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'ClO Match' An examination of chlorine kinetics using the Self-Match flight during EUPLEX II 2004

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The kinetics of chlorine dimer reaction under highly activated polar stratospheric spring conditions is critical to understanding the dramatic ozone losses that lead to the formation of the stratospheric 'ozone hole'. Previous studies of nighttime stratospheric observations have found levels of ClO that can only be explained with a lower equilibrium constant than that recommended from laboratory studies. In this study we examine in-situ ClO measurements made on the 30th January 2004 in the Arctic during the SOLVE II/VINTERSOL-EUPLEX campaign using a trajectory Match technique combined with a non-linear optimal estimator. Over the 3 hour flight 72 Match pairs were identified with temperatures ranging between 200-206 K and SZAs between 840 and 950. Along each trajectory defined for a Match pair the total active chlorine ClOx is assumed to be constant. The kinetic parameters controlling the ClO concentration - Keq, kf and J as well as ClOx for each Match pair were then retrieved. We found that no combination of Keq, kf and J was consistent with the JPL 2006 recommendations for Keq and kf. This result challenges the chlorine dimer chemistry as we know it. With our fundamental understanding of chlorine chemistry being challenged our ability to predict the future recovery of the polar springtime ozone hole is therefore grossly impeded.