

The Reaction of HO₂ with CH₃O₂: CH₃OOH formed from the singlet electronic state surface

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High-level coupled-cluster calculations in combination with E,J-resolved two-dimensional master equation simulations were used to study the HO₂ + CH₃O₂ reaction, which plays an important role in the oxidation of methane and hydrocarbons in the Earth's atmosphere and low-temperature combustion. The main reaction pathways taking place on the lowest-lying triplet and singlet potential energy surfaces (PES) were characterized. Interestingly, methyl hydroperoxide (CH₃OOH), the sole product, could be produced from both the triplet and singlet PESs, with a ratio of roughly 9:1. Formaldehyde is not made as a primary product, but can be formed via secondary chemistry. The formation of methyl tetraoxide (MTO) from the singlet PES is unimportant. The calculated reaction rate coefficients were found to be practically pressure-independent for $p \leq 760$ Torr and can be given by $k(T) = 2.75 \times 10^{-13} \times e^{+1.75 \text{ kcal mol}^{-1} / RT}$ (in cm³/s), an expression useful for kinetics modeling over the range T = 200–800 K. The rate constant has a slight negative Arrhenius energy dependence of about $-1.75 \text{ kcal mol}^{-1}$, falling about a factor of 30 from 200 K to 800 K.