



Laboratory Studies on the IO self reaction and the fate of its products: evidence for OIO nucleation.

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The atmospherically relevant chemistry generated by photolysis of I₂/O₃ mixtures has been studied by using a laboratory flash photolysis set up combining molecular optical absorption spectroscopy and atomic resonance absorption spectroscopy. The temporal behaviours of I, I₂, IO(X²Π_{3/2}, v''=0,1,2) and OIO have been analysed by conventional kinetic analysis (steady state analysis, pseudo-first and second order fitting, cumulative integration) and by complex kinetic modelling to investigate the IO self reaction and to propose a plausible mechanism describing the complex behaviour observed for IO and OIO, consistent with theoretical predictions and previous laboratory and field observations. For the overall reaction rate of the IO self reaction, a pressure independent value of $k(\text{IO}+\text{IO}) = (7.5^{+1.3}_{-0.6}) \cdot 10^{-11} \text{ molec}^{-1} \text{ s}^{-1} \text{ cm}^3$ at 298 K has been determined. The branching ratios of two channels of this reaction have been found to be pressure dependent between 10 and 400 hPa, having at 400 hPa the following values: $k_{\text{I}+\text{OIO}}/k = 0.45 \pm 0.10$ (decreases with increasing P) and $k_{\text{IOIO}}/k = 0.44 \pm 0.13$ (increases with increasing P). The other two branching ratios do not show a systematic dependence on pressure, with averaged values of $k_{\text{I}_2+\text{O}_2}/k = 0.09 \pm 0.06$ and $k_{\text{I}_2+\text{O}_2}/k < 0.05 \pm 0.03$. The mechanistic information collected indicates that IOIO is thermally stable and can participate in other processes. The OIO addition steps mechanism proposed in previous studies to explain new particle formation in the marine boundary layer has been found to be consistent with the temporal behaviours of OIO recorded in this study. A common bimolecular rate coefficient for the first addition steps $(\text{OIO})_n + \text{OIO} \rightarrow (\text{OIO})_{n+1}$ ($n=1,2,3,4$) has been determined at 298 K in the range of pressures indicated above, with value of $(1.2 \pm 0.3) \cdot 10^{-11} \text{ molec}^{-1} \text{ s}^{-1} \text{ cm}^3$ at 400

hPa. However, evaporation reactions $(\text{OIO})_{n+1} \rightarrow (\text{OIO})_n + \text{OIO}$ are not required to explain the observed data, which in terms of the theory of homogeneous nucleation implies a small critical cluster size of the order of magnitude of the diameter of the OIO monomers. Evidence for the participation of IO in the polymerization mechanism has been found. A global rate coefficient for IO attachment to nascent polymers has been determined to be $(5 \pm 2) \cdot 10^{-12} \text{ molec}^{-1} \text{ s}^{-1} \text{ cm}^3$ at 400 hPa and 298 K. These results suggest that the ultra-fine particles observed in the MBL could be formed as a result of nucleation induced by polymeric iodine oxides.