CHEMILUMINESCENT REACTIONS OF OXYGEN-IODINE SYSTEMS

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The reactions of O atoms with iodine containing molecules and the kinetics of the IO radical are of relevance to the removal of tropospheric ozone. These reactions, along with energy transfer processes involving electronically excited states of O$_2$, are also relevant to a new class of oxygen-iodine lasers that employ discharge excitation.

Pulsed photolysis of CF$_3$I/N$_2$O/N$_2$ mixtures and direct laser excitation of O$_2$ in the presence of I$_2$ have been used to investigate the iodine oxygen kinetics. The primary findings of this study are that O$_2$($a'\Delta$) is generated by the reactions IO+O $\rightarrow$ I+O$_2$(a) and I+I+O$_2$ $\rightarrow$ I$_2$+O$_2$(a). O$_2$(b) and O$_2$(a) are removed by I$_2$ with rate constants of 5.8x10$^{-11}$ and $< 5x10^{-16}$ cm$^3$ s$^{-1}$, respectively. The branching fraction for the physical quenching channel O$_2$(b)+I$_2$ $\rightarrow$ O$_2$(a)+I$_2$ was found to be 0.4. Re-measurement of the rate constant for O$_2$(a)+O$_2$(X) $\rightarrow$ 2O$_2$(X) yields a value of 9.3x10$^{-19}$ cm$^3$ s$^{-1}$. This result is somewhat lower than previous estimates.