shell as it is built, providing a connection between the behavior of these small clusters and atmospherically relevant systems. Vibrational spectroscopic signatures of key intermediates are discussed and compared to recent and ongoing experiments.[a]

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[b] R. B. Gerber, L. McCaslin, N. V. Karimova, *Faraday Discuss.* (Accepted).

[c] L. M. McCaslin, M. A. Johnson, R. B. Gerber, (In review)