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Reactions rates and mechanisms of product formation in the gas phase I_2/O_3 photochemistry

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To evaluate the relevance of atmospheric iodine chemistry in ozone depleting cycles and in aerosol formation it is necessary to gain a previous understanding of the kinetics and mechanisms involved. The chemistry generated by flash photolysis of I_2 in the presence of O_3 has been studied by using multichannel time-resolved absorption spectroscopy in order to compile such information. This chemical system was previously studied in order to determine absolute absorption cross sections of IO, IO*, OIO and higher iodine oxides. Therefore, time dependent concentration curves of relevant gas phase species are available.

These data have been analysed to derive a mechanism which explains the homogeneous aerosol nucleation observed. The mathematical formulation of the proposed mechanism as a set of differential rate equations enabled to derive by numerical integration and optimisation methods the rate constants of the reactions considered. Results obtained include the following rate constants: k(I_2+O), k(I+O_3), k(I+O_2), k(O+IO), k(I+IO), k(IO+IO), branching ratios of the IO self reaction, k(IO+OIO) and k(OIO+O_3). The results obtained for the IO source reactions and the IO self reaction are in agreement with the IUPAC recommended values.

A main result of these studies is the determination of rate constants of reactions involving OIO, which plays a key role in the iodate enrichment of aerosol and the ozone destroying power of iodine species. In this work the reactions IO+OIO+M$\rightarrow$$I_2O_3$+M (k(400mbar)=(1.5$\pm$0.5)$10^{-10}$cm^{3}molec^{-1}s^{-1}) and OIO+O_3 $\rightarrow$$IO_3$+$O_2$ (k=(2.0$\pm$0.5)10^{-13}cm^{3}molec^{-1}s^{-1}) are propossed as plausible paths to higher iodine oxides and aerosol formation.