

Temperature and Pressure Dependence Study of the Reaction of IO Radicals with Dimethyl Sulfide by Cavity Ring-Down Laser Spectroscopy

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The oxidation of dimethyl sulfide (DMS) is of particular importance to the production of atmospheric aerosols, especially in the marine boundary layer (MBL) because DMS is the main sulfur containing species emitted from the oceans.¹ DMS is a relatively reduced form of sulfur and is produced biologically.² When oxidized, however, the organic sulfur species become hygroscopic and may form condensation nuclei, leading to the production of aerosols and possibly clouds.³ The effects of aerosols and clouds remain as the largest uncertainty in climate forecasting today.⁴ For this reason, the understanding of DMS oxidation is important to the understanding of our atmosphere. Many aspects of these processes remain incompletely understood however, including the oxidation of DMS.⁵ For example, a recent work by James *et al.*⁶ comparing measured and modeled results at a site in Mace Head, Ireland show that the daytime oxidation rate of DMS is underestimated by models by over a factor of three. Nighttime oxidation of DMS is thought to be dominated by reaction with nitrate radical (NO₃).^{7,8} In the daytime, DMS is thought to be oxidized by reaction with the hydroxyl radical (OH).^{9,10} This reaction has a recommended¹¹ room temperature rate constant of $5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Due to an absence of a known alternative, it is common for models include only OH and NO₃ as an oxidation sources for DMS.⁶ Field measurements¹² have been made of iodine oxide (IO) in the MBL, also at the Mace Head site. However, because of small number of measurements made to this point, and the fact that these measurements are close to the current detection limit of IO in

the field, how representative these concentrations are for the entire MBL is unknown. The authors of reference 12 speculate that IO is ubiquitous in the MBL. The main source of IO is biogenic,^{13,14} in the form of organic iodine compounds such as CH₂I₂. Emission of these compounds correlates with times of high biogenic activity.¹⁵ These compounds are photochemically converted to active iodine by photolysis to produce the I atom¹⁶ followed by reaction with ozone (O₃) to produce IO.¹⁷ A large fraction of iodine is thought to be in its active form (i.e. IO and I), due to the fast rate of photolysis of HOI,^{18,19} a major reservoir species for iodine. Less is known about iodine chemistry than the chemistry of the other natural halogen species, chlorine and bromine. A more comprehensive explanation of IO studies, with special attention given to the IO radical self reaction, can be found a recent work by Bloss *et al.*²⁰

At one time, it was thought that DMS oxidation by IO,^{21,22}



is an important reaction in the atmosphere. The measured rate constant in those works was on the order of 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. Those measurements were found to be in error and the current recommended value of this rate constant is 1.2 x 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ at room temperature,¹¹ with the temperature dependency of this reaction remaining unknown. The major obstacles in the earlier studies of reaction 1 include: 1) the uncertainty of the absorbance cross section of IO radical, 2) the uncertainty of the rate constant for the self-reaction of IO radical, and 3) wall loss of the IO radical. This recommended value is based on three measurements by Maguin *et al.*,²³ Barnes *et al.*,²⁴ and Knight and Crowley²⁵, as well as an upper limit set by Daykin and Wine.²⁶ The former three studies were done at low pressures (2 Torr or lower) and the study by Daykin and Wine (at 40, 100, 300 Torr) found no pressure dependence.

In this work, we examine the reaction of IO radicals with DMS using Cavity-Ring Down Spectroscopy (CRDS). This technique was employed in a previous study,²⁷ performed in this laboratory, of the reaction of Br atoms and BrO radicals with DMS. In that work, the reaction of BrO radicals with DMS was found to have a pressure dependence. In this work, both the pressure and the temperature effects of reaction 1 are examined. In the process, we examine the high-resolution spectrum of the IO radical using laser spectroscopy. The low detection limit achieved by using the CRDS technique allows us to spectroscopically observe IO radical directly, and in a quantitative manner.