Temperature-dependent rate constants of regular and fully-deuterated methoxy radical reacting with O_2

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The methoxy radical is an intermediate in the atmospheric oxidation of methane, and as the simplest alkoxy species, its behavior is fundamental to understanding the degradation of alkoxy radicals. The temperature-dependent rate constants for methoxy radicals reacting with O_2 have been studied both experimentally and theoretically. However, all previous experiments were carried out at room temperature and above, which may fail to represent the situation in the atmosphere. Furthermore, the mechanism of this fundamental reaction remains uncertain: the fitted experimental Arrhenius equation suggests a small pre-exponential factor (10^{-14} $cm^3molecule^{-1}s^{-1}$), and previous theoretical studies suggest that tunneling effects play a significant role in this reaction. The rate constants of CD_3O (the fully deuterated isotopologue of CH_3O) with O_2 are expected to be much smaller due to zero-point energy effects and the reduced tunneling effect, which may provide insights into the mechanism of the reaction.

Using the FT-IR smog chamber technique, we measured the relative rate constants of CH_3O reacting with O_2 and NO_2 at 250-333 K, as well as the relative rate constants of CD_3O reacting with O_2 and NO_2 at 277-335 K. Applying the IUPAC recommended rate constants of CH_3O and NO_2, the absolute rate constants of CH_3O and CD_3O reacting with O_2 are fitted (see the attached plot) by the Arrhenius expression, giving $k_{CH_3O+O_2} = 1.89^{+0.89}_{-0.60} \times 10^{-14} \exp[-(751 \pm 107)/T]$ $cm^3molecule^{-1}s^{-1}$; $k_{CD_3O+O_2} = 2.58^{+1.57}_{-0.98} \times 10^{-15} \exp[-(667 \pm 145)/T]$ $cm^3molecule^{-1}s^{-1}$, respectively. Over the range 277-333 K, the kinetic isotope effect associated with deuterium substitution is about 5, and not sensitive to temperature.

References

(1) Orlando, J.J.; Tyndall, G.S.; Wallington, T.J. *Chem. Rev*. **2003**, 103, 4657-4689.

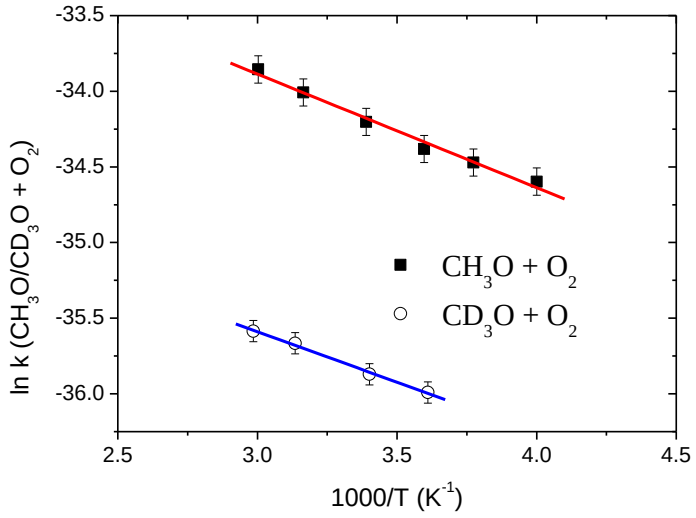

Figure 1: Fitted Arrhenius plot of the temperature-dependent rate constants of the two title reactions: $CH_3O + O_2$ and $CD_3O + O_2$.

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