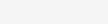
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# The potential impact of $CIO_x$ radical complexes on polar stratospheric ozone loss processes

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Abstract. The importance of radical-molecule complexes for atmospheric chemistry has been discussed in recent years. In particular, the existence of a CIO·O<sub>2</sub> and CIO<sub>x</sub> water radical complexes like CIO·H<sub>2</sub>O, OCIO·H<sub>2</sub>O,  $OCIO \cdot (H_2O)_2$ , and  $CIOO \cdot H_2O$  could play a role in enhancing the CIO dimer (Cl<sub>2</sub>O<sub>2</sub>) formation and therefore may constitute an important intermediate in polar stratospheric ozone loss cycles. Model simulations performed with the Chemical Lagrangian Model of the Stratosphere (CLaMS) will be presented to study the role of radical complexes on polar stratospheric ozone loss processes. The model simulations are performed for the Arctic winter 2002/2003 at a level of 500 K potential temperature and the results are compared to observed ozone loss rates determined by the Match technique. Moreover, recently reported values for the equilibrium constant of the CIO dimer formation are used to restrict the number of possible model results caused by large uncertainties about radical complex chemistry. Our model simulations show that the potential impact of  $CIO \cdot O_2$ on polar ozone loss processes is small (dO<sub>3</sub>/dt≪0.5 ppb/sunlight h) provided that the CIO·O2 complex is only weakly stable. Assuming that the binding energies of the  $\text{CIO}_{\mathbf{x}}$  water complexes are much higher than theoretically predicted an enhancement of the ozone loss rate by up to  $\approx$ 0.5 ppb/sunlight h is simulated. Because it is unlikely that the ClO<sub>x</sub> water complexes are much more stable than predicted we conclude that these complexes have no impact on polar stratospheric ozone loss processes. Although large uncertainties about radical complex chemistry exist, our findings show that the potential impact of  $\text{CIO}_{\mathbf{x}}$  radical molecule complexes on polar stratospheric ozone loss processes is very small considering pure gas-phase chemistry. However the existence of CIO<sub>x</sub> radical-molecule complexes could possibly explain discrepancies for the equilibrium constant of the CIO dimer formation found between recent laboratory and stratospheric measurements.

■ Final Revised Paper (PDF, 3609 KB) ■ Discussion Paper (ACPD)

Citation: Vogel, B., Feng, W., Streibel, M., and Müller, R.: The potential impact of CIO<sub>x</sub> radical complexes on polar stratospheric ozone loss processes, Atmos. Chem. Phys., 6, 3099-3114,

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