Characterization of VMS oxidation reveals unexpected oxidation mechanism. Additional oxygen incorporation could affect aerosol partitioning and environmental impacts

**Introduction**

- More than two million tons of volatile methyl siloxanes (VMS) are produced globally each year\(^1\).
- Due to their high vapor pressures and low water solubilities, >90% of released VMS partition into the atmosphere - gas phase oxidation dominates the environmental loss of these compounds\(^2\).
- VMS are oxidized by hydroxyl (OH) radicals and chlorine (Cl) atoms, quickly forming a compound called a peroxy radical, with different products formed from this radical\(^3\).
- Little is known about the fate of this peroxy radical and how it forms previously observed oxidation products, limiting our understanding of the environmental fate of these compounds.
- Isotopically labeled VMS can assist with structure determination.
- Measuring lifetimes of VMS radicals could lead to unexpected observations.

**Methods**

- Three cyclic VMS were oxidized by photolyzing either Cl\(_2\), H\(_2\)O\(_2\), or HONO.

**Results**

- Formation of Silanol: Silanol is formed in higher levels with shorter RO\(_2\) lifetimes.
- Formation of silylester and silanol: Two main products previously detected: silanol and silylester.
- Unclear how to form the silanol from peroxy radical.

**Deuterated L2 (\(\text{D}_2\text{O}_2\)) Oxidation as silylester structure confirmation**

- Isotopically labeled VMS can assist with structure identification from molecular formulas.
- Oxidized \(\text{D}_2\text{O}_2\) with Cl atoms.
- Charge carrier is always a proton from toluene.
- Any other protons in the molecular formula are from H exchanges with ambient water.
- Aldehydic H/D do not exchange with water, alcoholic H/D do.
- Main product structures shown below, with only one or two protons, validating the structures.

**Peroxy radical reactions suggested by previous theoretical and experimental studies**\(^4,5\):

- Our experiments suggest that all the reactions occur except for the two rearrangements indicated by the blue arrow.

**Alkoxyl radical rearrangement to form ether peroxy radical**

- The rearrangement of this alkoxy radical (formed from the reaction of the peroxy radical with NO or HO\(_2\)) is predicted to be very rapid according to theory,\(^4,5\) and is a unique reaction to the Si-containing molecules.

**Time series of two expected organonitrates formed during the oxidation of D5 by OH in the presence of NO**

- The red signal corresponds to the D5 organonitrates in the absence of NO.
- The black is without the rearrangement (structures below). This is the first time these products have been detected experimentally.

**Alkoxy radical rearrangement**

- Reaction of the peroxy radical with NO or HO\(_2\)) is predicted to be very rapid according to theory,\(^4,5\) and is a unique reaction to the Si-containing molecules.