Kinetics of the Self-Reaction of Hydroxyl Radicals

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Hydroxyl radical plays a central role both in atmospheric and in combustion chemistry. Self reaction of hydroxyl radical is very important in the laboratory kinetic studies as well as for fundamental chemical kinetics:

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\begin{align*}
\text{OH} + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O} \quad (1a) \\
& \rightarrow \text{H}_2\text{O}_2 \quad (1b)
\end{align*}
\]

Channel 1b is pressure dependent, while channel 1a is assumed to be pressure independent. Despite the large number of experimental and theoretical studies of reaction 1 there is still a significant uncertainty in the rate constant of the disproportionation channel 1a. The IUPAC recommended value of $k_{1a} = 1.45 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K\textsuperscript{1} is in significant discrepancy with the most recent measurement\textsuperscript{2} ($2.7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$).

In this work, we determined the rate constant of channel 1a by measuring the ozone yield in the photolysis of the reactive mixture N$_2$O/H$_2$O/O$_2$/He at 193.3 nm. Attempts to measure the rate constant of reaction 1a at low pressures (0.01 bar) were unsuccessful due to the non-stationary wall activity towards the radical decay, which was unambiguously demonstrated using the two-pulse photolysis technique. High pressure of a bath gas (1 bar, He) allowed prevention of the losses of hydroxyl radical on the walls of the reactor and avoiding complications associated with heterogeneous processes. Oxygen atoms formed in channel 1a were converted to ozone in fast reaction 3:

\[\text{O} + \text{O}_2 \rightarrow \text{O}_3\]  

Transient absorption profiles of OH (308 nm) and O$_3$ (253 nm) were recorded at the same experimental conditions. The ozone build-up profiles were fitted using a small reaction mechanism with explicit temporal profiles of OH. Preliminary results are consistent with the low value of the rate constant of reaction 1a.

References