Identifying Criegee intermediates as potential oxidants in the troposphere

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1. Introduction

Criegee intermediates (CI) are formed during the ozonolysis of unsaturated compounds and have been intensively studied in the last few years due to their possible role as oxidants in the troposphere. Still, it remains challenging to assess their effective oxidative capacity, as CI chemistry is complex, spans a large range of rate coefficients, and different CI conformers react with water dimers and trace gases, and currently there is no reliable measurement technique able to detect ambient SCI concentrations.

2. Estimate of the SCI steady state concentration

1. From the unexplained H2SO4 gas phase concentration observed when restraining the sources for H2SO4 in the gas phase to the OH radicals only

\[ [H_2SO_4] = \left( \sum k_{exp} \times [VOC] \times [OH] \right) \times \frac{[SO_2]}{[OH]} \]

2. From the measured unsaturated VOCs

\[ [SC] = \left( \sum k_{exp} \times [VOC] \right) \times [O_3] \times [Y] \]

3. From the measured OH reactivity

\[ R_{measured} = k_{exp} \times [VOC] \times [O_3] \]

4. From unexplained OH production rate

\[ P_{measured} = k_{exp} \times [VOC] \times [O_3] \times [Y] \]

3. Field data

The background OH signal measured with an IPI-LIF-FAGE® when injecting propane to remove ambient OH is proposed to be caused by SCI. During both the HUMPPA-COPEC 2010 and HOPE 2012 campaigns the background OH correlates exponentially with temperature at a rate of ~0.77 0.08°C⁻¹.

During the HOPE 2012 campaign the background OH correlates with the product of measured VOC, mainly monoterpenes and isoprene, and ozone. Occasional addition of SO2, a known SCI scavenger, to the air before sampling led to removal of the background signal during the campaign.

4. SCI fate in a boreal forest

5. Conclusions

- Using four different approaches, i.e. unaccounted (i.e. non-OH) H2SO4 oxidant, measured VOC concentrations, unexplained OH reactivity and unexplained production rate of OH, we estimated the concentration of SCI to be between ~10⁻² and ~10⁻⁶ molecules cm⁻³.
- Ambient background OH measured with IPI-LIF-FAGE correlates with the unexplained production rate of sulfuric acid and with the production rate of SCI and can be scavenged with SO2.
- Further studies are necessary to obtain the relationship between the OH background concentration detected within our LIF-FAGE instrument and the ambient abundance of SCI.

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References

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Image 1: Criegee intermediates (CI) are formed during the ozonolysis of unsaturated compounds and have been intensively studied in the last few years due to their possible role as oxidants in the troposphere. Still, it remains challenging to assess their effective oxidative capacity, as CI chemistry is complex, spans a large range of rate coefficients, and different CI conformers react with water dimers and trace gases, and currently there is no reliable measurement technique able to detect ambient SCI concentrations.

Image 2: The background OH signal measured with an IPI-LIF-FAGE® when injecting propane to remove ambient OH is proposed to be caused by SCI. During both the HUMPPA-COPEC 2010 and HOPE 2012 campaigns the background OH correlates exponentially with temperature at a rate of ~0.77 0.08°C⁻¹.

Image 3: The background OH signal measured with an IPI-LIF-FAGE® when injecting propane to remove ambient OH is proposed to be caused by SCI. During both the HUMPPA-COPEC 2010 and HOPE 2012 campaigns the background OH correlates exponentially with temperature at a rate of ~0.77 0.08°C⁻¹.

Image 4: The background OH signal measured with an IPI-LIF-FAGE® when injecting propane to remove ambient OH is proposed to be caused by SCI. During both the HUMPPA-COPEC 2010 and HOPE 2012 campaigns the background OH correlates exponentially with temperature at a rate of ~0.77 0.08°C⁻¹.

Image 5: The background OH signal measured with an IPI-LIF-FAGE® when injecting propane to remove ambient OH is proposed to be caused by SCI. During both the HUMPPA-COPEC 2010 and HOPE 2012 campaigns the background OH correlates exponentially with temperature at a rate of ~0.77 0.08°C⁻¹.