Identifying Criegee intermediates as potential oxidants in the troposphere

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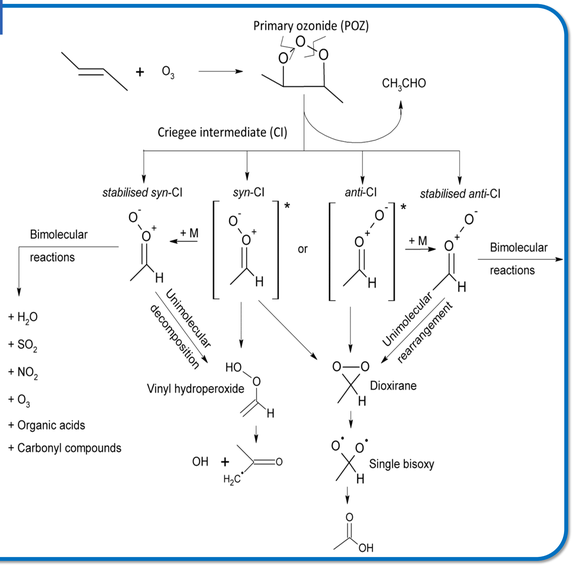
1. Introduction

Criegee intermediates[1](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 for different SCI conformers reacting 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 H_2SO_4 gas phase concentration[2] observed when restraining the sources for H_2SO_4 in the gas phase to the OH radicals only

$$[H_2SO_4] = \frac{(k_{OH+SO_2} \times [OH] + k_{SCI+SO_2} \times [SCI]) \times [SO_2]}{CS}$$

2. From the measured unsaturated VOC[3]

$$[SCI] = \frac{(\sum_i k_{VOC_i+O_3} \times [VOC_i]) \times [O_3] \times Y_{SCI}}{L_{SCI\,syn}}$$

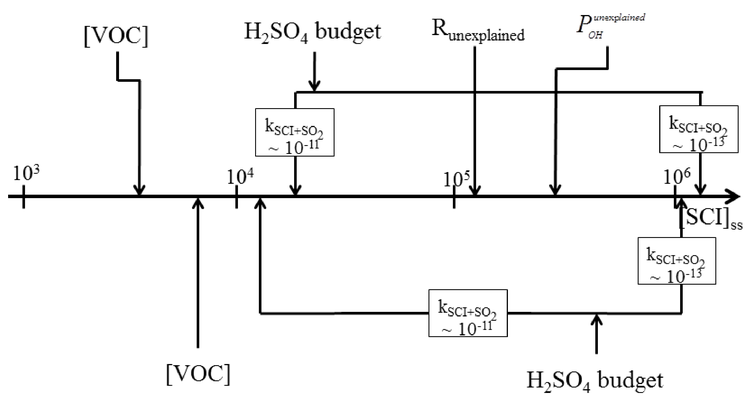
3. From the measured OH reactivity[4]

$$R_{unexplained} = k_{VOC+OH} \times [VOC_{unidentified}]$$

4. From unexplained OH production rate[3]

$$P^{unexplained} = k_{voc+O_3} \times [VOC_{unidentified}] \times [O_3] \times Y_{OH}$$

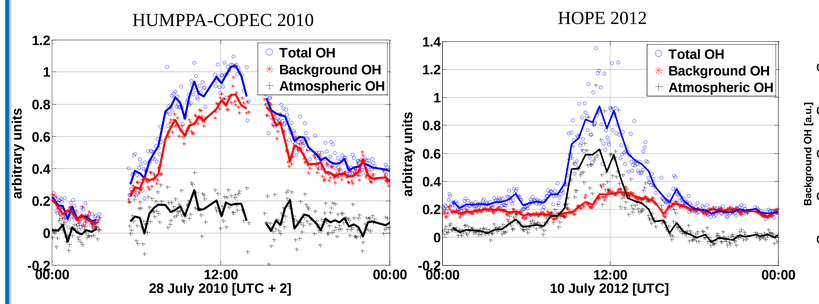
Boreal Forest (HUMPPA-COPEC 2010)

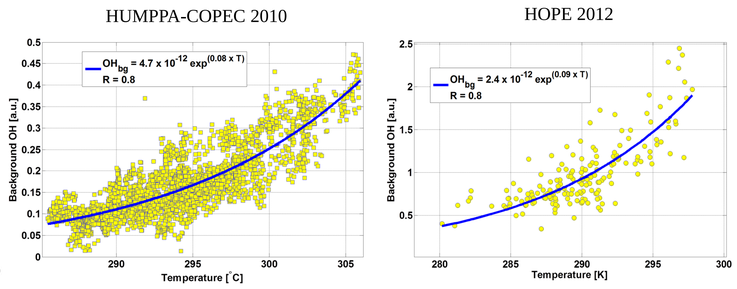


(Rural Europe) HOPE 2012

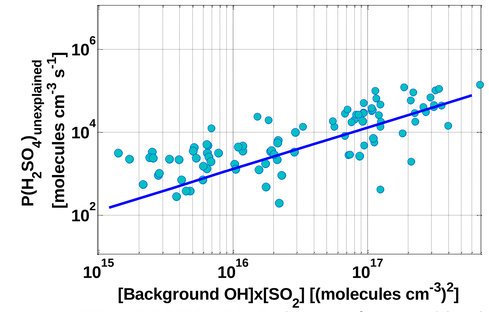
3. Field data

The background OH signal measured with a IPI-LIF-FAGE[5] when injecting propane to remove ambient OH is proposed to be caused by SCI[6]. During both the HUMPPA-COPEC 2010 and HOPE 2012 campaigns the background OH correlates exponentially with temperature





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 just before sampling led to removal of the background signal during the campaign.



During HUMPPA-COPEC 2010 it correlates with the missing H_2SO_4 oxidant[7] that was hypothesized to be Criegee intermediate due to their fast reaction rate[4] with SO_2 and the subsequent formation of SO_3 which is rapidly converted in H_2SO_4 with H_2O.

4. SCI fate in a boreal forest

Loss path contribution (fraction) as a function of SCI substituents

	Day	Night	
H_2COO			
H_2O	0.01	0.01	OH formation
$(H_2O)_2$	0.99	0.99	
***anti*-CH_3CHOO**			
H_2O	0.25	0.39	50 % of measured H_2SO_4
$(H_2O)_2$	0.75	0.6	
Ester channel		0.01	
***syn*-CH_3CHOO**			
H_2O	0.01		Main chemical removal process for carboxylic acids
$(H_2O)_2$	0.11	0.08	
Vinyl hydroperoxyde channel	0.42	0.77	
SO_2	0.01	0.01	Formation of LVOC
O_3	0.01	0.01	
Carboxylic acids	0.42	0.12	
Hydroxyl compounds	0.02	0.01	

5. Conclusions

- Using four different approaches, i.e. unaccounted (i.e. non-OH) H_2SO_4 oxidant, measured VOC concentrations, unexplained OH reactivity and unexplained production rates of OH, we estimated the concentration of SCI to be between ~ 10^3 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 SO_2.
- 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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