HOOCH$_2$SCHO formation in the marine boundary layer: Rate coefficient measurement of the intramolecular Hydrogen-shift in the CH$_3$SCH$_2$OO radical

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Introduction

- DMS (CH$_3$SCH$_3$) is a major tropospheric source of sulfur and sulfate aerosol in the atmosphere.
- The kinetics and mechanism of DMS oxidation is, therefore, of critical importance to developing a comprehensive understanding of climate and climate change.

Simplified OH initiated DMS atmospheric oxidation mechanism:
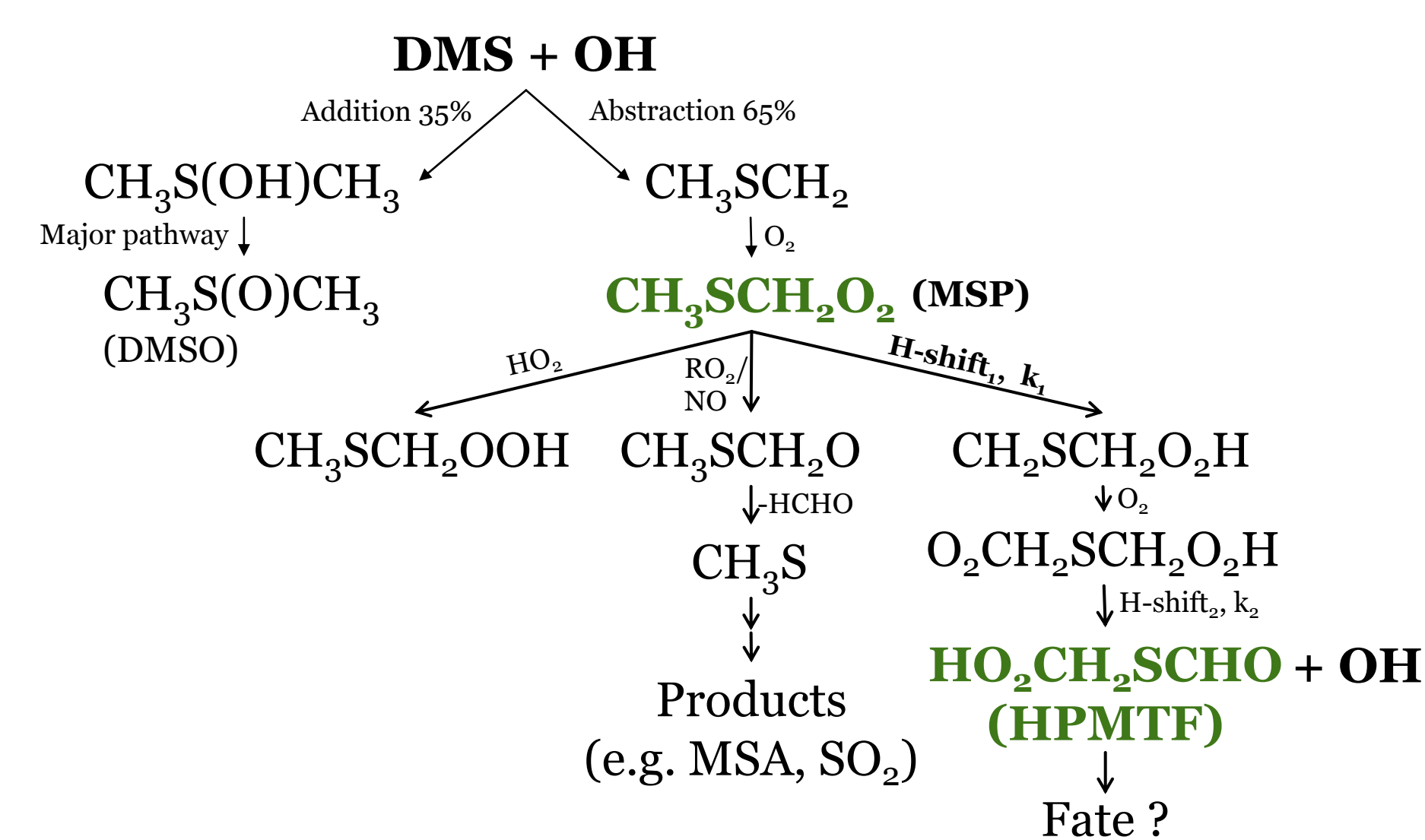
What is the fate of CH$_3$SCH$_2$O$_2$ (MSP)?

high-NO$_X$: CH$_3$SCH$_2$O$_2$ + NO reaction dominant

low-NO$_X$ (e.g. remote marine environment): H-shift reaction pathways possible

Previous studies:

- Wu et al. (2014): Theoretical study

    Proposed H-shift reactions, hydroperoxymethyl thioformate (HOOCH$_2$SCHO, HPMTF) formation

    k$_1$(298 K) = 2.1 s^{-1}

    k$_2$(298 K) >> k$_1$(298 K)

- Veres et al. (2019): ATOM field campaign

    I$^-$-ToF-CIMS detection

    Observed HPMTF in the marine boundary layer

    k$_1$(298 K) = 0.04 s^{-1} (calculated theoretically)

- Berndt et al. (2019): Experimental study

    free-jet flow system coupled to I$^-$-CI-API-TOF mass spectrometer

    k$_1$(298 K) = 0.23 s^{-1}

Motivations and objectives

The H-shift chemical pathway is currently not included in CCM atmospheric models

⟹ potential impact on sulfate aerosol formation and climate

The discrepancy between the calculated and measured rate coefficient calls for additional experimental measurement of k$_1$ and its temperature dependence

In this study:

- k$_1$ was measured over a range of temperature using a photolysis flow tube reactor coupled to a chemical ionization mass spectrometer

- k$_1$(T) was theoretically investigated with the M06-2X/aug-cc-pVTZ level of density functional theory and W1 energies

Experimental details

- Pulsed laser photolysis used to generate Cl radicals in presence of excess DMS in a slow-flow tube reactor
- Formation of HPMTF measured with a quadrupole or a high-resolution time-of-flight chemical ionization mass spectrometer (quad-CIMS or HR-ToF-CIMS)
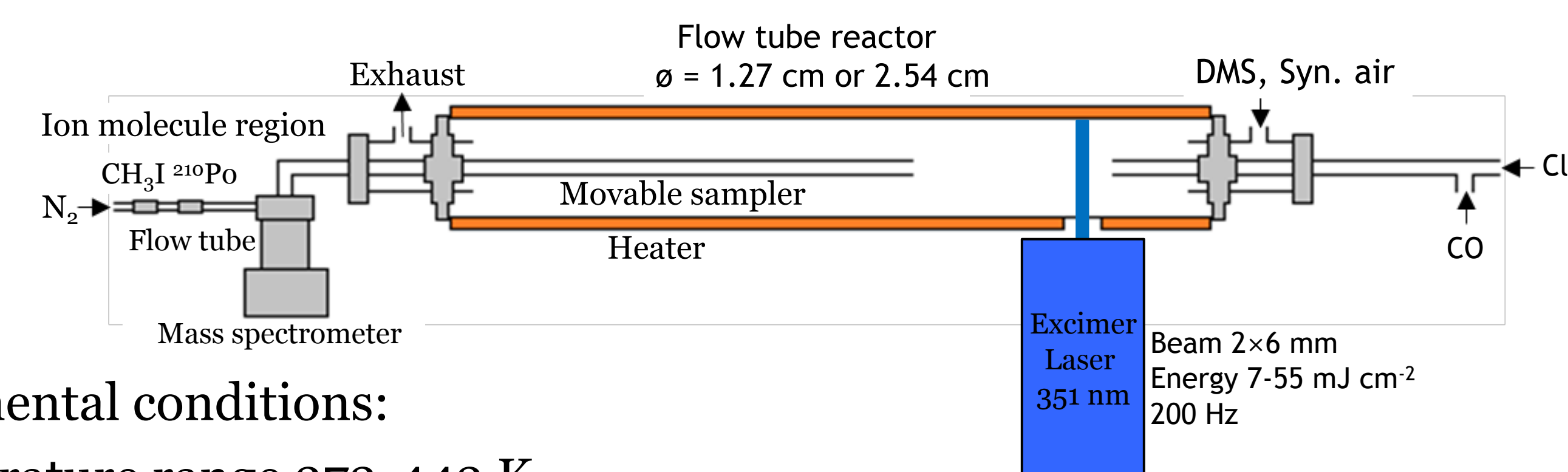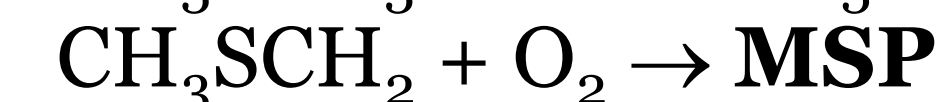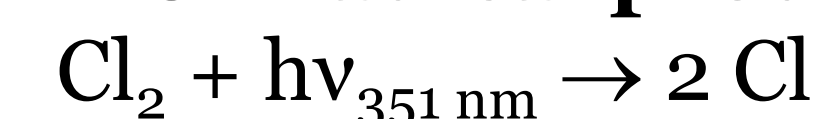

Experimental conditions:
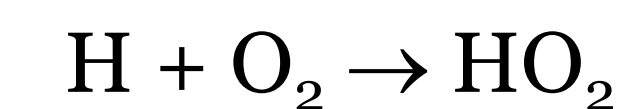
- Temperature range 373-443 K

- Pressure 620 Torr

- [DMS] = 4-12 × 10^{14} molecule cm^{-3}, [Cl$_2$] = 2-7 × 10^{11} molecule cm^{-3}, [Cl]$_0$ = 0.2-4 × 10^{10} molecule cm^{-3}, [O$_2$] = 4 × 10^{18} molecule cm^{-3}, [CO] = 2 × 10^{17} molecule cm^{-3}

MSP radical production:

Cl$_2$ + hv$_{351\,nm}$ → 2 Cl

CH$_3$SCH$_3$ + Cl → CH$_3$SCH$_2$

CH$_3$SCH$_2$ + O$_2$ → **MSP**

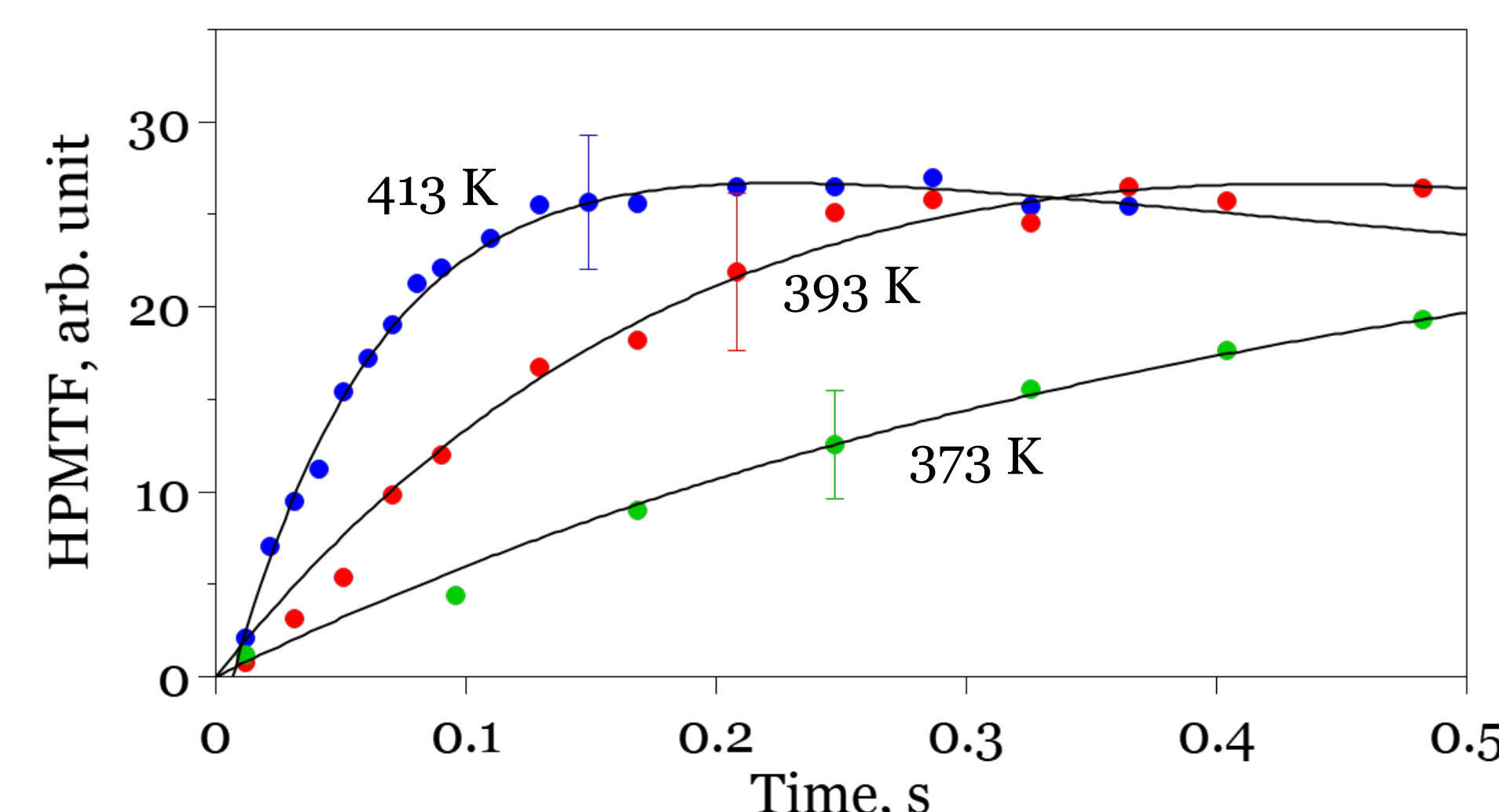CO added to the system as OH scavenger: OH + CO → CO$_2$ +H

H + O$_2$ → HO$_2$

Low radical concentrations:

MSP + MSP and MSP + HO$_2$ minimized (confirmed with box model calculations)

Results

Representative HPMTF formation profiles


Different conditions tested for each T:

- concentration of reactants
- laser energy
- flow tube reactor diameter
- thermal decomposition of HPMTF

⟹ No impact on obtained k$_i$(T)

Lines are fits of the HPMTF profiles for pseudo-first order formation and loss of HPMTF

$$S(t) = S_{asy} \times \frac{k_1(T)}{k_{loss} - k_1(T)} \times (\exp(-k_1(T)\,t) - \exp(-k_{loss}t))$$

where S$_{asy}$ is the asymptote value of HMPTF and k$_{loss}$ is the rate coefficient of HPTMF first-order loss

Arrhenius plot of k$_1$(T), CH$_3$SCH$_2$O$_2$ → CH$_2$SCH$_2$OOH
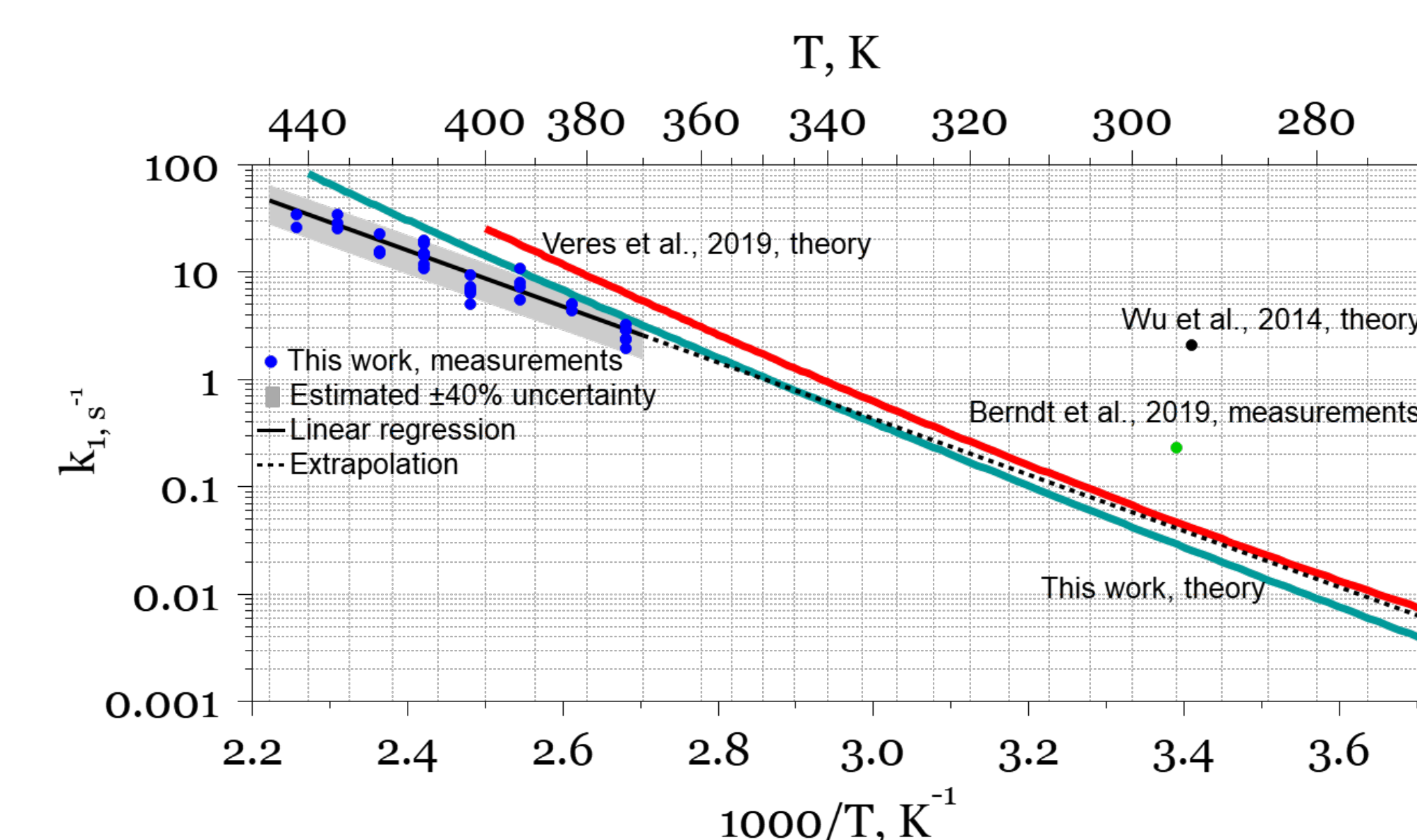
Experimental (373−443 K):

$k_1(T) = 2.98 \times 10^7 \exp(-\frac{6020}{T})$ s^{-1}

k$_1$(298 K) = 0.05 s^{-1} (extrapolated value)

Theory:

$k_1(T) = 8120 \times \frac{T}{298} \times 9.62 \exp(-\frac{3670}{T})$ s^{-1}

k$_1$(298 K) = 0.037 s^{-1}

⟹ agreement between our experiment extrapolation and theory

agreement with Veres et al. (theory)

significantly less than Wu et al. (theory) and Berndt et al. (experiments)

Atmospheric Implications

Marine boundary layer loss processes for CH$_3$SCH$_2$O$_2$ (MSP)

Reactant	k # cm^3 molecule^{-1} s^{-1}	Concentration * molecule cm^{-3}	First Order Rate Coefficient s^{-1}
NO	1 × 10^{-11}	10^8-10^9	0.001-0.01
HO$_2$	1 × 10^{-11}	10^8-10^9	0.001-0.01
RO$_2$	1 × 10^{-11}	10^8-10^9	0.001-0.01
OH	1 × 10^{-10}	10^6	0.0001
H-shift (k$_1$)	-	-	0.05

Estimated values for NO/HO$_2$/RO$_2$ reactions; OH rate coefficient from Fittschen (2019)
* Estimated values vary with season and location

- H-shift reaction is fast enough to impact the fate of CH$_3$SCH$_2$O$_2$ in remote environments, where NO$_X$ concentrations are low

- Fate of HPMTF needs to be determined to fully evaluate the impact of the H-shift reaction pathway on sulfate aerosol formation and climate

References:

Wu, R., S. Wang, and L. Wang (2015), New mechanism for the atmospheric oxidation of dimethyl sulfide. The importance of intramolecular hydrogen shift in a CH3SCH2OO radical, J. Phys. Chem. A, 119(1), 112-117, doi:10.1021/jp511616j

T. Berndt et al. (2019), Fast Peroxy Radical Isomerization and OH Recycling in the Reaction of OH Radicals with Dimethyl Sulfide, J. Phys. Chem. Lett., 10 (21), 6478-6483, doi:10.1021/acs.jpclett.9b02567

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C. Fittschen (2019), The reaction of peroxy radicals with OH radicals, Chem. Phys. Lett., 725, 102-108, doi:10.1016/j.cplett.2019.04.002