Direct observation of OH formation from stabilised Criegee intermediates

Supporting information

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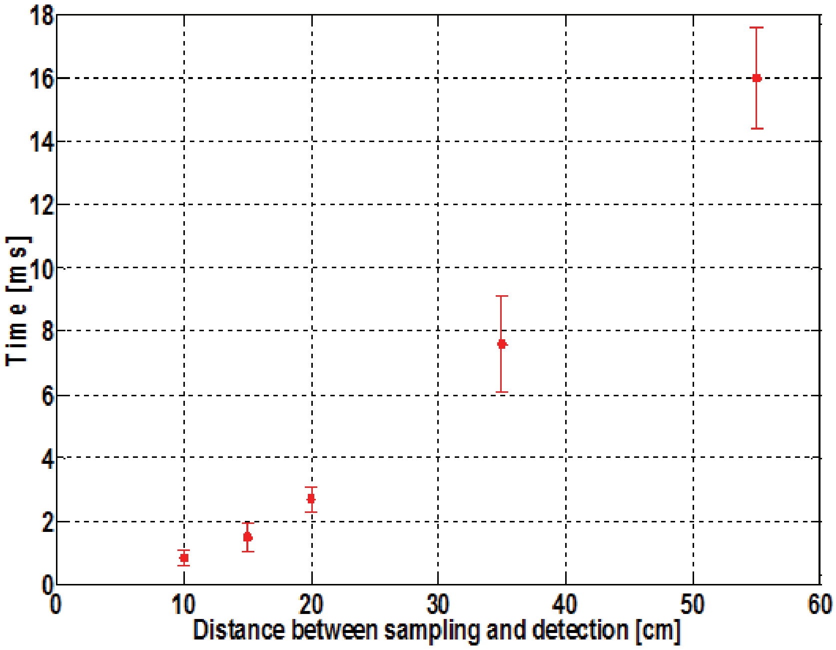

Figure SI-1. Residence time between the sampling point and the detection of OH radicals for five different inlet lengths.

HO_x losses

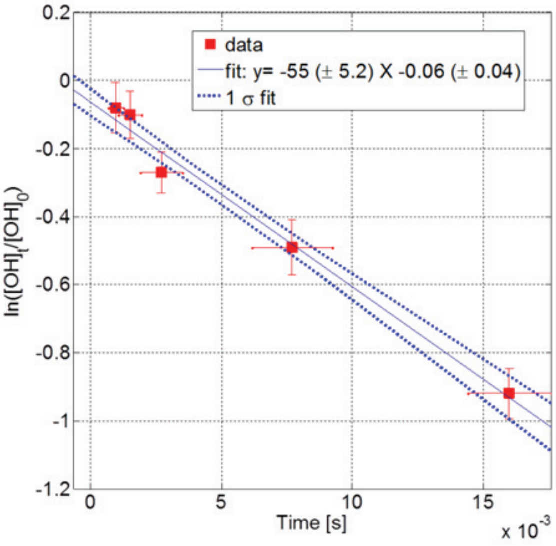

Figure SI-2. Wall loss of OH with residence time in the low-pressure segment of the LIF-FAGE instrument.

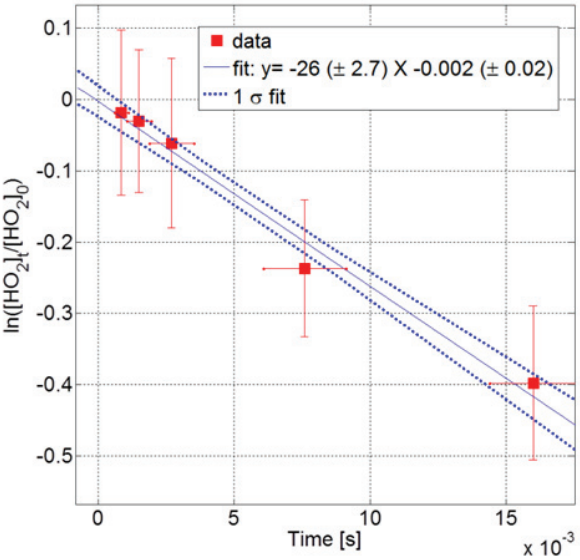

Figure SI-3. Wall loss of HO_2 with residence time in the low-pressure segment of the LIF-FAGE instrument.

Propene + Ozone – Additional figures and table

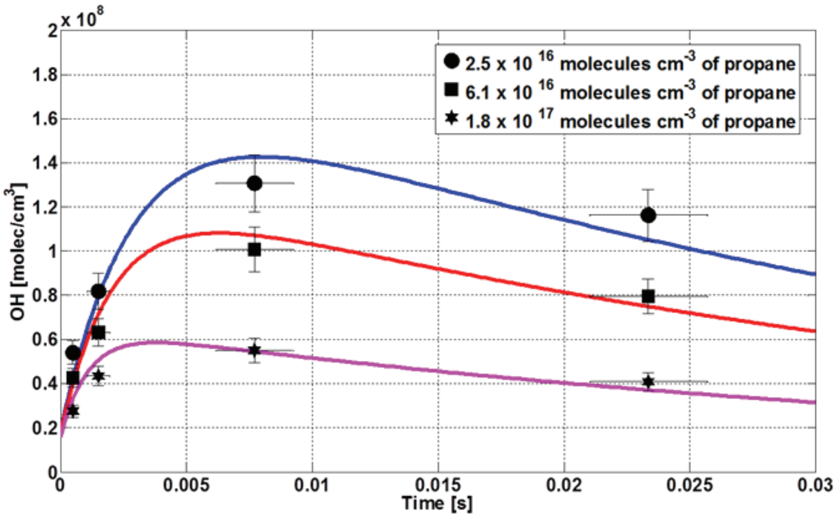

Figure SI-4. Temporal profiles of the OH signal (solid symbols) inside the detection cell of the LIF-FAGE instrument for the ozonolysis reaction of propene (3.5 x 10^{15} molecules cm^{-3}) and model simulations (lines) for three different concentrations of propane.

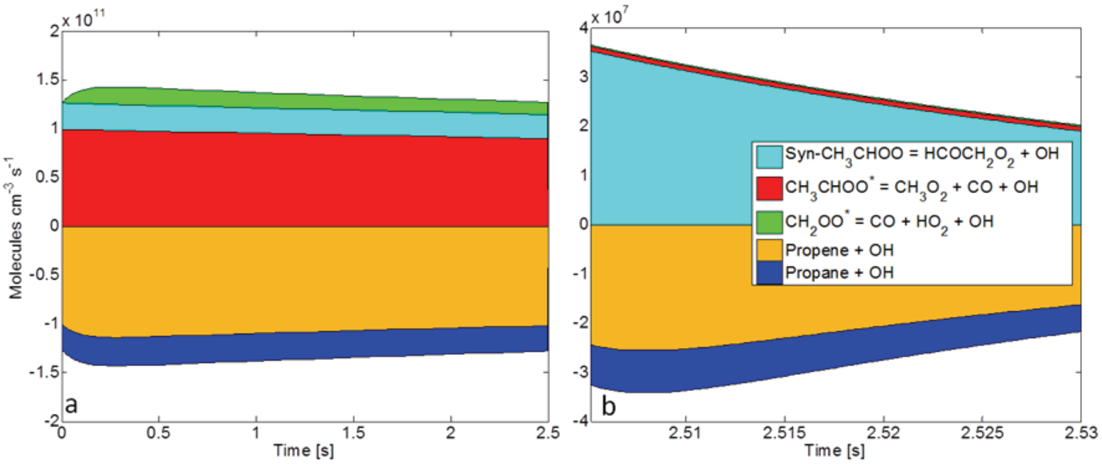

Figure SI-5. a, cumulative formation (positive contribution) and loss (negative contribution) pathways of OH in the flow tube at ambient pressure and b, formation and loss path of OH in the instrument inlet at ~ 3.5 hPa during the ozonolysis of propene.

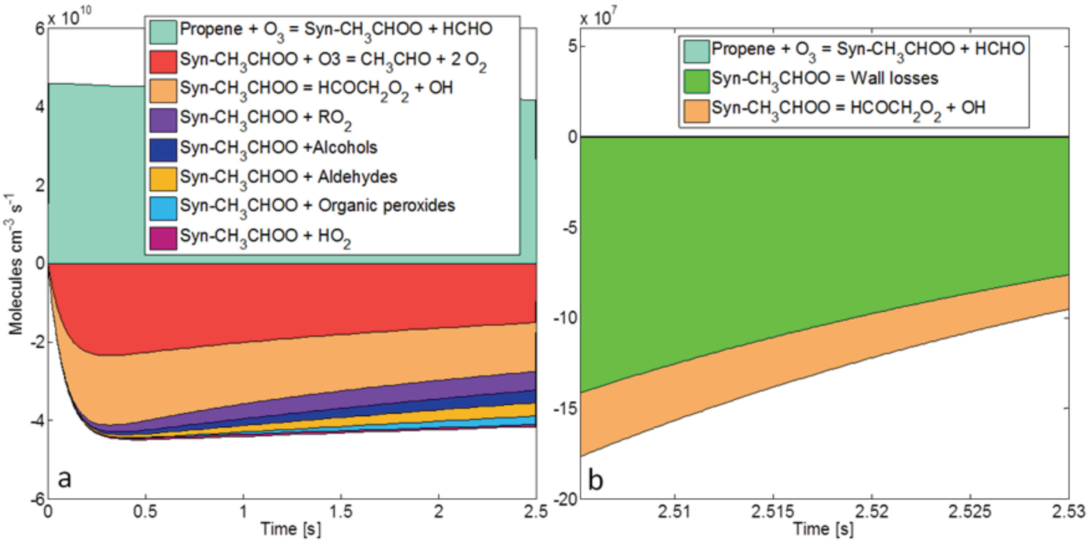

Figure SI-6. a, cumulative formation (positive contribution) and loss (negative contribution) pathway of *syn*-CH_3CHOO in the flow tube at ambient pressure and b, formation and loss path of *syn*-CH_3CHOO in the instrument inlet at ~ 3.5 hPa during the ozonolysis of propene.

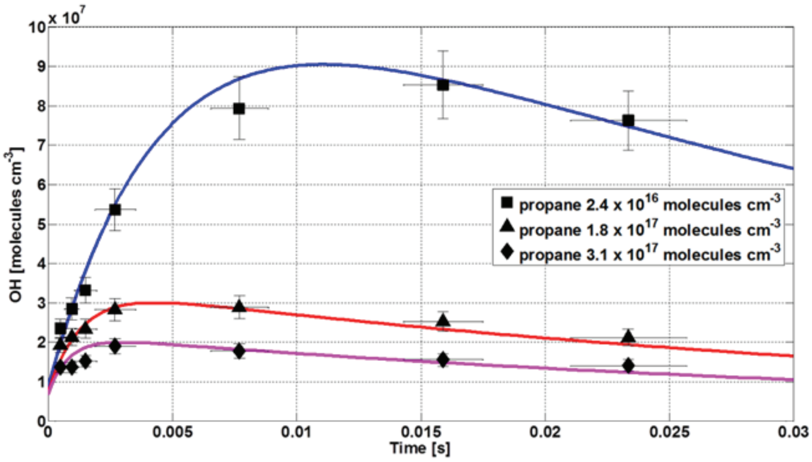

Figure SI-7. Temporal profiles of the OH signal (solid symbols) inside the detection cell of the LIF-FAGE instrument for the ozonolysis reaction of propene (1.8 x 10^{15} molecules cm^{-3}) and model simulations (lines) for three different concentrations of propane.

Table SI 1. Concentrations (molecules cm^{-3}) of SCIs at the sampling point together with the peak OH concentration observed during the ozonolysis experiments.

Propene	**Propane**	***Syn*-CH_3CHOO**	***Anti*-CH_3CHOO**	**CH_2OO**	**OH**
3.5×10^{15}	2.5×10^{16}	1.8×10^{9}	2.5×10^{8}	4.1×10^{9}	1.3×10^{8}
	6.1×10^{16}	1.8×10^{9}	2.5×10^{8}	4.2×10^{9}	1.0×10^{8}
	1.8×10^{17}	1.6×10^{9}	2.5×10^{8}	4.2×10^{9}	5.7×10^{7}
1.8×10^{15}	2.5×10^{16}	9.3×10^{8}	1.6×10^{8}	1.3×10^{9}	8.5×10^{7}
	1.8×10^{17}	9.3×10^{8}	1.6×10^{8}	1.3×10^{8}	3.0×10^{7}
	3.0×10^{17}	9.3×10^{8}	1.6×10^{8}	1.3×10^{8}	2.0×10^{7}

(E)-2-butene + Ozone – Additional figures and table

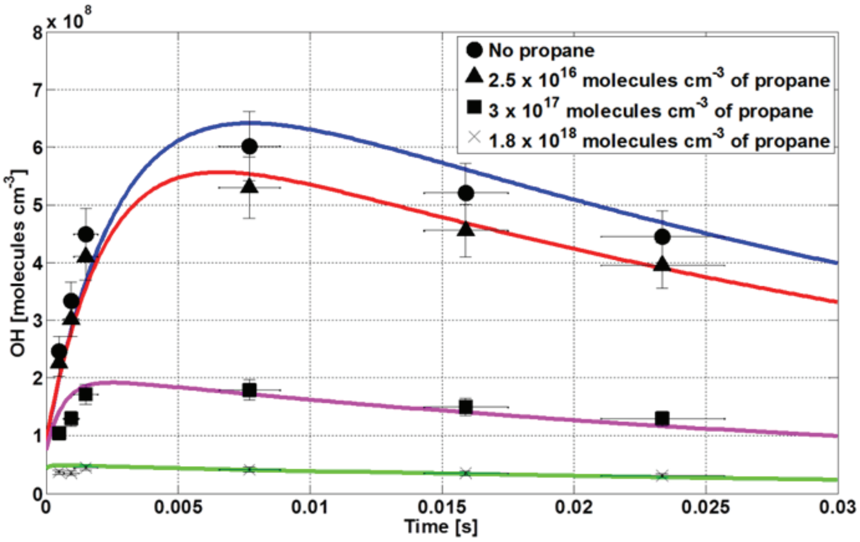

Figure SI-8. Temporal profiles of the OH signal (solid symbols) inside the detection cell of the LIF-FAGE instrument for the ozonolysis reaction of (E)-2-butene (1.4 x 10^{15} molecules cm^{-3}) and model simulations (lines) for four different concentrations of propane.

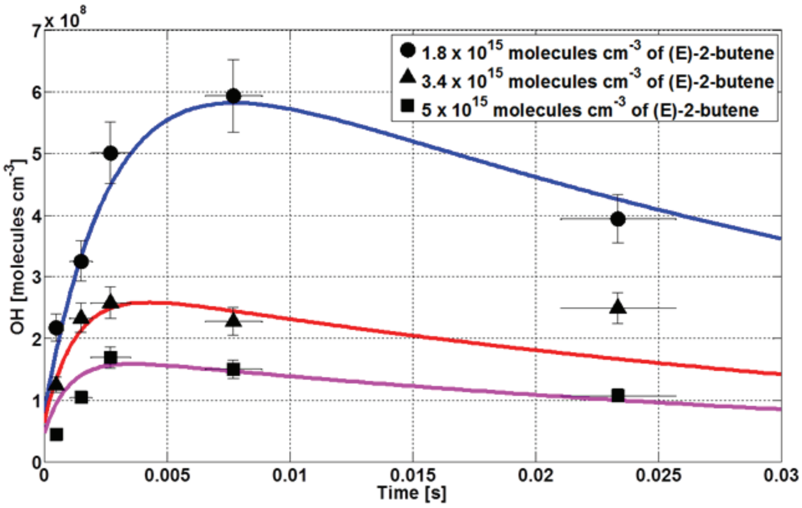

Figure SI-9. Temporal profiles of the OH signal (solid symbols) inside the detection cell of the LIF-FAGE instrument for the ozonolysis reaction of (E)-2-butene and model simulations (lines) for three different concentrations of (E)-2-butene at a constant concentration of propane of 2.5 x 10^{16} molecules cm^{-3}.

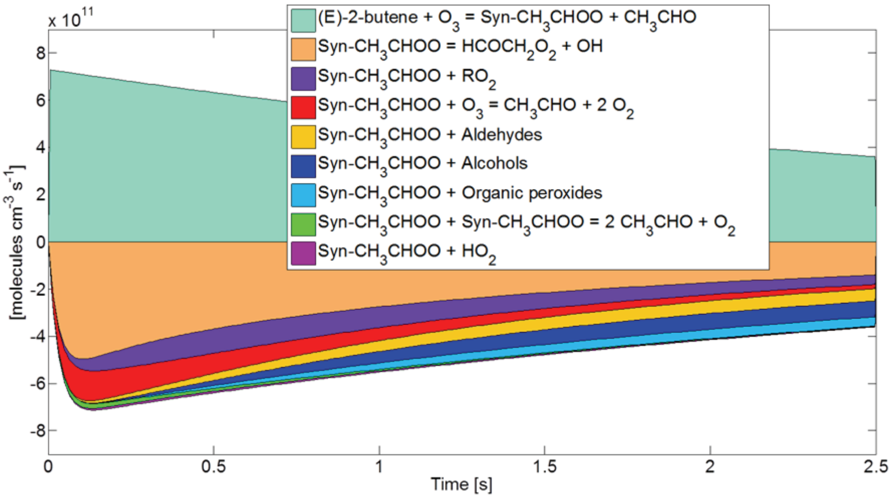

Figure SI-10. Cumulative formation (positive contribution) and loss path (negative contribution) of *syn*-CH_3CHOO in the flow tube at ambient pressure and b, formation and loss path of *syn*-CH_3CHOO in the instrument inlet at ~ 3.5 hPa during the ozonolysis of (E)-2-butene.

Table SI 2. Concentrations (molecules cm^{-3}) of SCIs at the sampling point together with the peak OH concentration observed during the ozonolysis experiments.

(E)-2-butene	Propane	*Syn*-CH_3CHOO	*Anti*-CH_3CHOO	OH
1.4×10^{15}	0	9.2×10^{9}	2.2×10^{9}	6.0×10^{8}
	2.5×10^{16}	9.0×10^{9}	2.2×10^{9}	5.3×10^{8}
	3.0×10^{17}	9.5×10^{9}	2.4×10^{9}	2.9×10^{8}
	1.8×10^{18}	9.7×10^{9}	2.4×10^{9}	5.8×10^{8}
1.8×10^{15}	2.5×10^{16}	9.2×10^{9}	9.0×10^{9}	5.9×10^{8}
3.4×10^{15}		9.0×10^{9}	6.8×10^{9}	2.5×10^{8}
5.0×10^{15}		9.5×10^{9}	4.4×10^{9}	1.8×10^{8}

Ethene + Ozone – Additional figures

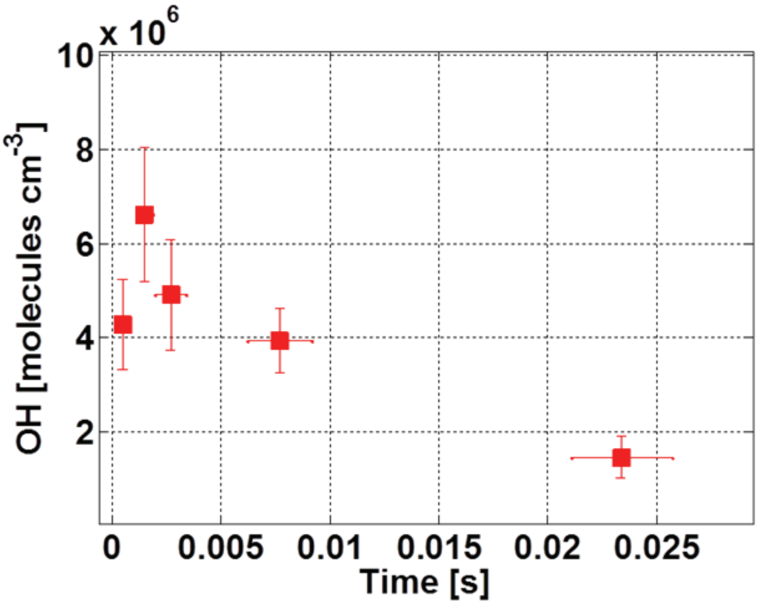

Figure SI-11. Temporal profile of the OH signal (red squares) inside the detection cell of the LIF-FAGE instrument for the ozonolysis reaction of ethene.

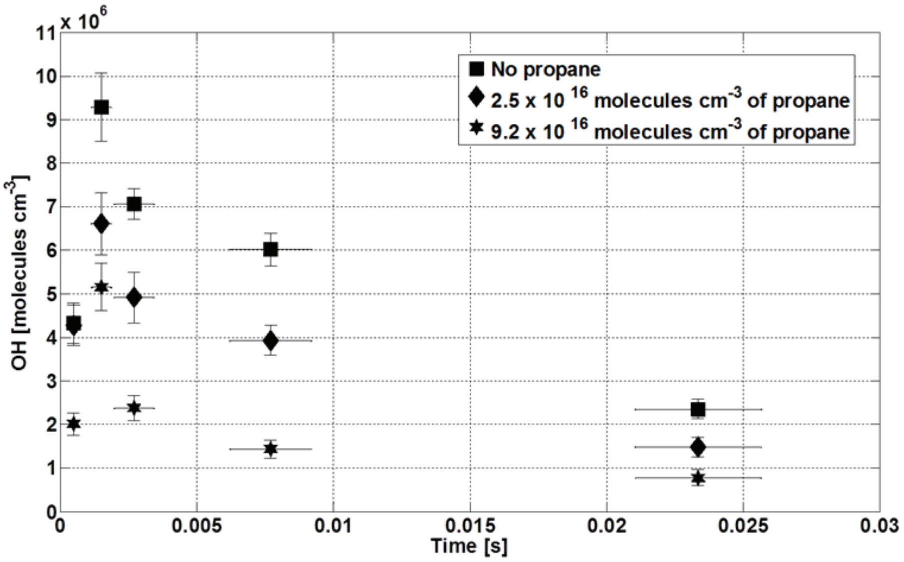

Figure SI-12. Temporal profiles of the OH signal (solid symbols) inside the detection cell of the LIF-FAGE instrument for the ozonolysis reaction of ethene (1.1 x 10^{16} molecules cm^{-3}) for three different concentrations of propane.

SCI + Scavengers – Additional figures

1. Scavenging experiment with water vapor

Figure SI-13 presents model simulations for three assumed rate coefficients of the reaction between *syn*-CH_3CHOO and water monomers and dimers. In these simulations, the ratio of k(H_2O) and k(($H_2O)_2$) is maintained as derived from Ryzhkov and Ariya[1] as detailed in the main text, while the ratio $[(H_2O)_2]/[H_2O]$ is obtained by the equilibrium constant for dimerization.[2] The best agreement is obtained for a rate coefficient between *syn*-CH_3CHOO and H_2O of ~ 3 x 10^{-17} cm^3 $molecules^{-1}$ s^{-1}, in agreement with the upper limit of 4 x 10^{-15} cm^3 $molecules^{-1}$ s^{-1} measured by Taatjes, et al.[3] The last experimental point at the highest humidity level (RH 46%) is not reproduced by the model simulation suggesting that the rate coefficient used for the *syn*-CH_3CHOO + $(H_2O)_2$ is too high, i.e. that the acceleration factor of 1.6 x 10^5 compared to the rate coefficient with water monomers (based on Ryzhkov and Ariya[1]), could be overestimated.

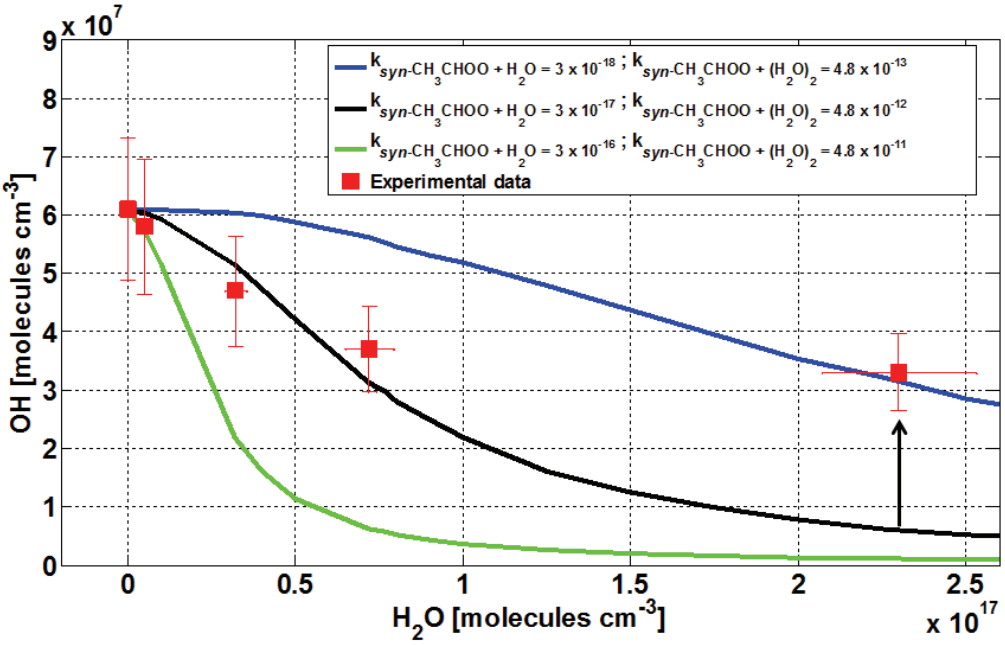

Figure SI-13. OH concentration observed at 2.4 ms as a function of water vapour (red square) together with model simulations (lines) for three different rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) between *syn*-CH_3CHOO and water monomers and dimers.

2. Scavenging experiment with SO_2

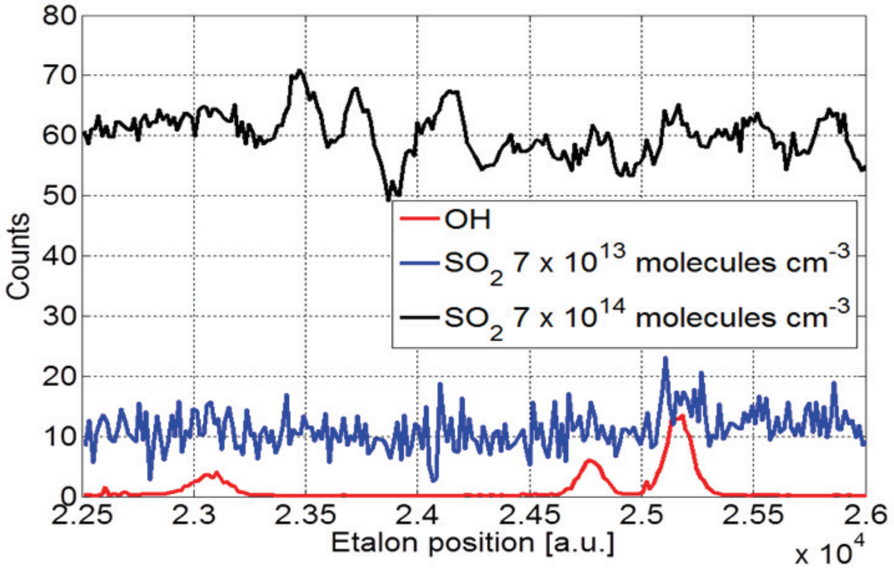

Figure SI-14. Fluorescence spectra at around 308 nm during ozonolysis of alkenes (red line), with the addition of 7 x 10^{13} molecules cm^{-3} (blue line) and 7 x 10^{14} molecules cm^{-3} (black line) of SO_2.

From Figure SI-14, it follows that the impact of SO_2 on the OH measurements cannot be easily subtracted. The measurement of the OH concentration is performed by tuning the excitation laser on and off resonance with the transition line at 308 nm (the high red peak in figure SI-14), thus allowing removal of the spectral background from the pure OH signal.

With SO_2 added, the signal differences between the on-resonance and off-resonance frequencies are not a straightforward superposition of an OH signal and a linearly increasing spectral background caused by SO_2, other compounds, and instrumental noise. In particular, the overall spectrum changes qualitatively with increasing [SO_2], i.e. the position and shape of the peaks changes as the contribution to the signal from each of the components changes with changing SO_2. As such, the spectral background measured off-resonance is not necessarily equal to the background signal underneath the on-resonance OH peak, nor can it be reduced to a fixed ratio between the two wavelengths employed. This occurs to a significant extent even for the lowest

SO_2 concentrations we used. As such, the subtracted signals obtained in these conditions are not a true measure of the OH concentration.

What can be observed from the spectra is that the OH peak is significantly reduced or even removed entirely even at the lowest SO_2 concentrations, i.e. the peak signal at 308 nm should be clearly visible above the noisy spectral background for $[SO_2] = 7 \times 10^{-13}$ molecules cm^{-3} if the OH concentration would remain unaffected. This loss of OH is corroborated by the model predictions which, using a rate coefficient k(*syn*-$CH_3CHOO+SO_2$) = 2.4×10^{-11} cm^3 $molecules^{-1}$ s^{-1},[3] predict a 100-fold decrease in *syn*-CH_3CHOO and concomitant OH decrease, i.e. at these SO_2 concentration the OH peak is expected to be near-vanishing in the spectrum, contributing only 1% of the signal for $[SO_2] = 7 \times 10^{-13}$ molecules cm^{-3} (blue curve, SI-14). Note that SO_2 does not react with OH directly, either in the high- or low-pressure regimes, and the lack of OH peak is thus directly related to removal of *syn*-CH_3CHOO by SO_2 in the high-pressure flow tube, removing the *syn*-CH_3CHOO decomposition as the OH source in the low-pressure cell.

A quantitative analysis might be possible using significantly lower concentrations of SO_2, provided a concentration range can be found where the spectral background caused by SO_2 remains negligible, while the *syn*-CH_3CHOO is still sufficiently scavenged to cause a measurable reduction in OH signal.

3. Scavenging experiment with acetic acid

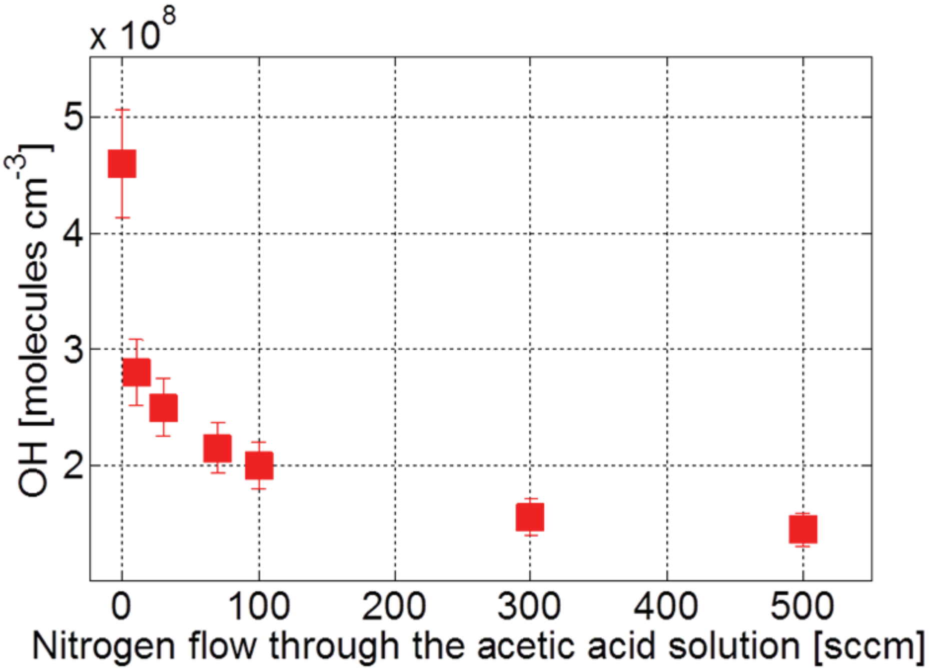

Figure SI-15. OH concentration observed at 2.4 ms as a function of acetic acid vapor.

Flow Tube Experiment – Kinetic Models

Ethene

Kinetic model added to the MCM chemistry to describe the CI chemistry in ethene ozonolysis, in Facsimile format. The MCM uses container species, i.e. class-specific-species that contain the sum of all individual species in this class, to describe certain reaction, e.g. for RO2. We have defined some additional container species to easily describe the generic reactions of CI with aldehyde, ketone, hydroxy, carboxylic acid and organic peroxide-compounds. These were calculated using the following MCM species names:

Ketones = CH3COCH3 + HCOCO3H + HCOCO2H + ACETOL + HYPERACET + IPROPOLPER + MGLYOX + CH3CO3H + GLYOX + HOC2H4CO3H + HOCH2CO3H + CH3CO2H + C2H5CO3 + CH3CHOHCO3 + CH3COCH2O + CO23C3CHO + HOC2H4CO3 + CH3COCH2O2;
Aldehydes = HCHO + CH3CHO + C2H5CHO + CH3CHOHCHO + HOCH2CHO + HOC2H4CHO + HCOCH2O + HCOCH2O2 + HCOCH2OOH;
Alcohols = CH3OH + C2H5OH + NPROPOL + IPROPOL + HOC2H4CO2H + ETHGLY + HYETHO2H + IPROPOLPER + IPROPOLO2H + HOC2H4CO3H + PROPGLY + CH3CHOHCHO + HOCH2CO2H + HO1C3OOH + HOC3H6OH + HOCH2CHO + C4ME22OH + HOC2H4CHO + HYPROPO2H + C4ME2OHOOH + ACETOL + HOCH2CO3H + CH3CHOHCO3 + HO1C3O + HO1C3O2 + HO1C3OOH + HOC2H4CO3 + HOCH2CH2O + HOCH2CH2O2 + HOCH2CO3 + HYPROPO2 + ETHGLY + HYPROPO + IPROPOLO2;
Acids = HCOOH + CH3CO2H + PROPACID + HOC2H4CO2H + HCOCO2H + HOCH2CO2H + HCOCO3H + PERPROACID;
Organic peroxides = HYPERACET + IPROPOLPER + CH3CO3H + HYETHO2H + IPROPOLO2H + HOC2H4CO3H + HO1C3OOH + HYPROPO2H + C4ME2OHOOH + HOCH2CO3H + C2H5OOH + CH3OOH + H2O2 + HCOCH2OOH + HO1C3OOH + IC3H7OOH;

For some of the CI reactions, the fate of the products was not explicitly modeled, as they didn't accumulate to a sufficiently high concentration to affect the kinetics. Future work will include the secondary chemistry explicitly; in many cases, the CI reactions lead to oxygenated compounds that should be part of the RO2, Aldehydes, Ketones, Alcohols, Acids or Organic Peroxides container species.
Finally, to merge the model below with the MCM, some reactions need to be removed from the original MCM model, as they are redefined or altered in our more explicit model: C2H4 + O3, all CH2OOA reactions, all CH2OO reactions.

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* ------------------------------------------------------------------------------------------------------------ ;
* Novelli, Vereecken, Lelieveld and Harder, "Direct observation of OH formation from ;
* stabilised Criegee intermediates" PCCP, submitted 2014 ;
* -------------------------------------------------------------------------------------------------------------;
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* Ozonolysis reaction yields excited CI (reactions as per the MCM) ;
* or forms stabilized CI ;
* YCH2 = fraction of CI stabilized  ;

YCH2 = 0.4; * The fraction of SCI formed during ozonolysis;

% 9.1D-15*EXP(-2580/TEMP)*(1-YCH2E) : C2H4 + O3 = HCHO + CH2OOA ;
% 9.1D-15*EXP(-2580/TEMP) : C2H4 + O3 = HCHO + CH2OO ;

* The chemistry of the excited Criegee intermediates, CH2OOA ;
* is taken from the MCM;

% KDEC*0.54/(1-YCH2) : CH2OOA = CO ;
% KDEC*0.10/(1-YCH2) : CH2OOA = HO2 + CO + OH ;

* Rate coefficients for the reaction of CI are discussed in the main paper ;

KEth = 1;
KSO2   = 4D-11;
KAcids = 2D-10;
KRO2 = 5D-12;
KHO2 = 5D-12;
KKeton = 2.3D-13;
KAlde = 1D-12;
KPerox = 3D-12;
KOH = 5D-12;
KAlco = 5D-12;
KCO  = 4D-14;
KH2O = 2D-16;
KAlke = 6D-16;
KCriegee = 4D-10;
KOzone = 4D-13;
KDime = 7D-11;
KNO2 = 2D-12;
KWall = 22;

* Where feasible, the MCM products are specified. For other reactions, we define product sinks;
* whose secondary chemistry is not considered further at this stage, (i.e. SOZ, Oligomers        ;
* Product1/2/3/4/5), as in our conditions they do not accumulate to relevant concentrations.     ;

% KEth : CH2OO = Dioxirane;
% KCO: CH2OO + CO   = HCHO + CO2;
% KH2O: CH2OO + H2O  = HOCH2OOH;
% KSO2 : CH2OO + SO2  = SO3 ;
% KKeton : CH2OO + Ketones = SOZ;
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% KAlde : CH2OO + Aldehydes = SOZ;
% KPerox : CH2OO + Peroxides = Oligomers;
% KAlco : CH2OO + Alcohols = Product1;
% KHO2 : CH2OO + HO2 = Oligomers;
% KRO2 : CH2OO + RO2 = Oligomers;
% KAcids : CH2OO + Acids = Product2;
% KOH : CH2OO + OH  = Product3;
% KAlke : CH2OO + C2H4 = Product4;
% KCriegee : CH2OO + CH2OO = CH2O + CH2O + O2 ;
% KOzone : CH2OO + O3 = CH2O + O2 + O2 ;
% KWall : CH2OO = Product5;
% KDime : CH2OO + Dime = Product6;
% KNO2 : CH2OO + NO2 = CH3CHO + NO3 ;


* For completeness, we also added two ozone reactions, with rate ;
* coefficients from IUPAC ;
% 2D-15 : HO2 + O3 = OH + O2;
% 7.3D-14 : OH + O3 = HO2 + O2;
* ---------------------------------------------------------------- ;
```

Propene

Kinetic model added to the MCM chemistry to describe the CI chemistry in propene ozonolysis, in Facsimile format. The MCM uses container species, i.e. class-specific-species that contain the sum of all individual species in this class, to describe certain reaction, e.g. for RO2. We have defined some additional container species to easily describe the generic reactions of CI with aldehyde, ketone, hydroxy, carboxylic acid and organic peroxide-compounds. These were calculated using the following MCM species names:

```
Ketones = CH3COCH3 + HCOCO3H + HCOCO2H + ACETOL + HYPERACET +
          IPROPOLPER + MGLYOX + CH3CO3H + GLYOX + HOC2H4CO3H +
          HOCH2CO3H + BIACET + BIACETO2 + BIACETOH + BIACETOOH +
          BUT2OLO +C2H5CO3 + CH3CHOHCO3 + CH3COCH2O + CO23C3CHO +
          HOC2H4CO3 + PERPROACID;
Aldehydes = HCHO + CH3CHO + C2H5CHO + CH3CHOHCHO + HOCH2CHO +
            HOC2H4CHO + HCOCH2O + HCOCH2O2 + HCOCH2OOH + PROPALO;
Alcohols = CH3OH + C2H5OH + NPROPOL + IPROPOL + HOC2H4CO2H + ETHGLY +
           HYETHO2H + IPROPOLPER + IPROPOLO2H + HOC2H4CO3H + PROPGLY +
           CH3CHOHCHO + HOCH2CO2H + HO1C3OOH + HOC3H6OH + HOCH2CHO +
           C4ME22OH + HOC2H4CHO + HYPROPO2H + C4ME2OHOOH + ACETOL +
           HOCH2CO3H + BIACETOH + BUT2OLAO + BUT2OLO + BUT2OLO +
           BUT2OLOH + BUT2OLOOH + CH3CHOHCO3 + HO1C3O + HO1C3O2 +
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          HO1C3OOH + HOC2H4CO3 + HOCH2CH2O + HOCH2CH2O2 + HOCH2CO3 +
          HYPROPO2 + IPROPOLO + IPROPOLO2;
Acids = HCOOH + CH3CO2H + PROPACID + HOC2H4CO2H + HCOCO2H + HOCH2CO2H
      + HCOCO3H;
Organic peroxides = HYPERACET + IPROPOLPER + CH3CO3H + HYETHO2H +
                    IPROPOLO2H + HOC2H4CO3H + HO1C3OOH + HYPROPO2H +
                    C4ME2OHOOH + HOCH2CO3H + BIACETOOH + C2H5OOH +
                    CH3OOH + H2O2 + HCOCH2OOH + HO1C3OOH + IC3H7OOH +
                    PERPROACID;
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For some of the CI reactions, the fate of the products was not explicitly modeled, as they didn't accumulate to a sufficiently high concentration to affect the kinetics. Future work will include the secondary chemistry explicitly; in many cases, the CI reactions lead to oxygenated compounds that should be part of the RO2, Aldehydes, Ketones, Alcohols, Acids or Organic Peroxides container species.

Finally, to merge the model below with the MCM, some reactions need to be removed from the original MCM model, as they are redefined or altered in our more explicit model: C3H6 + O3, all CH2OOB reactions, all CH2OO reactions, all CH3CHOOA reactions, all CH3CHOO.

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* ------------------------------------------------------------------------------------------------------;
* Novelli, Vereecken, Lelieveld and Harder, "Direct observation of OH formation from;
* stabilised Criegee intermediates" PCCP, submitted 2014 ;
* ------------------------------------------------------------------------------------------------------;
* Ozonolysis reaction yields excited CI (reactions as per the MCM) ;
* or forms stabilized syn-CI or stabilized anti-CI ;
* YPropSCI = fraction of CI stabilized ;
* YPropSS = fraction of syn-CI in the CI formed ;

YPropSCI = 0.24;   * The fraction of SCI formed during ozonolysis;
YPropSS = 0.4;     * The fraction of syn or anti in the SCI;

% (5.5D-15*EXP(-1880/TEMP)*(1-YPropSCI)*0.5) : O3 + C3H6 =
CH3CHOOB + HCHO ;
% (5.5D-15*EXP(-1880/TEMP)*(1-YPropSCI)*0.5) : O3 + C3H6 =
CH2OOB + CH3CHO ;
% (5.5D-15*EXP(-1880/TEMP)*(YPropSCI)*(YPropSS)) : O3 + C3H6 =
CH3CHOOS + HCHO ;
% (5.5D-15*EXP(-1880/TEMP)*(YPropSCI)*(0.5-YPropSS)) : O3 + C3H6 =
CH3CHOOA + HCHO ;
% (5.5D-15*EXP(-1880/TEMP)*(YPropSCI)*0.5) : O3 + C3H6 =
CH2OO + CH3CHO ;


* The chemistry of the excited Criegee intermediates, CH3CHOOB ;
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* and CH2OOB is taken from the MCM;

% KDEC*0.3/(1-YPropSCI) : CH3CHOOB = CH3O2 + CO + OH;
% KDEC*0.125/(1-YPropSCI) : CH3CHOOB = CH3O2 + HO2;
% KDEC*0.125/(1-YPropSCI) : CH3CHOOB = CH4;
% KDEC*0.57/(1-YPropSCI) : CH2OOB = CO ;
% KDEC*0.10/(1-YPropSCI) : CH2OOB = HO2 + CO + OH ;

* Rate coefficients for the reaction of CI are discussed in the main paper ;
* Some rate coefficients are specific for CH2OO or syn or anti-CH3CHOO, as indicated ;
* by suffix E/S/A ;

KSCIS = 3;
KSCIA = 3;
KSO2E   = 4D-11;
KSO2S   = 2D-11;
KSO2A   = 7D-11;
KAcids = 2.5D-10;
KRO2 = 5D-12;
KHO2 = 5D-12;
KOH = 9D-12;
KKeton = 2D-13;
KAlde = 1D-12;
KPerox = 3D-12;
KAlco = 5D-12;
KCO  = 4D-14;
KH2OE = 2D-16;
KH2OS = 2D-19;
KH2OA = 1D-14;
KAlkeE = 2D-15;
KAlkeS = 2D-18;
KAlkeA = 9D-15;
KCriegee = 2.7D-11;
KCriegeeE = 4D-10;
KOzone = 3.8D-13;
KDimeS = 3.2D-14;
KDimeA = 5.1D-11;
KDimeE = 7D-11;
KNO2 = 2D-12;
KWall = 22;

* Syn- and anti-CI-specific chemistry. Where feasible, the MCM ;
* products are specified. For other reactions, we define product sinks;
* whose secondary chemistry is not considered further at this stage, ;
*(i.e. SOZ, Oligomers, Product1/2/3/4/5/6), as in our conditions they do;
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* not accumulate to relevant concentrations. ;

% KEth : CH2OO = Dioxirane;
% KCO: CH2OO + CO   = HCHO + CO2;
% KH2OE: CH2OO + H2O  = HOCH2OOH;
% KSO2E : CH2OO + SO2  = SO3 ;
% KKeton : CH2OO + Ketones = SOZ;
% KAlde : CH2OO + Aldehydes = SOZ;
% KPerox : CH2OO + Peroxides = Oligomers;
% KAlco : CH2OO + Alcohols = Product1;
% KHO2 : CH2OO + HO2 = Oligomers;
% KRO2 : CH2OO + RO2 = Oligomers;
% KAcids : CH2OO + Acids = Product2;
% KOH : CH2OO + OH  = Product3;
% KAlkeE : CH2OO + C3H6 = Product4;
% KCriegeeE : CH2OO + CH2OO = CH2O + CH2O + O2 ;
% KCriegee : CH2OO + CH3CHOOS = CH2O + CH3CHO + O2 ;
% KCriegee : CH2OO + CH3CHOOA = CH2O + CH3CHO + O2  ;
% KOzone : CH2OO + O3 = CH2O + O2 + O2 ;
% KWall : CH2OO = Product5;
% KDimeE : CH2OO + Dime = Product6;
% KNO2 : CH2OO + NO2 = CH3CHO + NO3 ;

% KSCIS : CH3CHOOS = OH + HCOCH2O2;
% KCO : CH3CHOOS + CO = CH3CHO + CO2;
% KH2OS : CH3CHOOS + H2O = HOCH3CHOOH;
% KSO2S : CH3CHOOS + SO2  = SO3 ;
% KAlco : CH3CHOOS + Alcohols = Product1;
% KKeton : CH3CHOOS + Ketones = SOZ;
% KAlde : CH3CHOOS + Aldehydes = SOZ;
% KPerox : CH3CHOOS + Peroxides = Oligomers;
% KHO2 : CH3CHOOS + HO2 = Oligomers;
% KRO2 : CH3CHOOS + RO2 = Oligomers;
% KAcids : CH3CHOOS + Acids = Product2;
% KOH : CH3CHOOS + OH = Product3;
% KAlkeS : CH3CHOOS + C3H6 = Product4;
% KCriegee : CH3CHOOS + CH3CHOOS = CH3CHO + CH3CHO + O2;
% KCriegee : CH3CHOOS + CH3CHOOA = CH3CHO + CH3CHO + O2;
% KOzone : CH3CHOOS + O3 = CH3CHO + O2 + O2;
% KWall : CH3CHOOS = Product5;
% KDimeS : CH3CHOOS + Dime = Product6;
% KNO2 : CH3CHOOS + NO2 = CH3CHO + NO3 ;

% KSCIA : CH3CHOOA = Dioxirane;
% KCO : CH3CHOOA + CO = CH3CHO + CO2;
```

```
% KH2OA : CH3CHOOA + H2O = HOCH3CHOOH;
% KSO2A : CH3CHOOA + SO2  = SO3 ;
% KAlco : CH3CHOOA + Alcohols = Product1;
% KKeton : CH3CHOOA + Ketones = SOZ;
% KAlde : CH3CHOOA + Aldehydes = SOZ;
% KPerox : CH3CHOOA + Peroxides = Oligomers;
% KHO2 : CH3CHOOA + HO2 = Oligomers;
% KRO2 : CH3CHOOA + RO2 = Oligomers;
% KAcids : CH3CHOOA + Acids = Product2;
% KOH : CH3CHOOA + OH = Product3;
% KAlkeA : CH3CHOOA + C3H6 = Product4;
% KCriegee : CH3CHOOA + CH3CHOOA = CH3CHO + CH3CHO + O2;
% KOzone : CH3CHOOA + O3 = CH3CHO;
% Kwall : CH3CHOOA = Product5;
% KDimeA : CH3CHOOA + Dime = Product6;
% KNO2 : CH3CHOOA + NO2 = CH3CHO + NO3 ;

* For completeness, we also added two ozone reactions, with rate ;
* coefficients from IUPAC ;
% 2D-15 : HO2 + O3 = OH + O2;
% 7.3D-14 : OH + O3 = HO2 + O2;
* ------------------------------------------------------------------ ;
```

(E)-2-butene

Kinetic model added to the MCM chemistry to describe the CI chemistry in (E)-2-butene ozonolysis, in Facsimile format. The MCM uses container species, i.e. class-specific-species that contain the sum of all individual species in this class, to describe certain reaction, e.g. for RO2. We have defined some additional container species to easily describe the generic reactions of CI with aldehyde, ketone, hydroxy, carboxylic acid and organic peroxide-compounds. These were calculated using the following MCM species names:

```
Ketones = CH3COCH3 + HCOCO3H + HCOCO2H + ACETOL + HYPERACET +
          IPROPOLPER + MGLYOX + CH3CO3H + GLYOX + HOC2H4CO3H +
          HOCH2CO3H + BIACET + BIACETO2 + BIACETOH + BIACETOOH +
          BUT2OLO + C2H5CO3 + CH3CHOHCO3 + CH3COCH2O + CO23C3CHO +
          HOC2H4CO3;
Aldehydes = HCHO + CH3CHO + C2H5CHO + CH3CHOHCHO + HOCH2CHO +
            HOC2H4CHO + HCOCH2O + HCOCH2O2 + HCOCH2OOH;
Alcohols = CH3OH + C2H5OH + NPROPOL + IPROPOL + HOC2H4CO2H + ETHGLY
           + HYETHO2H + IPROPOLPER + IPROPOLO2H + HOC2H4CO3H + PROPGLY
           + CH3CHOHCHO + HOCH2CO2H + HO1C3OOH + HOC3H6OH + HOCH2CHO
           + C4ME22OH + HOC2H4CHO + HYPROPO2H + C4ME2OHOOH + ACETOL +
           HOCH2CO3H + BIACETOH + BUT2OLAO + BUT2OLO + BUT2OLO +
```

```
            BUT2OLOH + BUT2OLOOH + CH3CHOHCO3 + HO1C3O + HO1C3O2 +
            HO1C3OOH + HOC2H4CO3 + HOCH2CH2O + HOCH2CH2O2 + HOCH2CO3 +
            HYPROPO2;
Acids = CH3CO2H + PROPACID + HOC2H4CO2H + HCOCO2H + HOCH2CO2H +
        HCOCO3H;
Organic peroxides = HYPERACET + IPROPOLPER + CH3CO3H + HYETHO2H +
                    IPROPOLO2H + HOC2H4CO3H + HO1C3OOH + HYPROPO2H +
                    C4ME2OHOOH + HOCH2CO3H + BIACETOOH + C2H5OOH +
                    CH3OOH + H2O2 + HCOCH2OOH + HO1C3OOH + IC3H7OOH;
```

For some of the CI reactions, the fate of the products was not explicitly modeled, as they didn't accumulate to a sufficiently high concentration to affect the kinetics. Future work will include the secondary chemistry explicitly; in many cases, the CI reactions lead to oxygenated compounds that should be part of the RO2, Aldehydes, Ketones, Alcohols, Acids or Organic Peroxides container species.
Finally, to merge the model below with the MCM, some reactions need to be removed from the original MCM model, as they are redefined or altered in our more explicit model: TBUT2ENE + O3, all CH3CHOO reactions, all CH3CHOOB reactions.

```
* ---------------------------------------------------------------------------------------------------------- ;
* Novelli, Vereecken, Lelieveld and Harder, “Direct observation of OH formation from ;
* stabilised Criegee intermediates” PCCP, submitted 2014 ;
* ----------------------------------------------------------------------------------------------------------;
* Ozonolysis reaction yields excited CI (reactions as per the MCM), ;
* or forms stabilized syn-CI or stabilized anti-CI ;
* YButSCI = fraction of CI stabilized ;
* YButSS = fraction of syn-CI in the CI formed ;

YButSCI = 0.18; * The fraction of SCI formed during ozonolysis;
YButSS = 0.8; * The fraction of syn or anti in the SCI;

% 6.64D-15*EXP(-1059/TEMP)*(1-YButSCI) : TBUT2ENE + O3 = CH3CHO +
CH3CHOOB ;
% 6.64D-15*EXP(-1059/TEMP)*(YButSCI*YButSS) : TBUT2ENE + O3 = CH3CHO +
CH3CHOOS ;
% 6.64D-15*EXP(-1059/TEMP)*(YButSCI*(1-YButSS)) : TBUT2ENE + O3 =
CH3CHO + CH3CHOOA ;

* The chemistry of the excited Criegee intermediates, CH3CHOOB ;
* is taken from the MCM ;

% KDEC*0.3/(1-YButSCI) : CH3CHOOB = CH3O2 + CO + OH;
% KDEC*0.125/(1-YButSCI) : CH3CHOOB = CH3O2 + HO2;
% KDEC*0.125/(1-YButSCI) : CH3CHOOB = CH4;
```

```
* Rate coefficients for the reaction of CI are discussed in the main ;
* paper. Some rate coefficients are specific for syn or anti-CI, as ;
* indicated by suffix S/A ;

KSCIS = 3;
KSCIA = 3;
KAlkeS = 1.7D-19;
KH2OS = 2D-19;
KAlkeA = 1.4D-15;
KH2OA = 1D-14;
KAcids = 2.5D-10;
KRO2 = 5D-12;
KHO2 = 5D-12;
KOH = 5D-12;
KKeton = 2D-13;
KAlde = 1D-12;
KPerox = 3D-12;
KAlco = 5D-12;
KCO = 4D-14;
KCriegee = 3D-11;
KOzone = 3.8D-13;
KDimeS = 3.2D-14;
KDimeA = 5.1D-11;
KSO2S = 2D-11;
KSO2A = 7D-11;
KNO2 = 2D-12;
KWall = 22;

* Syn- and anti-CI-specific chemistry. Where feasible, the MCM ;
* products are specified. For other reactions, we define product sinks;
* whose secondary chemistry is not considered further at this stage, ;
*(i.e. SOZ, Oligomers, Product1/2/3/4/5), as in our conditions they do;
* not accumulate to relevant concentrations. ;

% KSCIS : CH3CHOOS = OH + HCOCH2O2;
% KCO : CH3CHOOS + CO = CH3CHO + CO2;
% KH2OS : CH3CHOOS + H2O = HOCH3CHOOH;
% KSO2S: CH3CHOOS + SO2  = SO3 ;
% KAlco : CH3CHOOS + Alco = Product1;
% KKeton : CH3CHOOS + Keton = SOZ;
% KAlde : CH3CHOOS + Alde = SOZ;
% KPerox : CH3CHOOS + Perox = Oligomers;
% KHO2 : CH3CHOOS + HO2 = Oligomers;
```

```
% KRO2 : CH3CHOOS + RO2 = Oligomers;
% KAcids : CH3CHOOS + Acids = Product2;
% KOH : CH3CHOOS + OH = Product3;
% KAlkeS : CH3CHOOS + TBUT2ENE = Product4;
% KCriegee : CH3CHOOS + CH3CHOOS = CH3CHO + CH3CHO + O2;
% KCriegee : CH3CHOOS + CH3CHOOA = CH3CHO + CH3CHO + O2;
% KOzone : CH3CHOOS + O3 = CH3CHO + O2 + O2;
% KWall : CH3CHOOS = Product5;
% KDimeS : CH3CHOOS + Dime = Product6;
% KNO2 : CH3CHOOS + NO2 = CH3CHO + NO3 ;

% KSCIA : CH3CHOOA = Dioxirane;
% KCO : CH3CHOOA + CO = CH3CHO + CO2;
% KH2OA : CH3CHOOA + H2O = HOCH3CHOOH;
% KSO2A: CH3CHOOA + SO2  = SO3 ;
% KAlco : CH3CHOOA + Alcohols = Product1;
% KKeton : CH3CHOOA + Ketones = SOZ;
% KAlde : CH3CHOOA + Aldehydes = SOZ;
% KPerox : CH3CHOOA + Peroxides = Oligomers;
% KHO2 : CH3CHOOA + HO2 = Oligomers;
% KRO2 : CH3CHOOA + RO2 = Oligomers;
% KAcids : CH3CHOOA + Acids = Product2;
% KOH : CH3CHOOA + OH = Product3;
% KAlkeA : CH3CHOOA + TBUT2ENE = Product4;
% KCriegee : CH3CHOOA + CH3CHOOA = CH3CHO + CH3CHO + O2;
% KOzone : CH3CHOOA + O3 = CH3CHO;
% Kwall : CH3CHOOA = Product5;
% KDimeA : CH3CHOOA + Dime = Product6;
% KNO2 : CH3CHOOA + NO2 = CH3CHO + NO3 ;

* For completeness, we also added two ozone reactions, with rate ;
* coefficients from IUPAC ;
% 2D-15 : HO2 + O3 = OH + O2;
% 7.3D-14 : OH + O3 = HO2 + O2;
* ------------------------------------------------------------------ ;
```

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