Assessing and improving the DMS oxidation mechanism in the MCM and CRI-Strat

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28 TgS of DMS is emitted annually.
Once in the atmosphere, DMS chemistry gets interesting
Aqueous phase adds to the complexity (but is important!!)
Closer to the poles, MSA can be deposited on ice
CRI-Strat and MCM are both useful, but have different uses.

**Master Chemical Mechanism (MCM):**
- 17,000 reactions
- 81 sulfur-based reactions
- Good for simple models: box models

**Common Representative Intermediates (CRI):**
- 1,183 reactions
- 38 sulfur-based reactions
- Good for more complicated models: global atmospheric models
Comparing the mechanisms to experiments: *Arsene et al.*

**Experimental Conditions:**
- DMS conc.: 6.5 ppm
- \( \text{H}_2\text{O}_2 \) conc.: 25 ppm
- \( \text{NO}_2 \) conc.: 350-500 ppb
- NO conc.: 900-1100 ppb
- Bath gas: synth. air
- Total pressure: 1000 mbar

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The MCM includes an additional reaction, forming DMSO₂

CRI-Strat:
DMS + OH = DMSO + HO₂

CRI-Strat Updated
DMS + OH = HODMSO₂
HODMSO₂ = DMSO + HO₂
HODMSO₂ + NO = DMSO₂ + HO₂ + NO₂

9.5 × 10⁻³⁹ [O₂]e^{5270/T} / (1 + 7.5 × 10⁻²⁹ [O₂]e^{5610/T})

9.5 × 10⁻³⁹ [O₂]e^{5270/T} / (1 + 7.5 × 10⁻²⁹ [O₂]e^{5610/T})

8.9 × 10⁻¹⁰ e⁻⁶⁰⁴⁰/T

2.7 × 10⁻¹² e⁻³⁶⁰/T
Adding a few reactions made a big difference to the output

CRI-Strat:
DMS + OH = DMSO + HO$_2$

CRI-Strat Updated:
DMS + OH = HODMSO$_2$
HODMSO$_2$ = DMSO + HO$_2$
HODMSO$_2$ + NO = DMSO$_2$ + HO$_2$ + NO$_2$

Experimental Conditions:
Temp: 290 K
DMS conc.: 15 ppm
$\text{H}_2\text{O}_2$ conc.: 25 ppm
Bath gas: synth. air
Total pressure: 1000 mbar

$\text{RO}_2$ reaction?
Comparing the mechanisms to experiments: Arsene et al.

Experimental Conditions:
DMS conc.: 6.5 ppm
H₂O₂ conc.: 25 ppm
NO₂ conc.: 350-500 ppb
NO conc.: 900-1100 ppb
Bath gas: synth. air
Total pressure: 1000 mbar
The differences in SO$_2$ formation can be explained by the reactions
The MCM assumes sulfur chemistry is similar to \( \text{RC(O)OH} \)
In the case of SO$_2$, one reaction is key:

**MCM:**
MSIA + OH = CH$_3$O$_2$ + SO$_2$

**MCM Updated:**
MSIA + OH = CH$_3$SO$_2$

Small steps to help us uncover the puzzle of DMS oxidation
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Talk about the state of what's in the models
- currently they are all over the place
- can we constrain the models by going back to older experiments
- compare Ben's study, showing a more qualitative evaluation (which is what is generally done on a global scale), to this, which is more of a quantitative assessment
The modelling of DMS oxidation is only as good as our knowledge of the chemistry

Aim: To improve the modelling of DMS oxidation chemistry

Objectives:
1. Assess the current uncertainties in the DMS oxidation pathway using box modelling
2. Perform fieldwork that can be compared to the atmospheric models
3. Assess the use of MSA as an ice core proxy using global atmospheric models
**CRI-Strat:**
DMS + OH = DMSO + HO2

**CRI-Strat Updated:**
DMS + OH = 
HODMSO2
HODMSO2 = DMSO + HO2
HODMSO2 + NO = 
DMSO2 + HO2 + NO2
One study that this relies on had 100% formation of SO2, however, that was done in the oxygen free experiment. In a bath gas of neat N2, the formation of CH3SO2 solely forms the above (CH3 + SO2) though with oxygen (or O3 and NO2) other products could be found.
Comparing the mechanisms to experiments: Albu et al.

Looking into the differences of MTF