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A re-evaluation of the ClO/Cl₂O₂ equilibrium constant based on stratospheric in-situ observations

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Abstract. In-situ measurements of ClO and its dimer carried out during the SOLVE II/VINTERSOL-EUPLEX and ENVISAT Validation campaigns in the Arctic winter 2003 suggest that the thermal equilibrium between the dimer formation and dissociation is shifted significantly towards the monomer compared to the current JPL 2002 recommendation. Detailed analysis of observations made in thermal equilibrium allowed to re-evaluate the magnitude and temperature dependence of the equilibrium constant. A fit of the JPL format for equilibrium constants yields $K_{EQ}=3.61 \times 10^{-27} \exp(8167/T)$, but to reconcile the observations made at low temperatures with the existing laboratory studies at room temperature, a modified equation, $K_{EQ}=5.47 \times 10^{-25} (T/300)^{-2.29} \exp(6969/T)$, is required. This format can be rationalised by a strong temperature dependence of the reaction enthalpy possibly induced by Cl₂O₂ isomerism effects. At stratospheric temperatures, both equations are practically equivalent. Using the equilibrium constant reported here rather than the JPL 2002 recommendation in atmospheric models does not have a large impact on simulated ozone loss. Solely at large zenith angles after sunrise, a small decrease of the ozone loss rate due to the ClO dimer cycle and an increase due to the ClO-BrO cycle (attributed to the enhanced equilibrium ClO concentrations) is observed, the net effect being a slightly stronger ozone loss rate.

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