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# **EFFECT OF CHLORINE SUBSTITUTION ON SULFIDE REACTIVITY WITH OH RADICALS**

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## ABSTRACT

Predicting plume migration and evolution of hazardous chemical species (toxic industrial compounds, pesticides, etc.) is challenging because current models cannot reliably predict reaction rate constants of these (often) complex organic molecules with atmospheric oxidants. In order to have a comprehensive approach for modeling plume migration and evolution of hazardous chemicals, rate constants need to be accurately predicted so that chemical degradation can be included. Here we present experimental and theoretical results of the reaction between OH radicals and organic sulfides to examine the effect of chlorine substitution. The results show appreciable reduction in the overall rate constant of the chlorine-substituted organics relative to their unmodified analogs. Both the theoretical calculations and experimental results show that the abstraction channel is similar for both compounds investigated suggesting that the addition channel is slower for the chlorine substituted sulfide.

## INTRODUCTION

Reduced sulfur compounds have both natural and anthropogenic sources,<sup>1</sup> and many toxic chemicals contain sulfur and halogen atoms. In order to predict the atmospheric reactivity of sulfur and halogen containing compounds, we must understand their mechanisms of degradation. This is best accomplished by starting with small representative molecules and incrementally increasing complexity. Many researchers have measured the reactivity of dimethyl sulfide (DMS) with atmospheric oxidants (OH, NO<sub>3</sub>, and O<sub>3</sub>) the most important of which is the OH radical during daylight. A convenient approach to measuring the effect of halogen substitution on reactivity is to measure the reaction rates of the substituted and unsubstituted analogs relative to one another. Relative rate experiments circumvent many experimental problems such as the need to accurately measure OH concentration or reaction time. Moreover, since the rate constant for DMS reacting with OH is known, the experimentally derived relative rate of chloromethyl methyl sulfide (CMMS) can be placed on an absolute scale.

## METHODS

Gas-phase reactions of OH + DMS/CMMS were carried out in a Teflon bag (80 L) mounted in a light box. UVB irradiation of methyl nitrite was used to provide the source of OH radicals. The organics were sampled from the chamber through a Teflon transfer line at 25 cm<sup>3</sup>/min and 100 cm<sup>3</sup> was collected on a cryogenically cooled trap at -90°C. The sample was then warmed to 50°C and transferred for analysis by GC-FID.

Theoretical structures were optimized at CCSD level of theory with the 6-31++G\*\* basis set. Rate constants were then calculated using a semiclassical flux-flux autocorrelation function approach.<sup>2</sup>

## RESULTS

Figure 1 shows a relative rate plot of CMMS and DMS reacting with OH where CMMS reacts at 0.225 times the rate of DMS. The reaction of reduced sulfur compounds with OH can proceed through either H-abstraction or addition to the sulfur. The addition channel is dependent on the oxygen concentration, so the experiment was repeated with 2% O<sub>2</sub> to examine the relative dependence on this channel. The lower O<sub>2</sub> concentration favors the H-abstraction channel. As shown in Figure 1, the relative rate of CMMS vs. DMS with low O<sub>2</sub> increases to 1.07 suggesting that the abstraction channel for CMMS is approximately the same as that for DMS. These relative rates are placed on an absolute scale in Table 1 by using the recommended DMS rate constants for these two conditions.

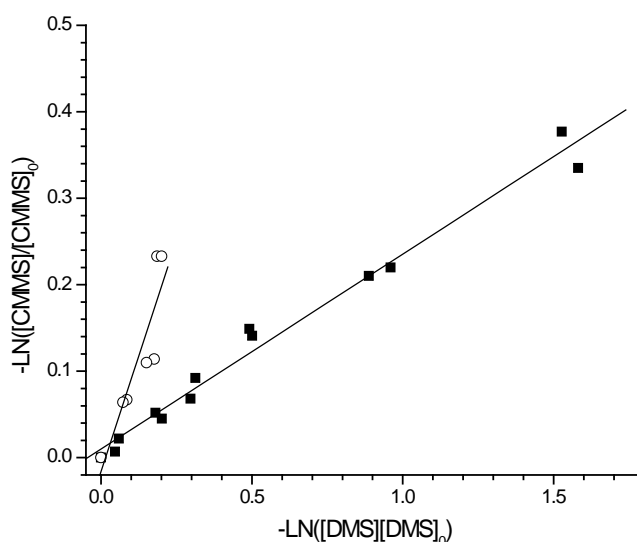


Figure 1. Relative rate plot of the reaction of CMMS and DMS with OH at 20.8% (■) and 2.0% (○) O<sub>2</sub>.

TABLE 1. OH rate constants determined in this work ( $\times 10^{12}$  cm<sup>3</sup>/molecule/sec.) at 20°C. Rate constants in parentheses are taken from the indicated reference. Abstraction rate constants for primary and secondary hydrogens are per hydrogen. ND = not determined.

Compound	Experiment		Theory				
	20.8% O <sub>2</sub>	2% O <sub>2</sub>	Abstraction			Addition	Total
			Primary	Secondary	Total		
DMS	(6.82) <sup>3</sup>	(4.97) <sup>3</sup>	0.65	N/A	3.9	2.1	6.0
CMMS	1.53	5.32	0.28	1.55	3.9	ND	3.9

These reactions were also examined theoretically with the results shown in Table 1. The theoretically determined rate constant for DMS at 20°C is in excellent agreement with the recommended value (6.0 and 6.82  $\times 10^{12}$  cm<sup>3</sup>/molecule/sec, respectively). The total theoretical

abstraction rate constants for DMS and CMMS are the same, corroborating the experimental results at low O<sub>2</sub> pressure. However, the primary hydrogens of CMMS react more slowly than those for DMS, and it is unclear what causes this. The secondary hydrogens in CMMS react much faster because the C-H bond is weakened by the electron-withdrawing chlorine atom. The calculated transition states for OH attack on DMS and CMMS are shown in Figure 2 where the chlorine atom in CMMS causes the OH radical to partially align with the C-Cl bond.

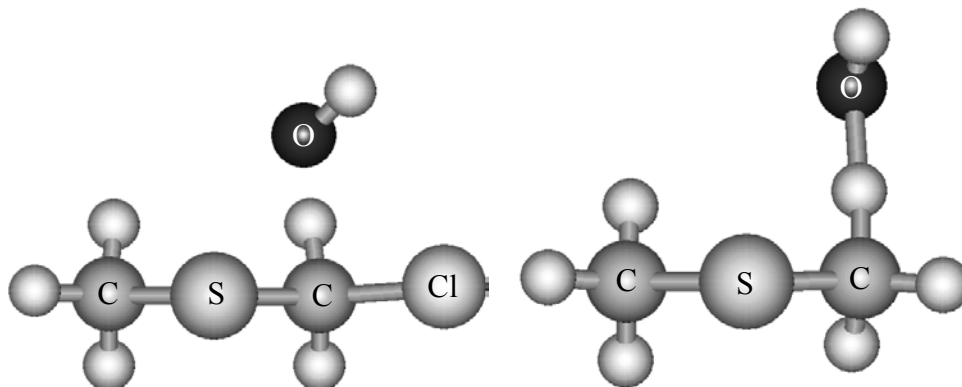


Figure 2. Calculated transition states for CMMS-OH (left) and DMS-OH (right). Unlabeled atoms are hydrogens.

The theoretical rate constant prediction is bracketed by the 20.8% and 2.0% O<sub>2</sub> measurements for CMMS. It is unclear what causes the increase in the rate constant at the lower O<sub>2</sub> concentration for CMMS. One possible explanation is the interference of NO<sub>x</sub> on the degradation of DMS or CMMS or both. NO<sub>x</sub> has been a problem with previous relative rate measurements of DMS, so these experiments need to be repeated with a NO<sub>x</sub> free OH source (H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub>). The rate constant for the CMMS + OH reaction has been determined at 2 Torr in argon ( $k = 2.5 \times 10^{-12}$  cm<sup>3</sup>/molecule/sec.) using an absolute technique.<sup>4</sup> Under these conditions, H-abstraction is expected to dominate the reaction and this compares well with the theoretical prediction and the relative measurement at low O<sub>2</sub> pressure (favoring H-abstraction).

## CONCLUSIONS

Chlorine substitution on a reduced sulfur compound reduces the overall rate of reaction with the OH radical. The abstraction channel is shown to be the same for DMS and CMMS, so the addition channel may be different for DMS and CMMS. Additional work needs to be done to quantify the contribution of the OH addition channel with CMMS in order to determine what effect the chlorine substitution has on it.

## REFERENCES

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3. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J. *Atmospheric Chemistry and Physics* **2004**, *4*, 1461.
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## Overview

Predicting plume migration and evolution of hazardous chemical species (toxic industrial compounds, pesticides, etc.) is challenging because current models cannot reliably predict reaction rate constants of these (often) complex organic molecules with atmospheric oxidants. In order to have a comprehensive approach for modeling plume migration and evolution of hazardous chemicals, rate constants need to be accurately predicted so that chemical degradation can be included. Here we present experimental and theoretical results of the reaction between OH radicals and organic sulfides to examine the effect of chlorine substitution. The results show appreciable reduction in the overall rate constant of chloromethyl methyl sulfide (CMMS) relative to dimethyl sulfide (DMS). Both the theoretical calculations and experimental results show that the abstraction channel is similar for both compounds investigated suggesting that the chlorine substituted sulfide has a slower addition channel.

## Methods

### Experimental:

• Rate law:  $\frac{d[DMS]}{dt} = -k_{DMS}[OH][DMS]$  [OH] difficult to measure

• Solution:  $-\ln\left(\frac{[DMS]}{[DMS]_0}\right) = k_{DMS}[OH]t$

• Relative:  $\frac{-\ln\left(\frac{[CMMS]}{[CMMS]_0}\right)}{-\ln\left(\frac{[DMS]}{[DMS]_0}\right)} = \frac{k_{CMMS}}{k_{DMS}}$  [OH] \*t cancels out!

• OH source: photolysis of methyl nitrite

• Detection: cryotrap, GC-FID

### Computational

• Structures optimized at CCSD/6-31++G\*\*

• Activation energy

• Single point energy: QCISD(T)/6-311G\*\* (QCI)

• Single point energy: MP2/6-311G\*\* (SML)

• Single point energy: MP2/6-311+G(3df,2p) (LRG)

• Zero Point Energy from a vibrational frequency analysis: MP2/6-31++G\*\* (ZPE)

• Extrapolated energy = E(QCI) + E(LRG) - E(SML) + ZPE

• Characterize the TS

• Use a three-point fit methodology – fit a harmonic potential to three CCSD single point energies (one at the TS and one on either “side” of the TS)

• Minimum Energy Path

• Use a reparameterized Hamiltonian (a variant of the AM1 NDDO Hamiltonian) to accurately reproduce coupled cluster theory to compute the reaction path

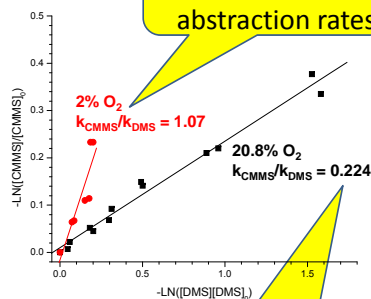
• Dynamics Modeling

• Semi-Classical Flux-Flux Autocorrelation Function (SCFFAF)

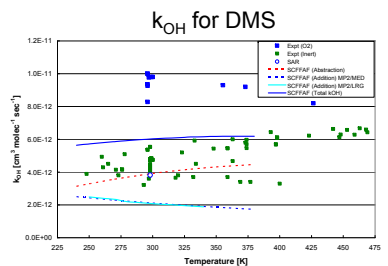
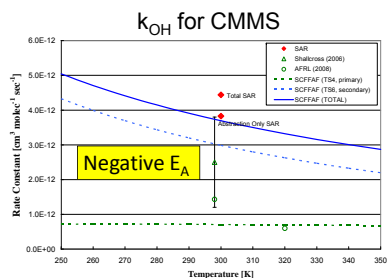
K Runge, MG Cory, and RJ Bartlett, *J. Chem. Phys.* 2001, 114, 5141.

## Results

CMMS and DMS have similar abstraction rates.

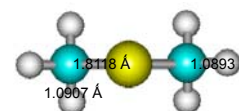


CMMS has a slower addition rate.



## Parent structures

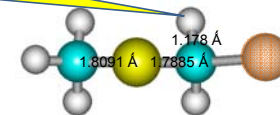
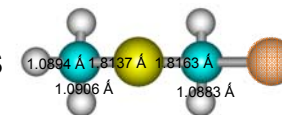
DMS



## Transition states

Secondary hydrogens react much faster than primary ones.

CMMS



## Rate constants (x 10<sup>12</sup> cm<sup>3</sup>/molecule/sec.)

Compound	Experiment		Theory			
	20.8% O <sub>2</sub>	2% O <sub>2</sub>	Abstraction	Addition	Total	
DMS	(6.82)	(4.97)	Primary: 0.65, Secondary: N/A	3.9	2.1	6.0
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DMS rate constants in parentheses are from Atkinson, R.; et al. *Atmospheric Chemistry and Physics* 2004, 4, 1461.

Theory predicts equivalent abstraction rates.

## Conclusions

✓ DMS and CMMS have similar abstraction rate constants

✓ CMMS has a slower addition rate constant

✓ CMMS has a negative activation energy

Need to...

• Determine theoretical addition rate for CMMS

• Measure temperature dependence of CMMS abstraction channel

• Measure relative rates with O<sub>3</sub> photolysis as OH source (NO<sub>x</sub> free!)