Supplement of Atmos. Chem. Phys., 17, 7807–7826, 2017
https://doi.org/10.5194/acp-17-7807-2017-supplement

Supplement of

Estimating the atmospheric concentration of Criegee intermediates and their possible interference in a FAGE-LIF instrument

Anna Novelli et al.

Correspondence to: Hartwig Harder (hartwig.harder@mpic.de)

Assessment of the available rate coefficients for the SCI + SO_2 reaction

The disagreement between the rate coefficient for the SCI + SO_2 reaction obtained by Mauldin III et al. (2012) and Berndt et al. (2012), 5.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, and the one obtained by a number of other groups (Welz et al., 2012;Taatjes et al., 2013;Liu et al., 2014b;Sheps et al., 2014;Stone et al., 2014;Chhantyal-Pun et al., 2015;Newland et al., 2015a;Newland et al., 2015b;Foreman et al., 2016;Zhu et al., 2016), 3.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, is not straightforward to explain.

A first factor is that Mauldin III et al. (2012) and Berndt et al. (2012) measure the rate of formation of H_2SO_4 rather than the loss of SCI by SO_2. Theoretical and experimental results (Carlsson et al., 2012;Ahrens et al., 2014) indicate that SO_3 is the main product of the SCI + SO_2 reaction, with a yield near 100% at all reaction conditions considered. Barring secondary chemistry removing SO_3 prior to its reaction with H_2O to form H_2SO_4, which seems unlikely under their reaction conditions, the H_2O_4 yield should match the SCI loss. Earlier theoretical work by Vereecken et al. (2012) suggested that the secondary ozonide (SOZ) formed as an intermediate from the reaction between larger SCI and SO_2 could stabilize and undergo bimolecular reaction without formation of SO_3; the loss of SOZ would then reduce SO_3 formation, explaining the difference in the rate coefficients for the different experiments. However, more recent theoretical work (Kuwata et al., 2015) found additional low-lying pathways that make collisional stabilization of the SOZ unlikely. Experiments by Carlsson et al. (2012) and Ahrens et al. (2014) observed high yields of SO_3 close to unity suggesting that the SOZ is not lost under the conditions used, i.e. in chambers with high concentrations of reactants and in the absence of water.

A second factor is that the reaction conditions used by Mauldin III et al. (2012) and Berndt et al. (2014) differ from the other studies, i.e. they were performed either at ambient air conditions or with lower concentrations of reagents and in the presence of water, while the remaining experiments were typically performed under lower pressures, without efficient colliders present. The mechanism of the SCI+SO_2 reaction as obtained by several authors (Vereecken et al., 2012;Kuwata et al., 2015;Jiang et al., 2010;Kurtén et al., 2011) all indicate a barrierless formation of a pre-reactive complex or cycloadduct. This type of reactions typically show faster rate coefficients at higher pressures due to lower redissociation of the adduct; this is corroborated by the theoretical study on the pressure dependence by Kuwata et al. (2015) who finds no pressure dependence up to 10132.5 hPa and an increase in the effective rate coefficient for higher pressures. Experimental studies of the pressure dependence (Liu et al., 2014b;Huang et al., 2015;Chhantyal-Pun et al., 2016) do not show extensive pressure dependence up to 300 Torr, and all show a positive pressure dependence, in line with the currently accepted reaction mechanism. The Carlsson et al. (2012) experiments at 1013.51 hPa likewise can be fitted using a faster CI + SO_2 rate coefficient of 1 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1}. This suggests that the reaction conditions used by Mauldin III et al. and Berndt et al. would likely lead to faster rate coefficients, especially for larger SCI as used in Mauldin III et al. due to the lower redissociation rate and hence higher thermalization yield of the intermediates.

A third factor is that the Mauldin III et al. examine SCI formed from larger terpenoids, rather than the smaller SCI examined in the remaining studies. A larger SCI should mean a longer lifetime for the SOZ intermediate, especially as this longer lifetime makes collisional thermalization more efficient. Hence the large SOZ might indeed live long enough to react in bimolecular reactions prior to dissociation to SO_3, contrary to smaller SOZ. Unfortunately, SOZ chemistry has not been studied in detail; for the current case the reaction with e.g. H_2O

could be a potential loss process. A prerequisite for this scavenging to be effective is that no H_2SO_4 precursor should be formed. This scavenging of the SOZ intermediate would however not apply to the experiments of Berndt et al., which examined CH_3CHOO and $(CH_3)_2COO$ Criegee intermediates, similar in size to those used in the studies yielding higher rate coefficients. For SCI of this size, the RRKM master equation analysis of (Kuwata et al., 2015) predicts very fast SOZ decomposition.

Finally, an alternative explanation could be based on analysis of the studies by Mauldin III et al. (2012) and Berndt et al. (2012). In their experiments, the rate of the SCI+SO_2 reaction is derived relative to the total loss rate of SCI, L_{SCI}, as it governs the steady-state concentration of SCI with negligible SO_2 present. This L_{SCI} has a value on the order of ~ 3 to 5 s^{-1} in both experiments. Since these studies, a large body of experimental and theoretical data has become available, regarding the reactivity of SCI towards many coreactants present in the reaction mixture (Taatjes et al., 2013;Ouyang et al., 2013;Ahrens et al., 2014;Buras et al., 2014;Liu et al., 2014a;Stone et al., 2014;Sheps et al., 2014;Welz et al., 2014;Lewis et al., 2015). From this new data, we should consider that a total loss rate of about 4 s^{-1} is an underestimate. In a previous study by Novelli et al. (2014) a value of L_{SCI} = 40 s^{-1} under atmospheric conditions was proposed. A re-analysis of the study by Mauldin III et al. (2012) using L_{SCI} = 40 s^{-1} and the measured yield of SCI for α-pinene of 0.1 (Donahue et al., 2011), results in a rate coefficient for the α-pinene-derived SCI + SO_2 reaction of 2.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Likewise, for the other compounds examined in the two studies (Berndt et al., 2012;Mauldin III et al., 2012), the derived rate of SCI+SO_2 would shift significantly towards the higher values obtained in the other studies (Welz et al., 2012;Taatjes et al., 2013;Liu et al., 2014b;Sheps et al., 2014;Stone et al., 2014). One must consider, though, that the study by Berndt et al. (2012) included a measurement of k_{loss}, based on the observed H_2SO_4 formation from the steady state SCI in the absence of SO_2. Hence, this second explanation is only viable if another source of H_2SO_4 exists in the system; this has already been suggested by Newland et al. (2015a) based on their SO_2 oxidation experiments.

Still, as these considerations for the lower values by Mauldin III et al. (2012) and Berndt et al. (2012) are merely speculative, we will consider both 3.3×10^{-11} cm^3 $molecule^{-1}$ s^{-1} and 5×10^{-13} cm^3 $molecule^{-1}$ s^{-1} as possible rate coefficients for the SCI + SO_2 reaction in the current budget analysis.

SCI time series

Time series of SCI were derived for two field campaigns, HUMPPA-COPEC 2010 and HOPE 2012, obtained based on different source data, i.e. the sulfuric acid budget, the speciated VOC concentrations measured, and the unexplained OH reactivity.

The time series for the HUMPPA-COPEC 2010 campaign (Figures SI-2, SI-4, and SI-7) are fairly well defined, at least in view of intrinsic uncertainty of the underlying data; as detailed in the main text, this is the campaign with the highest expected SCI concentrations. Fig SI-2, using the H_2SO_4 budget as data source, shows a less pronounced diurnal cycle, but figure SI-4 and SI-7 both show a clear diurnal cycle of the predicted SCI concentration, as well as some daily differences. These plots both link [SCI] to VOC concentrations, and the SCI concentration follows the diel variation of these VOCs, as expected from the ozonolysis chemistry as a source of SCI. Our analysis is not able to account for different yields or lifetimes of SCI as a function of VOC speciation differences from day to night, due to lack of data. In principle this could superimpose an additional SCI concentration diel variation, but we anticipate this to be minor considering that the VOC speciation does not change drastically between day and night. Both plots also show clear daily differences.

The [SCI] time series for the HOPE 2012 campaign are characterized mostly by their statistical noise. As discussed in the main paper, the SCI concentration during this campaign was expected to be low, and the SCI concentration estimates are typically derived from a small difference between large numbers, each with their own statistical noise, leading to highly variable data with very large relative uncertainties even when the absolute numbers remain small. Under these conditions, neither diurnal cycles, day-to-day variations, nor even minimum and peak values carry strong significance, and no meaningful in-depth analysis can be done beyond stating that the concentrations are predicted to be low indeed.

Across all SCI time series, we find that the minimum and maximum values of the predicted SCI concentration remains within a relatively modest factor of the median and the average [SCI], only exceeding a factor of 5 for a handful of data points. Considering the uncertainties already incurred through the analysis methodology itself, and the variability and uncertainties on the source data underlying these studies, secondary effects such as day-to-day variability, diurnal cycles, or multi-day variations have only a moderate to small impact on the overall uncertainty of the CI estimates proposed in the main paper, where we indicate uncertainties that exceed an order of magnitude.

Sensitivity study on the unexplained OH reactivity SCI estimate

The estimate of SCI from the unexplained OH reactivity data contains larger uncertainties compared to the previous estimates as the rate coefficient for ozonolysis of unsaturated compounds varies by up to three orders of magnitude. In addition, the rate coefficient between OH and unsaturated compounds, depending on whether these are unsaturated NMHC or OVOC, primary emissions, or secondary oxidation products, varies by an order of magnitude. A sensitivity study was done on the SCI estimates from the unexplained OH reactivity to attempt to account for this uncertainty in rate coefficients. It is possible to calculate a lower limit for the SCI concentration by using the highest rate coefficient between OH and unsaturated compounds, 1.0 x 10^{-10} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006) combined with a slow rate coefficient for the unsaturated compounds and ozone, 1.0 x 10^{-17} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006), leading to a [SCI] = (8.7 ± 8.0) x 10^3 molecules cm^{-3}. For the upper limit, a slower rate coefficient for OH and unsaturated OVOC, ~ 3.0 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006;Teruel et al., 2006) together with a higher rate coefficient with O_3, 1.0 x 10^{-16} cm^3 $molecule^{-1}$ s^{-1} (Atkinson et al., 2006) results in a concentration of [SCI] = (3.0 ± 3.0) x 10^5 molecules cm^{-3}. These are the values obtained for the HUMPPA-COPEC 2010 campaign. For the HOPE 2012 campaign, the same assumptions would yield a lower and an upper limit of (1.0 ± 0.2) x 10^3 molecules cm^{-3} and (2.9 ± 0.7) x 10^4 molecules cm^{-3}, respectively.

Table SI-1. Average concentrations with 1σ standard deviation of measured unsaturated VOC during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, together with the rate coefficients of the reaction with ozone (IUPAC recommended values) (Atkinson et al., 2006).

Compound	**[molecule cm^{-3}]**		**Rate coefficient with O_3 [cm^3 molecule^{-1} s^{-1}]**
	HUMPPA-COPEC 2010	**HOPE 2012**	
isoprene	(1.8 ± 1.8) x 10^{9}	(2.2 ± 2.2) x 10^{9}	1.0 x 10^{-14} exp(-1995/T)
α-pinene	(2.7 ± 3.0) x 10^{9}	(1.5 ± 1.5) x 10^{9}	8.1 x 10^{-16} exp(-640/T)
β-pinene	(1.9 ± 6.6) x 10^{8}	(9.0 ± 9.0) x 10^{8}	1.4 x 10^{-15} exp(-1270/T)
3-carene	(1.7 ± 2.0) x 10^{9}	(5.6 ± 4.7) x 10^{8}	4.8 x $10^{-17,\, b}$
myrcene	(2.6 ± 2.7) x 10^{8}	(2.2 ± 1.6) x 10^{8}	2.7 x 10^{-15} exp(-520/T)
limonene	n.a.	(2.9 ± 2.1) x 10^{8}	2.8 x 10^{-15} exp(-770/T)
sabinene	n.a.	(9.2 ± 9.6) x 10^{8}	8.2 x $10^{-17,\, b}$
γ-terpinene	n.a.	(1.0 ± 1.0) x 10^{8}	1.5 x $10^{-16,\, b}$
2-methylpropene	n.a.	(4.2 ± 2.5) x 10^{8}	2.7 x 10^{-15} exp(-1630/T)
but-1-ene	n.a.	(1.4 ± 4.2) x 10^{8}	1.2 x $10^{-17,\, a,b}$
propene	n.a.	(4.7 ± 3.7) x 10^{8}	5.5 x 10^{-15} exp(-1880/T)
cis-2-butene	n.a.	(6.1 ± 3.0) x 10^{7}	3.2 x 10^{-15} exp(-965/T)
ethene	n.a.	(7.3 ± 9.0) x 10^{9}	9.1 x 10^{-15} exp(-2580/T)

a, rate coefficient from Adeniji et al. (1981).
b, at 298 K
1 ppbv = 2.46 x 10^{10} molecules cm^{-3} at 295K and 1013 hPa.

Table SI-2. Average concentrations with 1σ standard deviation of measured trace gas during the HUMPPA-COPEC 2010 and HOPE 2012 campaigns, with the rate coefficients of the reaction with OH (IUPAC recommended values) (Atkinson et al., 2006;Atkinson et al., 2004)

Compound	**[molecule cm^{-3}]** **HUMPPA-COPEC 2010**	**HOPE 2012**	**Rate coefficient with OH [cm^3 molecule^{-1} s^{-1}]**
isoprene	$(1.8 \pm 1.8) \times 10^{9}$	$(2.2 \pm 2.0) \times 10^{9}$	2.7×10^{-11} exp(390/T)
α-pinene	$(2.7 \pm 3.0) \times 10^{9}$	$(1.5 \pm 1.5) \times 10^{9}$	1.2×10^{-11} exp(440/T)
β-pinene	$(1.9 \pm 6.6) \times 10^{8}$	$(9.0 \pm 9.0) \times 10^{8}$	$7.4 \times 10^{-11,\ a,b}$
3-carene	$(1.7 \pm 2.0) \times 10^{9}$	$(5.6 \pm 4.7) \times 10^{8}$	$8.8 \times 10^{-11,\ a,b}$
myrcene	$(2.6 \pm 2.7) \times 10^{8}$	$(2.2 \pm 1.6) \times 10^{8}$	$3.3 \times 10^{-10,\ b,c}$
limonene	n.a.	$(2.9 \pm 2.1) \times 10^{8}$	3×10^{-11} exp(515/T),[d]
sabinene	n.a.	$(9.2 \pm 9.6) \times 10^{8}$	$1.2 \times 10^{-10,\ a,b}$
γ-terpinene	n.a.	$(1.0 \pm 1.0) \times 10^{8}$	$1.7 \times 10^{-10,\ b}$
MACR	$(1.0 \pm 0.9) \times 10^{10}$	$(1.4 \pm 0.9) \times 10^{9}$	8×10^{-12} exp(380/T)
ethanol	$(3.6 \pm 2.2) \times 10^{10}$	$(1.8 \pm 1.1) \times 10^{10}$	3.2×10^{-12} exp(20/T)
methanol	$(1.0 \pm 1.4) \times 10^{11}$	$(9.0 \pm 3.4) \times 10^{10}$	$9.0 \times 10^{-13,\ b}$
ozone	$(1.1 \pm 0.2) \times 10^{12}$	$(1.1 \pm 0.3) \times 10^{12}$	1.7×10^{-12} exp(-940/T)
SO_2	$(1.4 \pm 1.7) \times 10^{10}$	$(2.3 \pm 2.2) \times 10^{9}$	$2.0 \times 10^{-12,\ b}$
H_2O_2	$(1.1 \pm 1.0) \times 10^{10}$	n.a.	$1.7 \times 10^{-12,\ b}$
HO_2	$(9.0 \pm 9.5) \times 10^{8}$	$(1.4 \pm 8.6) \times 10^{8}$	4.8×10^{-11} exp(250/T)
NO	$(6.5 \pm 7.0) \times 10^{8}$	$(3.8 \pm 5.0) \times 10^{9}$	$1.3 \times 10^{-11,\ b}$
NO_2	$(9.5 \pm 5.0) \times 10^{9}$	$(3.8 \pm 2.4) \times 10^{10}$	$1.1 \times 10^{-11,\ b}$
CO	$(3.0 \pm 1.2) \times 10^{12}$	$(2.8 \pm 0.4) \times 10^{12}$	$2.1 \times 10^{-13,\ b}$
HONO	$(3.4 \pm 3.1) \times 10^{9}$	n.a.	$6.0 \times 10^{-12,\ b}$
propanal	n.a.	$(5.8 \pm 3.0) \times 10^{9}$	4.9×10^{-12} exp(405/T)

acetaldehyde	$(1.8 \pm 1.0) \times 10^{10}$	$(2.9 \pm 1.4) \times 10^{10}$	$1.5 \times 10^{-11, b}$
formaldehyde	$(1.4 \pm 1.6) \times 10^{10}$	$(2.1 \pm 0.4) \times 10^{10}$	$8.5 \times 10^{-12, b}$
acetone	$(8.2 \pm 3.8) \times 10^{10}$	$(6.0 \pm 2.2) \times 10^{10}$	$1.8 \times 10^{-13, b}$
CH_4	$(4.4 \pm 0.07) \times 10^{13}$	$(4.3 \pm 0.1) \times 10^{13}$	$6.4 \times 10^{-15, b}$
2-methylpropene	n.a.	$(4.2 \pm 2.5) \times 10^{8}$	$6.1 \times 10^{-11, a,b}$
but-1-ene	n.a.	$(1.4 \pm 4.2) \times 10^{8}$	$3.1 \times 10^{-11, a,b}$
propene	n.a.	$(4.7 \pm 3.7) \times 10^{8}$	$2.9 \times 10^{-11, b}$
cis-2-butene	n.a.	$(6.1 \pm 3.0) \times 10^{7}$	$6.4 \times 10^{-11, b}$
ethene	n.a.	$(7.3 \pm 9.0) \times 10^{9}$	$7.8 \times 10^{-12, b}$
p-xylene	n.a.	$(7.2 \pm 5.2) \times 10^{8}$	$2.0 \times 10^{-11, a,b}$
benzene	$(2.1 \pm 1.9) \times 10^{9}$	$(8.0 \pm 4.0) \times 10^{8}$	$1.2 \times 10^{-12, a,b}$
ethylbenzene	n.a.	$(2.3 \pm 2.1) \times 10^{8}$	$7.0 \times 10^{-12, a,b}$
Toluene	$(6.1 \pm 3.0) \times 10^{9}$	$(1.2 \pm 0.7) \times 10^{9}$	$5.6 \times 10^{-12, a,b}$
ethane	n.a.	$(1.8 \pm 0.3) \times 10^{10}$	$4.8 \times 10^{-11} \exp(250/T),^{a}$
propane	n.a.	$(5.6 \pm 3.6) \times 10^{9}$	$1.1 \times 10^{-12, a,b}$
methylpropane	$(1.8 \pm 2.3) \times 10^{9}$	$(1.4 \pm 0.9) \times 10^{9}$	$2.1 \times 10^{-12, a,b}$
butane	$(1.8 \pm 1.6) \times 10^{9}$	$(2.0 \pm 1.2) \times 10^{9}$	$2.3 \times 10^{-12, a,b}$
2-methylbutane	$(1.6 \pm 1.2) \times 10^{9}$	n.a.	$3.6 \times 10^{-12, a,b}$
n-pentane	$(1.0 \pm 0.9) \times 10^{9}$	$(5.6 \pm 5.0) \times 10^{9}$	$3.8 \times 10^{-12, a,b}$

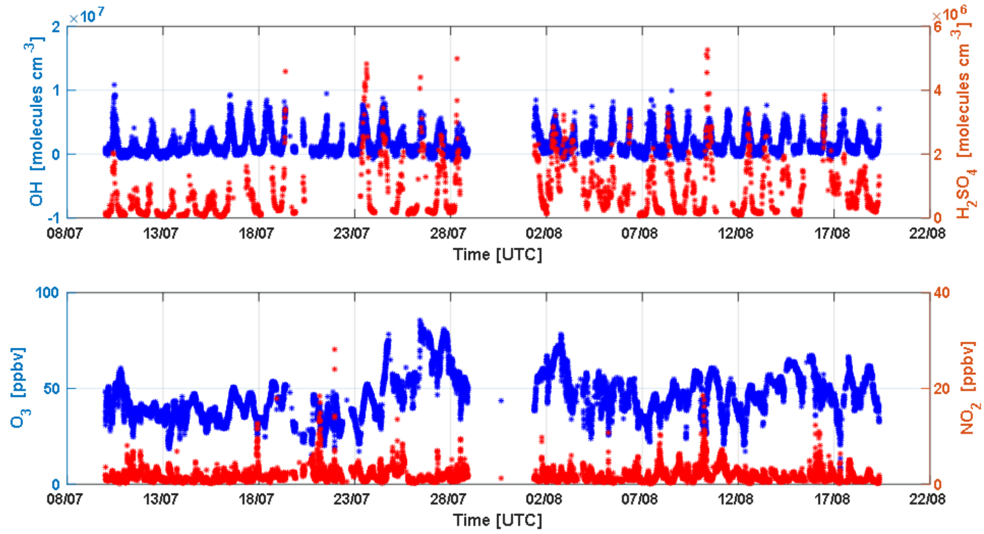
---

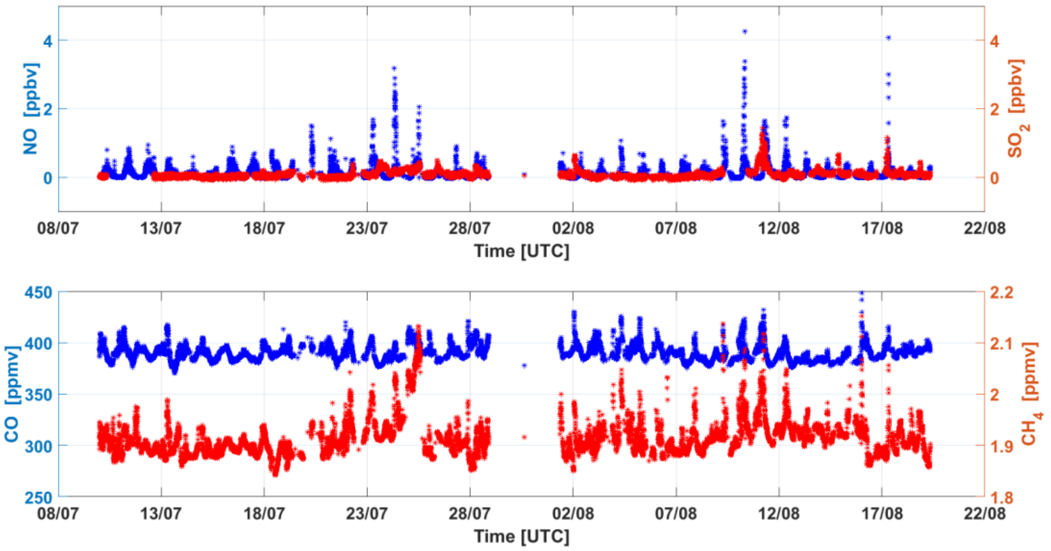
a, rate coefficient from (Atkinson and Arey, 2003).
b, at 298 K.
c, rate coefficient from (Hites and Turner, 2009)
d, rate coefficient from (Braure et al., 2014)
1 ppbv = 2.46×10^{10} molecules cm^{-3} at 295K and 1013 hPa.

Table SI-3. Average sum of concentrations with 1σ standard deviation of BVOC (isoprene, α-pinene, β-pinene, 3-carene, myrcene, limonene, sabinene, γ-terpinene) and temperature for the entire HOPE 2012 field campaign excluding the period between 26th to 28th of July 2012.

	Σ[VOC] [molecules cm^{-3}]	Temperature [ºC]
HOPE 2012 campaign	$(5.0 \pm 4.0) \times 10^{9}$	16 ± 3.0
26th to 28th of July 2012	$(1.3 \pm 0.9) \times 10^{10}$	22 ± 3.0

1 ppbv = 2.46×10^{10} molecules cm^{-3} at 295K and 1013 hPa.





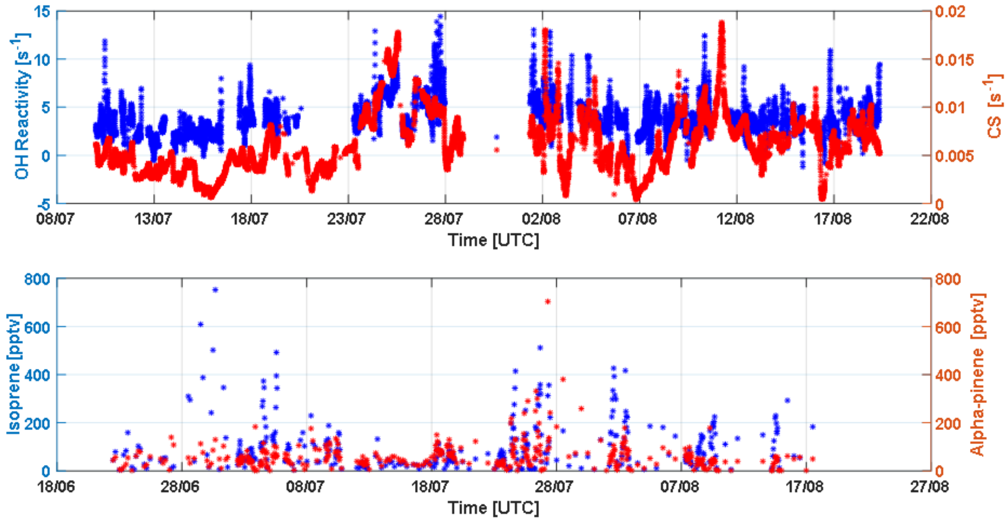


Figure SI-1. Time series of trace gases measured during the HOPE 2012 campaign.

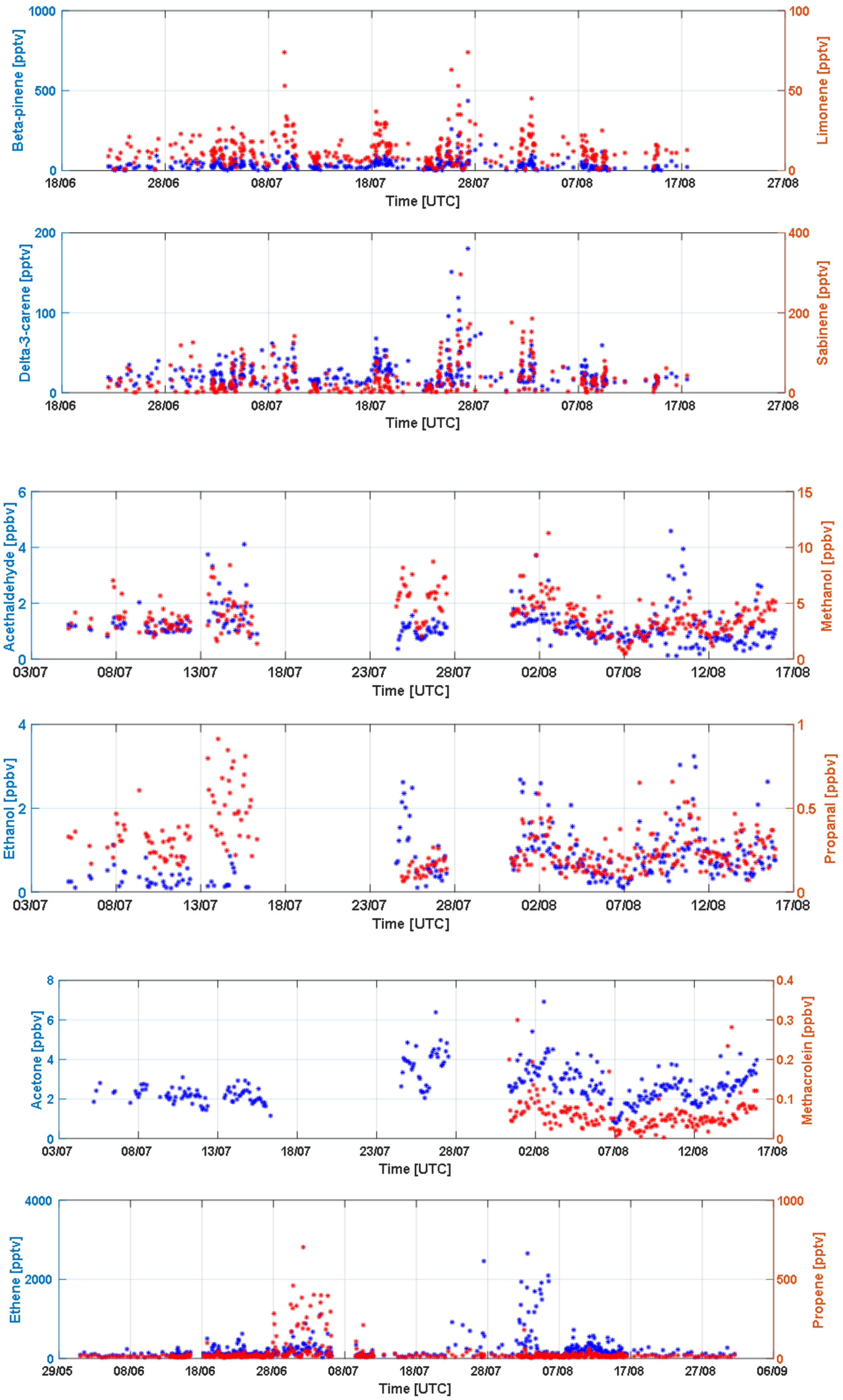


Figure SI-1, continued

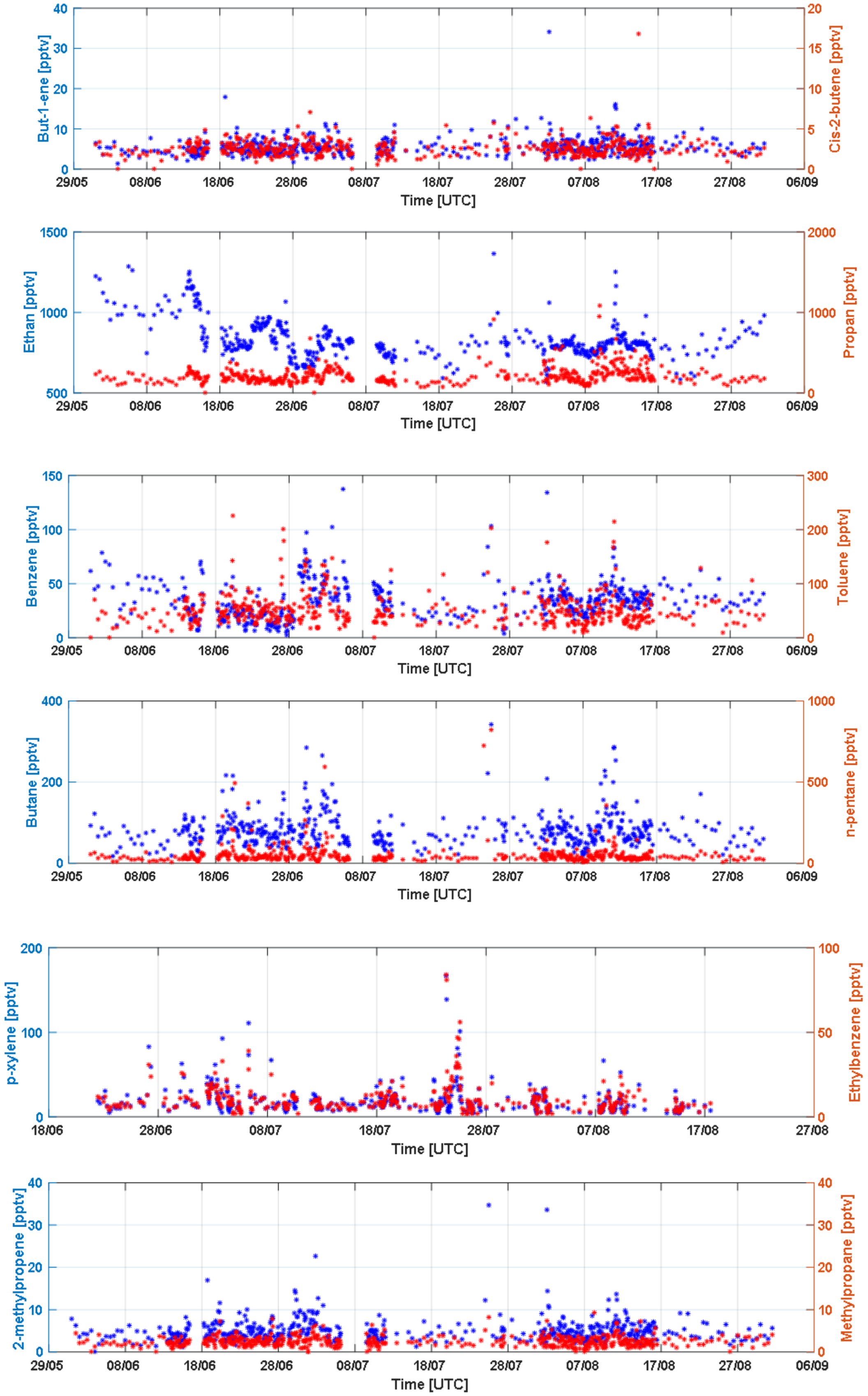


Figure SI-1, continued

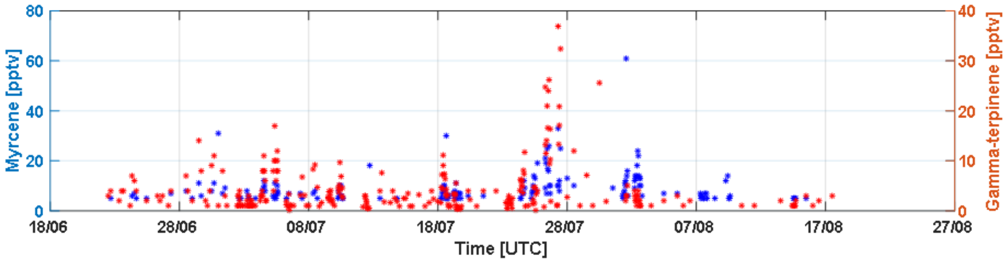


Figure SI-1, continued

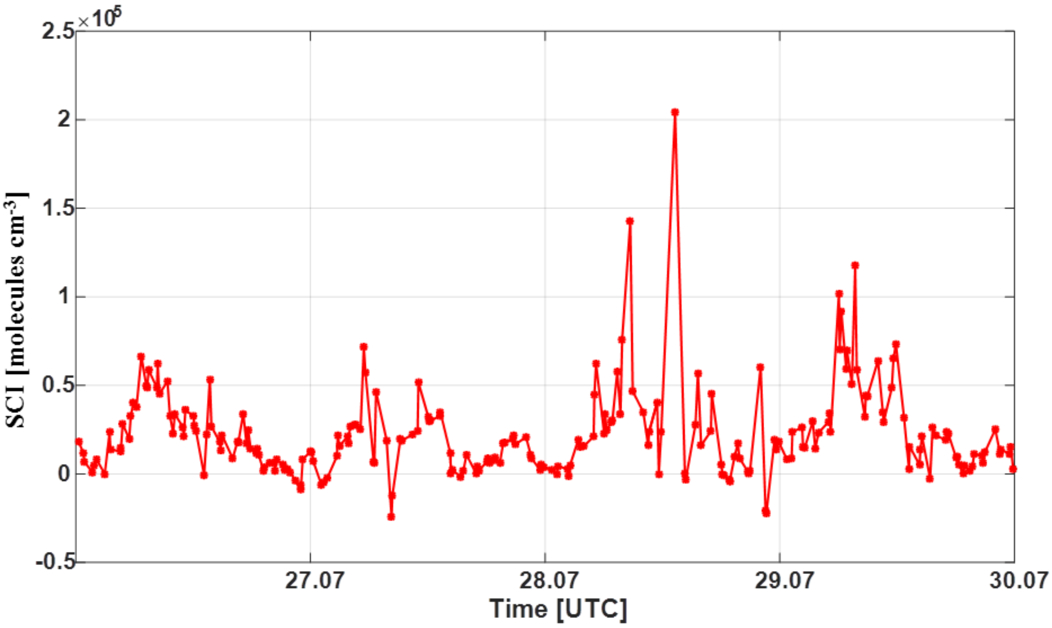


Figure SI-2. SCI time series as calculated from the sulfuric acid budget during the HUMPPA-COPEC 2010 campaign.

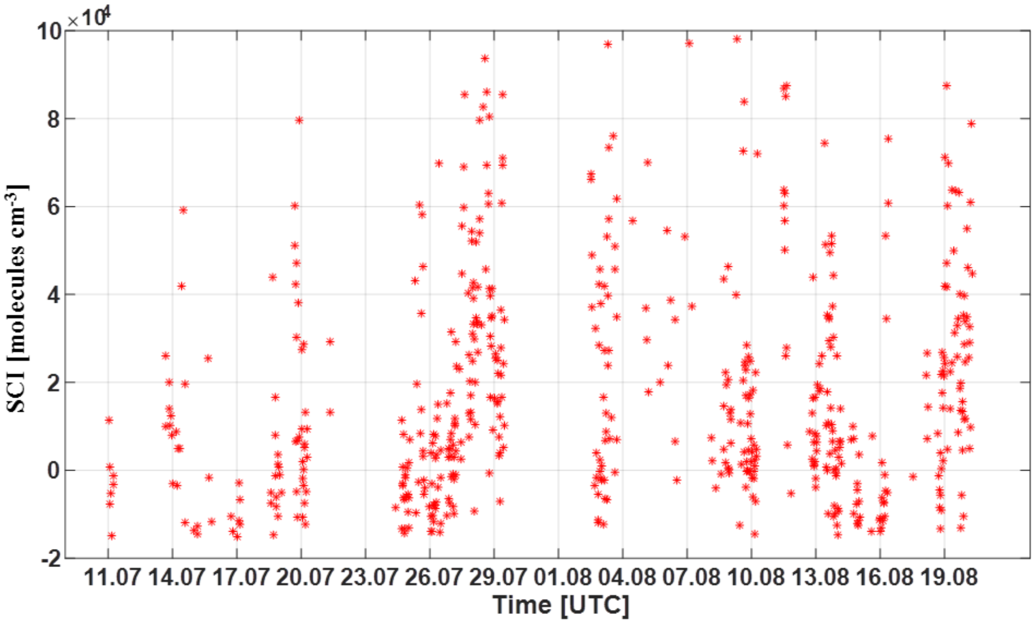


Figure SI-3. SCI time series as calculated from the sulfuric acid budget during the HOPE 2012 campaign.

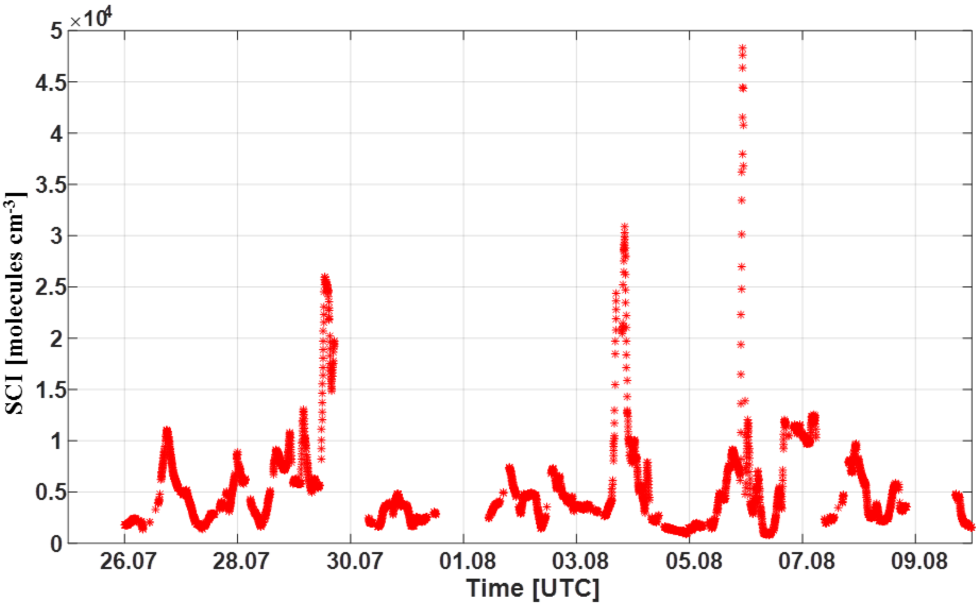


Figure SI-4. SCI time series as calculated from the measured unsaturated VOC during the HUMPPA-COPEC 2010 campaign.

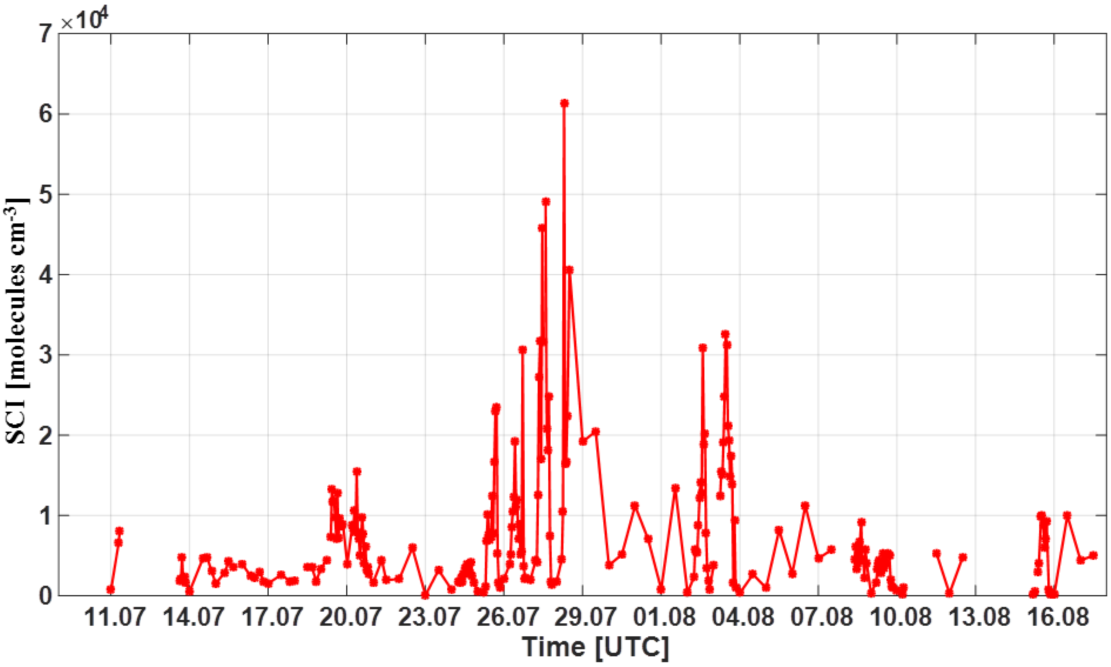


Figure SI-5. SCI time series as calculated from the measured unsaturated VOC during the HOPE 2012 campaign.

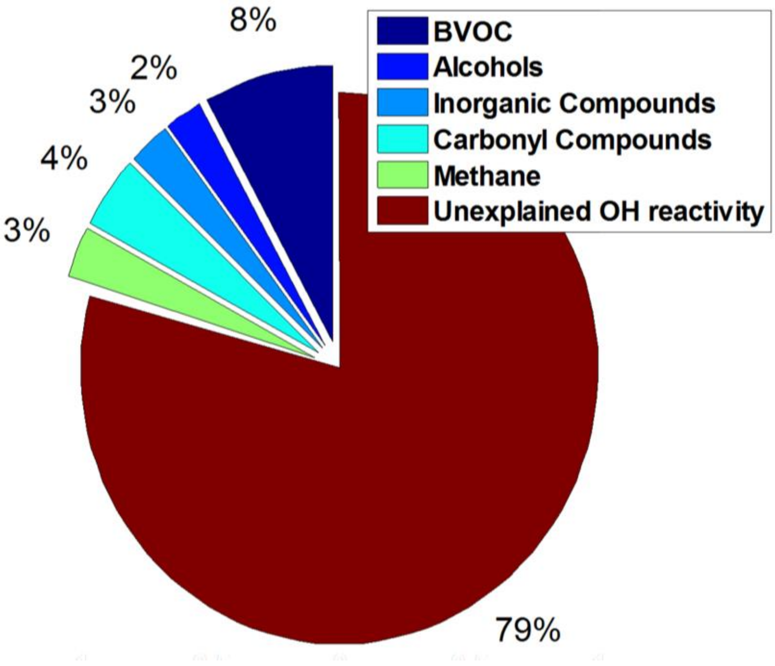


Figure SI-6. Contributions of measured trace gases to the measured OH reactivity during the HUMPPA-COPEC 2010.

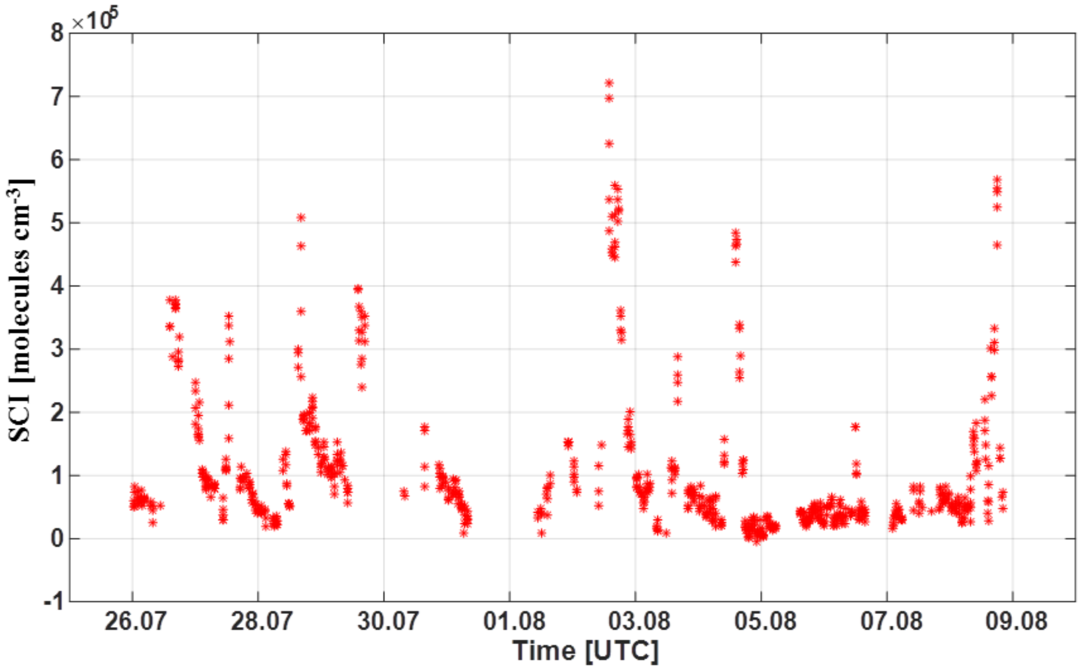


Figure SI-7. SCI time series as calculated from the unexplained OH reactivity during the HUMPPA-COPEC 2010 campaign.

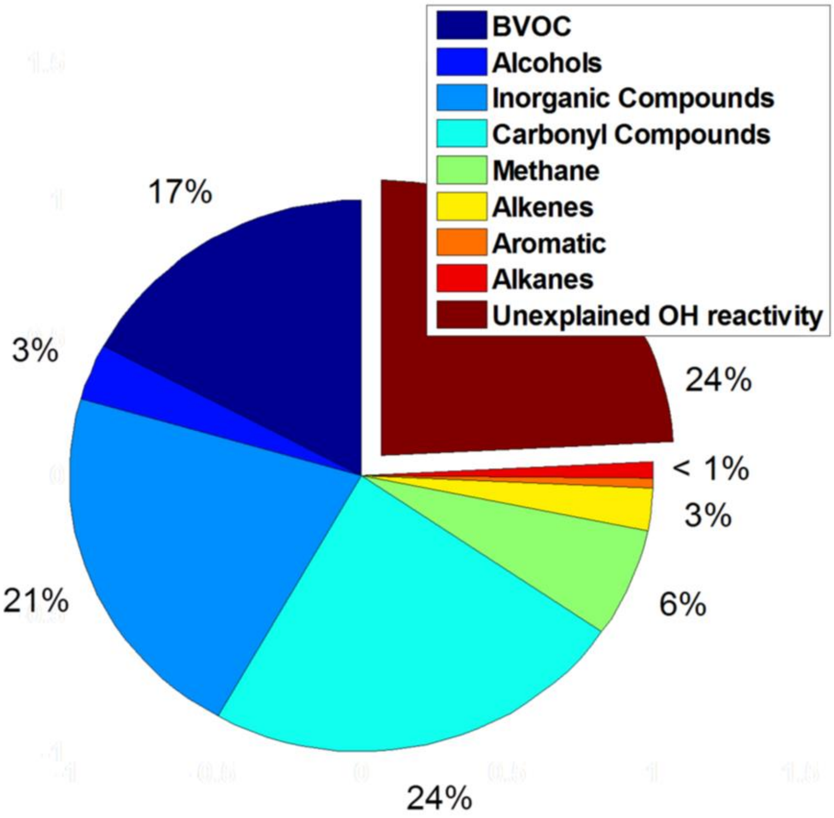


Figure SI-8. Contributions of measured trace gases to the measured OH reactivity during the HOPE 2012.

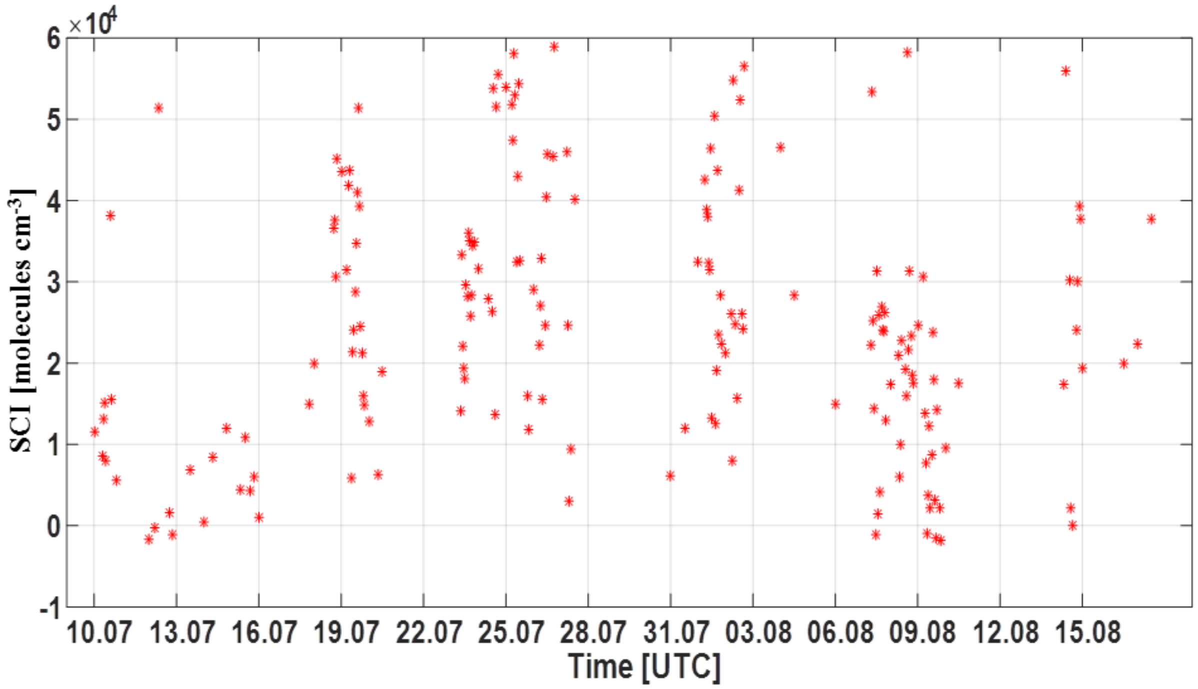


Figure SI-9. SCI time series as calculated from the unexplained OH reactivity during the HOPE 2012 campaign.

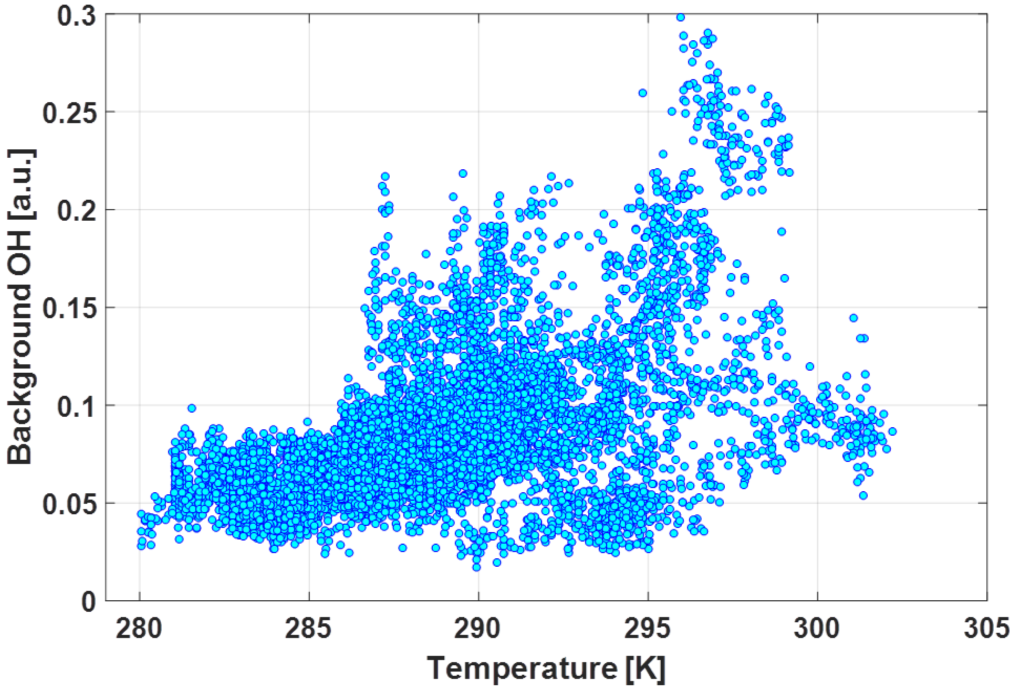


Figure SI-10. Background OH as a function of temperature during the HOPE 2012 campaign.

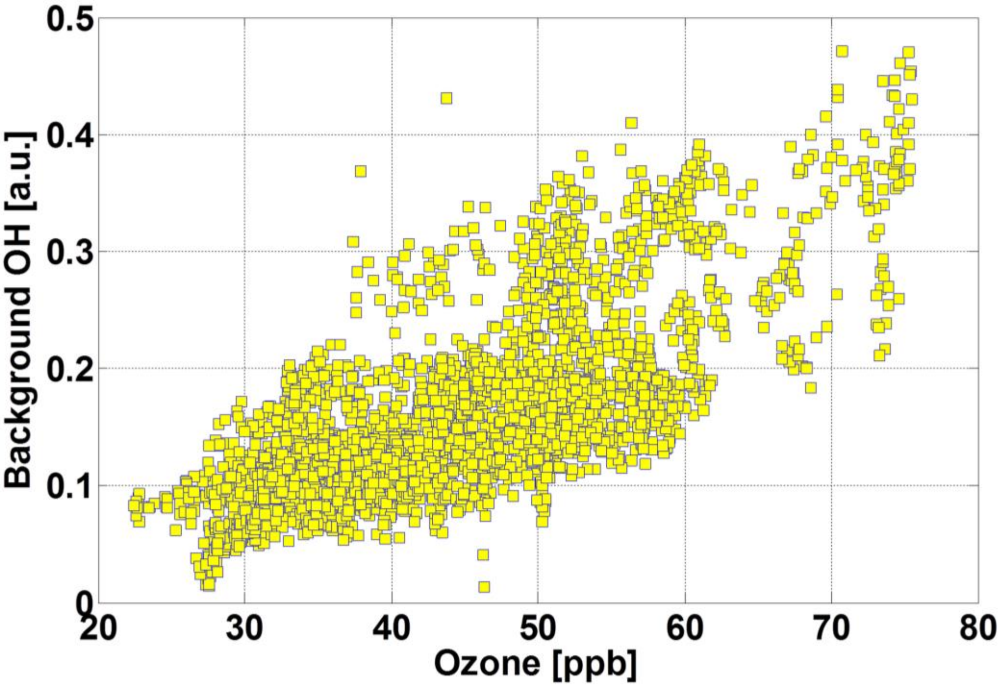


Figure SI-11. Background OH as a function of the ozone concentration during the HUMPPA-COPEC 2010 campaign.

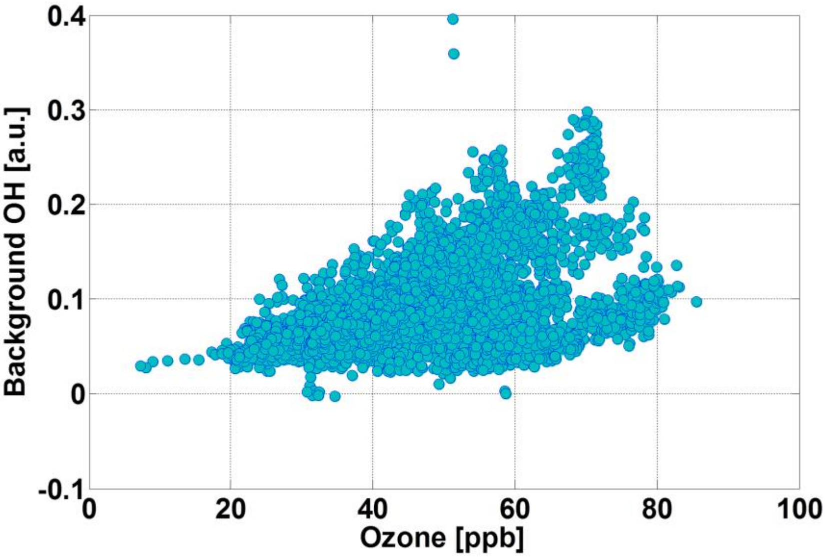


Figure SI-12. Background OH signal as a function of ozone concentration during the HOPE 2012 campaign.

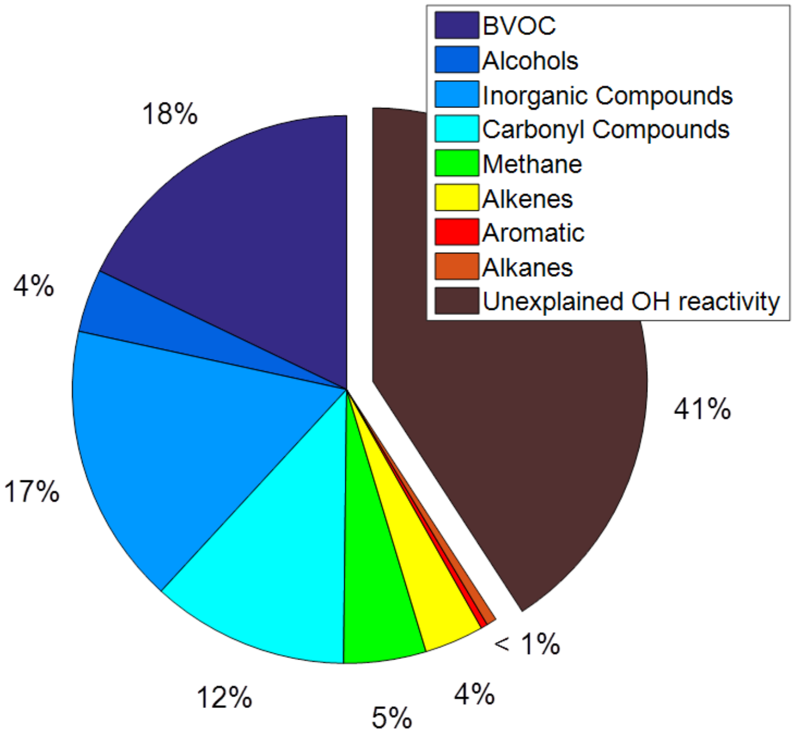


Figure SI-13. Contribution of measured trace gases to the measured OH reactivity during HOPE 2012 between the 1st and 3rd of August 2012.

References

Adeniji, S. A., Kerr, J. A., and Williams, M. R.: Rate constants for ozone–alkene reactions under atmospheric conditions, Int J Chem Kinet, 13, 209-217, 10.1002/kin.550130210, 1981.

Ahrens, J., Carlsson, P. T., Hertl, N., Olzmann, M., Pfeifle, M., Wolf, J. L., and Zeuch, T.: Infrared detection of Criegee intermediates formed during the ozonolysis of beta-pinene and their reactivity towards sulfur dioxide, Angew Chem Int Ed Engl, 53, 715-719, 10.1002/anie.201307327, 2014.

Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chemical Reviews, 103, 4605-4638, 10.1021/cr0206420, 2003.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species, Atmos. Chem. Phys., 4, 1461-1738, 10.5194/acp-4-1461-2004, 2004.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, 10.5194/acp-6-3625-2006, 2006.

Berndt, T., Jokinen, T., Mauldin, R. L., Petaja, T., Herrmann, H., Junninen, H., Paasonen, P., Worsnop, D. R., and Sipila, M.: Gas-Phase Ozonolysis of Selected Olefins: The Yield of Stabilized Criegee Intermediate and the Reactivity toward SO_2, J. Phys. Chem. Lett., 3, 2892-2896, 10.1021/jz301158u, 2012.

Berndt, T., Jokinen, T., Sipilä, M., Mauldin Iii, R. L., Herrmann, H., Stratmann, F., Junninen, H., and Kulmala, M.: H_2SO_4 formation from the gas-phase reaction of stabilized Criegee Intermediates with SO_2: Influence of water vapour content and temperature, Atmos Environ, 89, 603-612, http://dx.doi.org/10.1016/j.atmosenv.2014.02.062, 2014.

Braure, T., Bedjanian, Y., Romanias, M. N., Morin, J., Riffault, V., Tomas, A., and Coddeville, P.: Experimental Study of the Reactions of Limonene with OH and OD Radicals: Kinetics and Products, The Journal of Physical Chemistry A, 118, 9482-9490, 10.1021/jp507180g, 2014.

Buras, Z. J., Elsamra, R. M., Jalan, A., Middaugh, J. E., and Green, W. H.: Direct kinetic measurements of reactions between the simplest Criegee intermediate CH_2OO and alkenes, J Phys Chem A, 118, 1997-2006, 10.1021/jp4118985, 2014.

Carlsson, P. T. M., Keunecke, C., Kruger, B. C., Maa, and Zeuch, T.: Sulfur dioxide oxidation induced mechanistic branching and particle formation during the ozonolysis of ß-pinene and 2-butene, Phys Chem Chem Phys, 14, 15637-15640, 2012.

Chhantyal-Pun, R., Davey, A., Shallcross, D. E., Percival, C. J., and Orr-Ewing, A. J.: A kinetic study of the CH_2OO Criegee intermediate self-reaction, reaction with SO_2 and unimolecular reaction using cavity ring-down spectroscopy, Phys Chem Chem Phys, 10.1039/c4cp04198d, 2015.

Chhantyal-Pun, R., Welz, O., Savee, J. D., Eskola, A. J., Lee, E. P. F., Blacker, L., Hill, H. R., Ashcroft, M., Khan, M. A. H. H., Lloyd-Jones, G. C., Evans, L. A., Rotavera, B., Huang, H., Osborn, D. L., Mok, D. K. W., Dyke, J. M., Shallcross, D. E., Percival, C. J., Orr-Ewing, A. J., and Taatjes, C. A.: Direct Measurements of Unimolecular and Bimolecular Reaction Kinetics of the Criegee Intermediate (CH3)2COO, The Journal of Physical Chemistry A, 10.1021/acs.jpca.6b07810, 2016.

Donahue, N. M., Drozd, G. T., Epstein, S. A., Presto, A. A., and Kroll, J. H.: Adventures in ozoneland: down the rabbit-hole, Phys Chem Chem Phys, 13, 10848-10857, 10.1039/c0cp02564j, 2011.

Foreman, E. S., Kapnas, K. M., and Murray, C.: Reactions between Criegee Intermediates and the Inorganic Acids HCl and HNO3: Kinetics and Atmospheric Implications, Angewandte Chemie International Edition, n/a-n/a, 10.1002/anie.201604662, 2016.

Hites, R. A., and Turner, A. M.: Rate constants for the gas-phase β-myrcene + OH and isoprene + OH reactions as a function of temperature, Int J Chem Kinet, 41, 407-413, 10.1002/kin.20413, 2009.

Huang, H.-L., Chao, W., and Lin, J. J.-M.: Kinetics of a Criegee intermediate that would survive high humidity and may oxidize atmospheric SO2, Proceedings of the National Academy of Sciences, 10.1073/pnas.1513149112, 2015.

Jiang, L., Xu, Y.-s., and Ding, A.-z.: Reaction of Stabilized Criegee Intermediates from Ozonolysis of Limonene with Sulfur Dioxide: Ab Initio and DFT Study, The Journal of Physical Chemistry A, 114, 12452-12461, 10.1021/jp107783z, 2010.

Kurtén, T., Lane, J. R., Jørgensen, S., and Kjaergaard, H. G.: A Computational Study of the Oxidation of SO2 to SO3 by Gas-Phase Organic Oxidants, The Journal of Physical Chemistry A, 115, 8669-8681, 10.1021/jp203907d, 2011.

Kuwata, K. T., Guinn, E. J., Hermes, M. R., Fernandez, J. A., Mathison, J. M., and Huang, K.: A Computational Re-examination of the Criegee Intermediate–Sulfur Dioxide Reaction, The Journal of Physical Chemistry A, 119, 10316-10335, 10.1021/acs.jpca.5b06565, 2015.

Lewis, T. R., Blitz, M., Heard, D. E., and Seakins, P.: Direct evidence for a substantive reaction between the C1 Criegee radical, CH2OO, and the water vapour dimer, Phys Chem Chem Phys, 10.1039/c4cp04750h, 2015.

Liu, F., Beames, J. M., Green, A. M., and Lester, M. I.: UV spectroscopic characterization of dimethyl- and ethyl-substituted carbonyl oxides, J Phys Chem A, 118, 2298-2306, 10.1021/jp412726z, 2014a.

Liu, Y., Bayes, K. D., and Sander, S. P.: Measuring rate constants for reactions of the simplest Criegee intermediate (CH_2OO) by monitoring the OH radical, J Phys Chem A, 118, 741-747, 10.1021/jp407058b, 2014b.

Mauldin III, R. L., Berndt, T., Sipila, M., Paasonen, P., Petaja, T., Kim, S., Kurten, T., Stratmann, F., Kerminen, V. M., and Kulmala, M.: A new atmospherically relevant oxidant of sulphur dioxide, Nature, 488, 193-196, http://www.nature.com/nature/journal/v488/n7410/abs/nature11278.html#supplementary-information, 2012.

Newland, M. J., Rickard, A. R., Alam, M. S., Vereecken, L., Munoz, A., Rodenas, M., and Bloss, W. J.: Kinetics of stabilised Criegee intermediates derived from alkene ozonolysis: reactions with SO2, H2O and decomposition under boundary layer conditions, Phys Chem Chem Phys, 10.1039/c4cp04186k, 2015a.

Newland, M. J., Rickard, A. R., Vereecken, L., Muñoz, A., Ródenas, M., and Bloss, W. J.: Atmospheric isoprene ozonolysis: impacts of stabilised Criegee intermediate reactions with SO_2, H_2O and dimethyl sulfide, Atmos. Chem. Phys., 15, 9521-9536, 10.5194/acp-15-9521-2015, 2015b.

Novelli, A., Vereecken, L., Lelieveld, J., and Harder, H.: Direct observation of OH formation from stabilised Criegee intermediates, Phys Chem Chem Phys, 16, 19941-19951, 10.1039/c4cp02719a, 2014.

Ouyang, B., McLeod, M. W., Jones, R. L., and Bloss, W. J.: NO_3 radical production from the reaction between the Criegee intermediate CH_2OO and NO_2, Phys Chem Chem Phys, 15, 17070-17075, 10.1039/c3cp53024h, 2013.

Sheps, L., Scully, A. M., and Au, K.: UV absorption probing of the conformer-dependent reactivity of a Criegee intermediate CH_3CHOO, Phys Chem Chem Phys, 10.1039/c4cp04408h, 2014.

Stone, D., Blitz, M., Daubney, L., Howes, N. U., and Seakins, P.: Kinetics of CH_2OO reactions with SO_2, NO_2, NO, H_2O and CH_3CHO as a function of pressure, Phys Chem Chem Phys, 16, 1139-1149, 10.1039/c3cp54391a, 2014.

Taatjes, C. A., Welz, O., Eskola, A. J., Savee, J. D., Scheer, A. M., Shallcross, D. E., Rotavera, B., Lee, E. P., Dyke, J. M., Mok, D. K., Osborn, D. L., and Percival, C. J.: Direct measurements of conformer-dependent reactivity of the Criegee intermediate CH_3CHOO, Science, 340, 177-180, 10.1126/science.1234689, 2013.

Teruel, M. A., Lane, S. I., Mellouki, A., Solignac, G., and Le Bras, G.: OH reaction rate constants and UV absorption cross-sections of unsaturated esters, Atmos Environ, 40, 3764-3772, http://dx.doi.org/10.1016/j.atmosenv.2006.03.003, 2006.

Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO, RO_2, and SO_2, and their fate in the atmosphere, Phys Chem Chem Phys, 14, 14682-14695, 10.1039/c2cp42300f, 2012.

Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Direct Kinetic Measurements of Criegee Intermediate (CH_2OO) Formed by Reaction of CH_2I with O_2, Science, 335, 204-207, 10.1126/science.1213229, 2012.

Welz, O., Eskola, A. J., Sheps, L., Rotavera, B., Savee, J. D., Scheer, A. M., Osborn, D. L., Lowe, D., Murray Booth, A., Xiao, P., Anwar H. Khan, M., Percival, C. J., Shallcross, D. E., and Taatjes, C. A.: Rate Coefficients of C1 and C2 Criegee Intermediate Reactions with Formic and Acetic Acid Near the Collision Limit: Direct Kinetics Measurements and Atmospheric Implications, Angewandte Chemie, 126, 4635-4638, 10.1002/ange.201400964, 2014.

Zhu, C., Kumar, M., Zhong, J., Li, L., Francisco, J. S., and Zeng, X. C.: New Mechanistic Pathways for Criegee–Water Chemistry at the Air/Water Interface, J Am Chem Soc, 10.1021/jacs.6b04338, 2016.