Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation

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Simulation chamber SAPHIR

Experiments were performed in the atmosphere simulation chamber SAPHIR in Jülich, Germany. A description of the chamber and its properties can be found elsewhere\textsuperscript{1–3}. The chamber offers the possibility to investigate chemical processes under near-natural atmospheric conditions. It uses solar radiation as a light source, allows experiments at radical- and trace gas concentrations that are typically found in clean to polluted tropospheric air, and is operated at nearly ambient temperature and pressure. SAPHIR consists of a double-wall Teflon (FEP) film of cylindrical shape (length 18 m, diameter 5 m, volume 270 m\textsuperscript{3}). The chamber has a roof that can be closed for weather protection, or to keep the chamber in the dark. The Teflon film has a high optical transmittance over the entire solar spectrum\textsuperscript{2}. Slight overpressure prevents leakages of outside air into the chamber. Air which is removed during the experiments by air-sampling instruments, or which is lost by small leaks, is continuously replenished with zero air leading to a dilution rate of approximately 5\% per hour. The dilution rate was calculated from the measured replenishment flow and was confirmed by the measured concentration of an inert tracer (CO\textsubscript{2}). A fan, which was continuously operated during all experiments, ensured a short mixing time of approximately 1 min. Radical and trace gas concentrations, OH reactivity (k(\text{OH})), and photolysis frequencies were measured by instruments listed in Table S1. OH reactivity denotes the pseudo first-order loss rate coefficient of OH (inverse chemical lifetime).

Before each isoprene experiment, the dark chamber was flushed with ultra-pure zero air, which is mixed from evaporated liquid nitrogen and oxygen (Linde, purity \textsuperscript{>\text{99.9999 \%}}). The chamber air was humidified by evaporating Milli-Q water, which was flushed into the chamber together with a high flow of zero air. After this preparatory phase, the chamber roof was opened and the photochemical experiment was started by exposing the humidified air to solar radiation. After 30 minutes, ozone from a silent-discharge ozone generator was added to the chamber air (mixing ratio in the chamber: 40-50 ppbv). Thereafter, OH reactants were injected several times and the photochemical evolution of the air compo-
osition was observed for several hours (cf., Fig 3). During some experiments a reference species (CO) was added first and isoprene (Sigma Aldrich, purity 99%) at later times (Fig. 2) and during one experiment isoprene was injected several times (Fig. 3). The experiments were finished by closing the chamber roof.

Several sources of trace gases are known and well-characterised for the sunlit chamber. Nitrous acid (HONO), formaldehyde (HCHO), and acetaldehyde (CH$_3$CHO) are formed by heterogeneous photochemical processes on the Teflon film. The corresponding source strengths depend on solar radiation and relative humidity, and are well-described by empirical functions$^{1,4}$. For model calculations of individual experiments, the source strengths were scaled to match the measured concentrations of the produced species during the experimental phase before OH reactants were added. The variability of the source strengths from experiment to experiment was approximately 20%. The chamber sources produced HCHO and CH$_3$CHO at rates of approximately 200 pptv/h for conditions during this campaign. The simultaneously observed formation of peroxy acyl nitrate (PAN) can be explained by the photochemical degradation of CH$_3$CHO.

The photolysis of HONO is the main source for OH and NO$_X$ in the chamber. During the experiments, maximum OH concentrations of (1-2) $\times$ 10$^7$ cm$^{-3}$ were reached in the absence of additional reactants and for clear sky conditions. NO mixing ratios typically ranged between 100 pptv and 200 pptv after ozone had been injected and photostationary state for NO, O$_3$ and NO$_2$ had been reached (Table S2).

The initial OH reactivity was approximately 1 s$^{-1}$ after filling the chamber with humidified clean air. This reactivity resulted from an unknown contamination, which was introduced into the chamber together with the water vapour. When the humidified clean air was exposed to sunlight, the background OH reactivity started to increase due to the photochemical production of known reactants (NO$_2$, HCHO, and CH$_3$CHO), leading to a background reactivity of 2 s$^{-1}$ over the course of the experiments. The chemically unidentified part of the measured OH background reactivity can be described as the reaction of an unknown species with constant concentration, which behaves like CO converting OH to HO$_2$$^1$. For model calculations, the concentration was adjusted to the measured OH reactivity at the beginning of the experiment after the addition of water vapour. The reactivity was typically equivalent to a CO mixing ratio of 80-120 ppbv.

RO$_2$ radicals of approximately (1-2) $\times$ 10$^6$ cm$^{-3}$ were immediately formed in the humidified clean air when the chamber roof was opened. They were partly formed by photolytic processes. This is evident from reference experiments with CO, in which the RO$_2$ radical concentrations persisted even though OH was completely scavenged by CO. For model calculations, the photolytic RO$_2$ source was described by a similar empirical function like the chamber sources for HONO and HCHO. The applicability of this procedure was confirmed in test experiments, for which the production rate was scaled to match measured RO$_2$ concentrations. All model parameters regarding the photolytical
RO$_2$ source were assumed to be constant for the experiments shown here.

Ozone loss in the clean chamber was determined in separate test experiments, which show that the lifetime of ozone was 35 hours for conditions during these experiments. Reference experiments also indicate that HO$_2$ was most likely lost at the Teflon film giving an HO$_2$ lifetime of 4 min in the clean sunlit chamber. Wall loss of other species were of negligible influence for the experiments shown here.

OH radical concentrations were measured by two independent instruments. One instrument used laser induced fluorescence (LIF) for OH detection requiring a calibration. The other technique was differential optical absorption spectroscopy (DOAS) which is regarded as an absolute reference. As discussed in Fuchs et al. 2012, measurements by both instruments well agreed during experiments in the SAPHIR chamber in 2011 including those of this study. In particular, no change in the agreement between measurements by the two instruments with increasing isoprene concentration was observed. This is also demonstrated by the correlation of OH concentrations in Fig. S1, where measurements each of the parts of the experiments follow the one-to-one line. Good agreement between OH measurements by LIF and DOAS was also found during several other comparisons of concurrent OH measurements in the chamber for various conditions (Schlosser et al. 2007, 2009).
Table S1  Performance of instruments used for the isoprene experiments.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Time Resolution</th>
<th>1σ Precision$^a$</th>
<th>1σ Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>DOAS$^{b,c}$</td>
<td>205 s</td>
<td>0.8 x 10$^6$ cm$^{-3}$</td>
</tr>
<tr>
<td>OH</td>
<td>LIF$^{d,e}$</td>
<td>47 s</td>
<td>0.3 x 10$^6$ cm$^{-3}$</td>
</tr>
<tr>
<td>HO$_2$, RO$_2$</td>
<td>LIF$^{f}$</td>
<td>47 s</td>
<td>1.5 x 10$^7$ cm$^{-3}$</td>
</tr>
<tr>
<td>k(OH)</td>
<td>Laser-photolysis + LIF$^{c,10}$</td>
<td>180 s</td>
<td>0.3 s$^{-1}$</td>
</tr>
<tr>
<td>NO</td>
<td>Chemiluminescence$^{11}$</td>
<td>180 s</td>
<td>4 pptv</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>Chemiluminescence$^{11}$</td>
<td>180 s</td>
<td>2 pptv</td>
</tr>
<tr>
<td>O$_3$</td>
<td>Chemiluminescence$^{12}$</td>
<td>180 s</td>
<td>60 pptv</td>
</tr>
<tr>
<td>isoprene</td>
<td>PTR+SRITOF-MS$^{d}$ (H$_3$O$^+$-mode)$^{13,14}$</td>
<td>30 s</td>
<td>30 pptv</td>
</tr>
<tr>
<td>MVK+ MACR</td>
<td>PTR+SRITOF-MS$^{d}$ (H$_2$O$^+$-mode)$^{13,14}$</td>
<td>30 s</td>
<td>15 pptv</td>
</tr>
<tr>
<td>MACR</td>
<td>PTR+SRITOF-MS$^{d}$ (NO$^+$-mode)$^{14,15}$</td>
<td>820 s</td>
<td>40 pptv</td>
</tr>
<tr>
<td>isoprene, MVK, MACR</td>
<td>GC-FID$^{f}$</td>
<td>32 min</td>
<td>2 %</td>
</tr>
<tr>
<td>HONO</td>
<td>LOPAP$^{x,16}$</td>
<td>300 s</td>
<td>1.3 pptv</td>
</tr>
<tr>
<td>HCHO</td>
<td>Hantzsch monitor$^{17}$</td>
<td>120 s</td>
<td>20 pptv</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
<td>PTR+SRITOF-MS$^{d}$ (H$_3$O$^+$-mode)$^{13,14}$</td>
<td>30 s</td>
<td>50 pptv</td>
</tr>
<tr>
<td>PAN</td>
<td>GC$^{l,18}$</td>
<td>600 s</td>
<td>25 pptv</td>
</tr>
</tbody>
</table>

Photolysis frequencies

- Spectroradiometer$^2$
- 60 s 10 % 10 %

$^a$ for zero measurements
$^b$ Differential-Optical-Absorption-Spectroscopy
$^c$ Laser-Induced Fluorescence
$^d$ Proton-Transfer-Reaction Switchable-Reagent-Ion Time-Of-Flight Mass-Spectrometry, H$_3$O$^+$-mode
$^e$ Proton-Transfer-Reaction Switchable-Reagent-Ion Time-Of-Flight Mass-Spectrometry, NO$^+$-mode
$^f$ Gas-Chromatography with Flame-Ionization-Detector
$^g$ Long-Path-Absorption-Photometer
$^h$ Gas-Chromatography

Figure S1  Correlation between OH measurements by DOAS and LIF colour-coded by the different parts of the experiment in Fig. 3 (zero air phase and three isoprene oxidation parts). Error bars give the 1σ precision of the individual data points. LIF data are averaged to the time grid of DOAS measurements.
Operational parameters of PTR+SRI-TOF-MS and GC-FID

Isoprene and its oxidation products were measured by a proton-transfer-reaction time-of-flight mass-spectrometer combined with switchable reagent ion capability (PTR+SRI-TOF-MS, IONICON, Innsbruck, Austria). The technique is extensively described in the literature\textsuperscript{13–15}. We refer only to some important aspects of the measurement. Isoprene and the sum of MVK and MACR were measured in the $\text{H}_3\text{O}^+$-mode. During that measurement the drift tube was held at an $E/N$ ratio of 136 Td (\(E\) being the electric field strength and \(N\) the buffer gas number density; 1 Td = $10^{-17}$ cm\(^2\)V molecule\(^{-1}\)). The protonation of isoprene results mainly in an m/z-signal of 69.06989, while for MVK and MACR protonation results both in an m/z-signal of 71.04914. To differentiate between MVK and MACR we used the NO\(^+\)-mode with an $E/N$ ratio of 68 Td. By ionization with NO\(^+\) MACR yields in a dehydrogenated cation (MACR-H)\(^+\) with an m/z-signal of 69.03349. Under the same conditions MVK only yields an association complex with NO\(^+\) with an m/z-signal of 100.03912. This signal is biased by a MACR-NO\(^+\) association complex and was therefore not being evaluated. The two modes were measured alternately while the $\text{H}_3\text{O}^+$-mode was measured for 12 min and the NO\(^+\)-mode for 3 min. Calibrations of isoprene, MVK and MACR were carried out in the low ppbv mixing ratio range using a diffusion source\textsuperscript{19} under the same conditions as being present during the SAPHIR experiments. Air was continuously sampled from the SAPHIR chamber via a 10 m long PFA tubing of 4 mm inner diameter. The tubing and the drift tube of the PTR+SRI-TOF-MS instrument were heated to 60°C. The sample flow rate was 800 ml/min.

Isoprene, methyl vinyl ketone and methacrolein were additionally quantified with an Agilent 7890N gas chromatographic system (Agilent, Santa Clara, CA. USA) equipped with a Gerstel TDS G thermodesorption unit (Gerstel, Mülheim, Germany). Air samples were trapped at 30°C at a flow rate of 100 ml/min on glass tubes with an internal diameter of 6 mm filled with Carbotrap C, Carbotrap and Carbosieve SIII. The adsorption tubes were heated with a rate of 180°C/min up to 350°C. The sample was transferred onto a second trap (cold injection system KAS4, Gerstel, Mülheim, Germany), which has a diameter of 2 mm filled with Carbotrap C kept at -130°C with a helium flow rate of 50 ml/min. The secondary trap was heated with a rate of 16°C/sec up to 150°C and with a rate of 12°C/min up to the maximum temperature of 300°C. The compounds were separated on a DB624 gas chromatographic column (length 30 m, inner diameter 0.25 mm, film thickness 1.4 µm). The GC oven was set to an initial temperature of -30°C. The column was heated with a rate of 20°C/min up to 50°C, with a rate of 30°C/min up to 170°C and with a rate of 40°C/min up to 240°C. This temperature was held for 2.25 min. The carrier gas was helium at a constant head pressure of 24 psi. Detection of trace gases were achieved by a flame ionization detector (FID) held at 250°C fueled with hydrogen (flow rate 45 ml/min) and air (flow rate 450 ml/min). Identification of species were confirmed by a mass spectrometric detector (MSD 5975c Agilent, Santa Clara, CA. USA), which was connected in parallel. The GC system was calibrated using certified gas standards (Apel-Riemer Environmental Inc., Broomfield, CO. USA).
Simulation experiments

The experiments were designed to simulate conditions similar to those encountered during the PRIDE-PRD2006 field campaign\textsuperscript{8,20}. Ozone was kept within the range of 40–50 ppbv, NO was typically between 0.1 and 0.2 ppbv, and the OH reactivity of VOCs was within the range of 10–30 s\textsuperscript{−1}. Natural sunlight is transmitted by the FEP film over the entire solar spectrum. The production rates of HO\textsubscript{X} from the photolysis of HONO and ozone were of similar magnitude as in the atmosphere, so that OH concentrations reached values up to $2 \times 10^7$ cm\textsuperscript{−3}. The experiments were designed in such a way that chamber specific properties had only a small influence on the results shown in this work. The dilution of trace gases due to the replenishment of chamber air and wall losses of reactive species were sufficiently small, so that the experiments could be run almost unperturbed for many hours. The OH background reactivity caused by the chamber was small compared to the OH reactivity of the main reactant (isoprene). For these conditions, the photochemistry of OH and isoprene in the chamber is expected to be similar compared to that in the natural atmosphere.

Table S2  Chemical conditions during the isoprene experiments in SAPHIR. Maximum values are given for isoprene, OH and $k$(OH). NO, O\textsubscript{3}, CO, and H\textsubscript{2}O mixing ratios were relatively constant over the course of each experiment. CO mixing ratios are only noted, if CO was added during the experiment. $k$(OH) denotes the measured total OH reactivity including the reactivity from added reactants, background reactivity in the chamber, and the reactivity of VOC oxidation products. The NO concentrations are given for the time period after the addition of ozone, when NO, O\textsubscript{3} and NO\textsubscript{2} had reached their photostationary state.

<table>
<thead>
<tr>
<th>Isoprene ppbv</th>
<th>OH $10^6$ cm\textsuperscript{−3}</th>
<th>$k$(OH) s\textsuperscript{−1}</th>
<th>NO\textsubscript{X} ppbv</th>
<th>NO pptv</th>
<th>O\textsubscript{3} ppbv</th>
<th>H\textsubscript{2}O %</th>
<th>CO ppmv</th>
<th>T K</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>6.5</td>
<td>18</td>
<td>0.5</td>
<td>20–100</td>
<td>34</td>
<td>1.4</td>
<td>n.a.</td>
<td>285–303</td>
<td>15 June</td>
</tr>
<tr>
<td>7</td>
<td>14</td>
<td>24</td>
<td>1.9</td>
<td>150–200</td>
<td>70</td>
<td>1.7</td>
<td>1550</td>
<td>300–311</td>
<td>27 June</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>21</td>
<td>2.0</td>
<td>100–300</td>
<td>52</td>
<td>1.7</td>
<td>800</td>
<td>293–310</td>
<td>30 June</td>
</tr>
<tr>
<td>4.6</td>
<td>13</td>
<td>18</td>
<td>1.6</td>
<td>130–190</td>
<td>57</td>
<td>1.5</td>
<td>800</td>
<td>298–308</td>
<td>5 July\textsuperscript{b}</td>
</tr>
<tr>
<td>11</td>
<td>13</td>
<td>31</td>
<td>0.9</td>
<td>80–110</td>
<td>42</td>
<td>1.5</td>
<td>n.a.\textsuperscript{a}</td>
<td>293–310</td>
<td>12 July\textsuperscript{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} [CO] $< 20$ ppbv
\textsuperscript{b} experiment shown in Fig. 2
\textsuperscript{c} experiment shown in Fig. 3
Model calculations

* Base model: Master Chemical Mechanism (MCM)

The main purpose of the SAPHIR experiments was to test photochemical isoprene degradation mechanisms by comparing modelled and measured radical concentrations and isoprene oxidation products. The base model for all calculations is the current version of the Master Chemical Mechanism (MCMv32)\textsuperscript{21,22} available at http://mcm.leeds.ac.uk/MCM. For the purpose of this study, only the inorganic chemistry and isoprene chemistry modules were used. The MCM has recently been updated with respect to the isoprene degradation mechanism. For example, a revised chemistry for isoprene-derived nitrates and hydroperoxides (OH-neutral formation of epoxides) as described by Paulot et al.\textsuperscript{26} was integrated. However, the formation of MVK, MACR, and OH from the reaction of isoprene peroxy radicals with HO\textsubscript{2}, postulated by the same authors, was not included. Paulot et al.\textsuperscript{26} demonstrated the formation of epoxides and suggested that epoxides would increase the aerosol yield from isoprene oxidation. The potential of epoxides to enhance aerosol formation have been shown in further studies by Surratt et al.\textsuperscript{23} and Lin et al.\textsuperscript{24}.

In order to account for recent experimental findings, small changes were applied in the present study to the base model as listed in Table S3, but these modifications have a negligible influence on our model results. Chamber-specific characteristics were implemented in the model, such as dilution, wall losses, photochemical chamber sources for HONO, HCHO, and CH\textsubscript{3}CHO, and initial background OH reactivity (see chamber description above). The model was constrained by measurements of temperature, pressure, calculated dilution rates, measured water vapour mixing ratios, and photolysis frequencies for NO\textsubscript{2}, HCHO, MACR, O\textsubscript{3}, and HONO. Photolysis frequencies and relative humidity constrained the calculated chamber sources for HONO, HCHO, and CH\textsubscript{3}CHO as described above. MACR photolysis frequencies for clear sky conditions were calculated using the absorption cross section by Gierczak et al.\textsuperscript{25} and a quantum yield of 0.01 (upper limit in Gierczak et al.\textsuperscript{25}). Photolysis frequencies that were not measured were first calculated by a MCM function (using parameterisations of MCMv31, because they have not been updated so far) for clear sky conditions and then scaled by the ratio of the measured and calculated NO\textsubscript{2} photolysis frequencies to account for reductions of the solar radiation by clouds and the transmission of the Teflon film. Constrained parameters were reinitialized on a 1 min time grid. The addition of trace gases (H\textsubscript{2}O, O\textsubscript{3}, CO, isoprene) was modelled as sources, which were turned on for the time of the injection. The source strength for ozone was adjusted to match the measured ozone concentration right after the ozone addition and the source strengths for CO and isoprene were adjusted to match the change in the measured OH reactivity. Otherwise, trace gas concentrations were calculated by the model.

Modelled HO\textsubscript{2} concentrations in this work were increased by a small fraction of mod-
elled \( \text{RO}_2 \) (30\% of \( \text{RO}_2 \) from isoprene and 10\% \( \text{RO}_2 \) from MACR and MVK), in order to account for an interference in the \( \text{HO}_2 \) measurement by LIF as described by Fuchs et al.\(^9\). Because \( \text{RO}_2 \) concentrations were calculated from the difference of measured \( \text{RO}_x \) (\( \text{HO}_2 \) plus \( \text{RO}_2 \)) and measured \( \text{HO}_2 \), resulting \( \text{RO}_2 \) values are also biased. Modelled \( \text{RO}_2 \) shown in Fig. 3 were corrected accordingly, in order to make modelled values comparable to experimental \( \text{RO}_2 \) data. In this work, the \( \text{RO}_2 \) interference was significantly smaller than during previous field campaigns\(^8\), because the LIF instrument was operated at optimized conditions, in order to minimize this interference, but on the cost of a reduced \( \text{HO}_2 \) sensitivity\(^9\).

* Model modifications: Leuven Isoprene Mechanism (LIM)

The base model (MCM) was modified to test the applicability of the Leuven Isoprene Mechanism (LIM) which was proposed by Peeters et al.\(^{27,28}\) from quantum-chemical calculations. For that purpose, the detailed formulation provided in the supplement of the publication by Peeters and Müller was adopted here (Table S3).

In the reaction of OH with 2-methyl-1,3-butadiene (isoprene), addition of OH to one of the two conjugated double-bonds is the most likely process leading to the formation of different isomers of hydroxy isoprene radicals. The preferred positions for OH addition are the terminal carbon atoms at positions 1 and 4, whereas addition to the inner C-atoms (position 2 and 3) are minor reaction channels, which are neglected in MCM. LIM, however, assumes a total yield of 10\% for the sum of the two minor channels. In the present work, the degradation scheme following the inner C-atom addition was adopted from Fan and Zhang 2004\(^{29}\) (Table S3). Except for a small additional production of MACR, the minor reaction channels do not further impact the results of the present work.

At atmospheric conditions, the isoprene radicals from the 1-OH and 4-OH addition react further with oxygen and produce six OH-isoprene peroxy radical isomers (E-1-OH-4-OO, Z-1-OH-4-OO, 1-OH-2-OO, E-4-OH-1-OO, Z-4-OH-1-OO, 4-OH-3-OO). The nomenclature of the isomers and their corresponding reactions listed in Table S3 follow those in the supplement of the publication by Peeters and Müller\(^{28}\). LIM postulates a fast interconversion of the RO\(_2\) isomers and H-migration in specific RO\(_2\) isomers followed by unimolecular decomposition. According to LIM, the H-migration can occur by a 1,5-H-shift in 1-OH-2-OO and 4-OH-3-OO radicals leading to the formation of OH+HCHO+MVK and OH+HCHO+MACR, respectively. Alternatively, a much faster 1,6-H-shift in Z-1-OH-4-OO and Z-4-OH-1-OO radicals leads to the formation of \( \text{HO}_2 \) and hydroxy peroxy aldehydes (HPALDs). The LIM mechanism predicts for NO-free conditions that due to the fast RO\(_2\) isomer equilibrium, the pool of all isomers would predominantly decay via the 1,6-H-shift reaction channels. HPALD can further undergo a reaction with OH, reproducing immediately OH, or is photolyzed at a fast rate producing \( \text{OH} \) and peroxyacid aldehydes (PACALDs). The proposed formation of HPALD from isoprene oxidation and its fast photolysis frequency was recently confirmed by laboratory measurements of Crounse et al.\(^{30}\)
and Wolfe et al.\textsuperscript{31}, respectively. Peeters and Müller suggested furthermore that PACALDs exclusively photolyze producing at least one or possibly up to three OH molecules. Here, we assumed that one OH radical is formed from PACALD photolysis. In any case, the 1,6-H-shift reaction channel leads to a strong enhancement in OH, because several OH radicals are formed in the photolysis reactions of HPALD and PACALD.

In the present study, the LIM mechanism was the basis for two further mechanistic modifications, called in the following LIM-CS and LIM-J. These are essentially identical to LIM, but with different rate constants.

LIM-CS (C = Crounse et al.\textsuperscript{30}, S = da Silva et al.\textsuperscript{32}) applies the significantly reduced rate constants for the 1,6-H-shift reactions measured by Crounse et al.\textsuperscript{30} in a laboratory study. This group measured the ratio of the formation rates of HPALD and hydroxyperoxides (ISOPOOH), which are produced from isoprene peroxy radicals either by a 1,6-H-shift or by competing reactions of RO\textsubscript{2} with HO\textsubscript{2}, respectively. The experimental result by Crounse et al. refers to a lumped RO\textsubscript{2} reaction, in contrast to the isomer specific isomerisation rates calculated by Peeters and Müller. In order to account for the bulk reaction rate coefficient specified by Crounse et al., the corresponding 1,6-H-shift rate coefficient is formally applied to all RO\textsubscript{2} isomers in LIM-CS (Table S3). This approach is valid, if RO\textsubscript{2} loss reactions like in our work do not perturb significantly the equilibrium between the RO\textsubscript{2} isomers (compare also Stavrakou et al. 2010\textsuperscript{33}). The determination of the 1,6-H-shift isomerisation rate by Crounse et al. assumes that there is only one decomposition channel with HPALD as a product subsequent to the H-migration. If there was another decomposition channel, the 1,6-H-shift rate would have been underestimated. The study by Crounse et al. did not allow an accurate determination of the isomerisation rate of the 1,5 H-shift reaction channel, but the authors estimated that the rate would be smaller than in the original LIM and would be more similar to calculations by da Silva et al.\textsuperscript{32}. Accordingly, the rate coefficient by da Silva was adopted in LIM-CS. As a consequence, the 1,6-H-shift remains the dominant unimolecular reaction channel like in the original LIM.

The LIM-J modification (J = Juelpich, this work) applies the upper limit of the measured isomerisation rate by Crounse et al. for the 1,6-H-shift and an optimised rate for the 1,5 H-shift (Table S4). Table S5 shows the calculated partitioning of the RO\textsubscript{2} radical isomers, which can be used to calculate lumped reaction rate constants from the isomer specific reaction rate coefficients.

* Model modifications: X mechanism for additional OH recycling

In the field campaign PRIDE-PRD2006, measured OH concentrations could be explained, when additional OH recycling is implemented in form of a two-step generic mechanism in RACM-MIM-GK\textsuperscript{8,20}. Hofzumahaus et al.\textsuperscript{20} assumed that peroxy radicals (HO\textsubscript{2}, RO\textsubscript{2}) react with a hypothetical species X in the same way as NO (Table S3). Because the reaction sequence with X does not produce NO\textsubscript{2}, the additional recycling does not produce ozone. In the present work, a constant amount of X, which is equivalent to 100 pptv
NO, was required to match the observations.

**Table S3**  Mechanistic modifications applied to the base model MCMv3.2. LIM denotes the original Leuven Isoprene Mechanism by Peeters and Müller\textsuperscript{28}. LIM-CS and LIM-J are essentially identical with LIM, but use different rate coefficients for the 1,5-H and 1,6-H-shift reactions of isoprene peroxy radicals (Table S4). The X mechanism proposed by Hofzumahaus et al.\textsuperscript{20} is an extension of the base model to represent additional OH recycling from peroxy radicals. In this work, an amount of X is used, which is equivalent to 100 pptv NO.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction rate constant / cm(^{3})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base model modifications</strong></td>
<td></td>
</tr>
<tr>
<td>HOCH(_2)CHO + OH \rightarrow GLYOX + HO(_2)</td>
<td>(8 \times 10^{-12} \times 0.29\textsuperscript{a})</td>
</tr>
<tr>
<td>HOCH(_2)CHO + OH \rightarrow HOCH(_2)CO(_3)</td>
<td>(8 \times 10^{-12} \times 0.71\textsuperscript{b})</td>
</tr>
<tr>
<td>OH + NO(_2) \rightarrow HNO(_3)</td>
<td>(9.2 \times 10^{-12}\textsuperscript{c})</td>
</tr>
<tr>
<td>RC(O)O(_2) + HO(_2) \rightarrow O(_2) + RCO(_2)H</td>
<td>KAPHO(_2)\textsuperscript{d} \times 0.12\textsuperscript{e,f}</td>
</tr>
<tr>
<td>RC(O)O(_2) + HO(_2) \rightarrow O(_3) + RCO(_2)H</td>
<td>KAPHO(_2)\textsuperscript{d} \times 0.18\textsuperscript{e,f}</td>
</tr>
<tr>
<td>RC(O)O(_2) + HO(_2) \rightarrow O(_2) + RCO(_2) + OH</td>
<td>KAPHO(_2)\textsuperscript{d} \times 0.70\textsuperscript{e,f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Karunanandan et al. 2007\textsuperscript{34}
\textsuperscript{b} Galloway et al. 2013\textsuperscript{35}
\textsuperscript{c} Mollner et al. 2010\textsuperscript{36}
\textsuperscript{d} KAPHO\(_2=5.2 \times 10^{-13} \exp(980/T),\) MCMv32
\textsuperscript{e} Dillon and Crowley 2008\textsuperscript{37}
\textsuperscript{f} Taraborrelli et al. 2012\textsuperscript{38}
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant (cm$^3$/s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISOP + OH $\rightarrow$ 2OHisoprene</td>
<td>$2.7 \times 10^{-11} \exp(390/T)$ $\times 0.03^k$</td>
</tr>
<tr>
<td>ISOP + OH $\rightarrow$ 3OHisoprene</td>
<td>$2.7 \times 10^{-11} \exp(390/T)$ $\times 0.07^k$</td>
</tr>
<tr>
<td>2OHisoprene + O$_2$ $\rightarrow$ HC4CCHO + HO$_2$</td>
<td>$2.5 \times 10^{-11}^h$</td>
</tr>
<tr>
<td>3OHisoprene + O$_2$ $\rightarrow$ HC4CCHO + HO$_2$</td>
<td>$1.4 \times 10^{-12} \times 0.4^h$</td>
</tr>
<tr>
<td>3OHisoprene + O$_2$ $\rightarrow$ B3OH4OO</td>
<td>$1.4 \times 10^{-12} \times 0.6^h$</td>
</tr>
<tr>
<td>B3OH4OO + NO $\rightarrow$ ISOPEO + HCHO + NO$_2$</td>
<td>like ISOPDO$_2$ in MCMv32</td>
</tr>
<tr>
<td>B3OH4OO + NO $\rightarrow$ ISOPENO3</td>
<td>KRO2NO$\times 0.866^h,i$</td>
</tr>
<tr>
<td>B3OH4OO + HO$_2$, RO$_2$, NO$_3$</td>
<td>$1.0 \times 10^{11h,i}$</td>
</tr>
<tr>
<td>ISOP + Oh $\rightarrow$ cis1OHisoprene</td>
<td>$2.7 \times 10^{-11} \exp(390/T)$ $\times 0.6 \times 0.5^l$</td>
</tr>
<tr>
<td>ISOP + OH $\rightarrow$ trans1OHisoprene</td>
<td>$2.7 \times 10^{-11} \exp(390/T)$ $\times 0.6 \times 0.5^l$</td>
</tr>
<tr>
<td>cis1OHisoprene + O$_2$ $\rightarrow$ Z1OH4OO</td>
<td>$7.8 \times 10^{13} \exp(-8660/T) \times 1.8 \times 10^{-26} \exp(8660/T)^i$</td>
</tr>
<tr>
<td>cis1OHisoprene + O$_2$ $\rightarrow$ 1OH2OO</td>
<td>$4.2 \times 10^{14} \exp(-9970/T) \times 3.6 \times 10^{-27} \exp(9970/T)^i$</td>
</tr>
<tr>
<td>trans1OHisoprene + O$_2$ $\rightarrow$ 1OH2OO</td>
<td>$3.7 \times 10^{14} \exp(-9570/T) \times 4.0 \times 10^{-27} \exp(9570/T)^i$</td>
</tr>
<tr>
<td>trans1OHisoprene + O$_2$ $\rightarrow$ E1OH4OO</td>
<td>$3.1 \times 10^{12} \exp(-7900/T) \times 9.8 \times 10^{-26} \exp(7900/T)^i$</td>
</tr>
<tr>
<td>Z1OH4OO $\rightarrow$ cis1OHisoprene + O$_2$</td>
<td>$7.8 \times 10^{13} \exp(-8660/T)^i$</td>
</tr>
<tr>
<td>1OH2OO $\rightarrow$ cis1OHisoprene + O$_2$</td>
<td>$4.2 \times 10^{14} \exp(-9970/T)^i$</td>
</tr>
<tr>
<td>1OH2OO $\rightarrow$ trans1OHisoprene + O$_2$</td>
<td>$3.7 \times 10^{14} \exp(-9570/T)^i$</td>
</tr>
<tr>
<td>E1OH4OO $\rightarrow$ trans1OHisoprene + O$_2$</td>
<td>$3.1 \times 10^{12} \exp(-7900/T)^i$</td>
</tr>
<tr>
<td>E1OH4OO + HO$_2$, RO$_2$, NO$_3$</td>
<td>like ISOPA02 in MCMv32$^k$</td>
</tr>
<tr>
<td>1OH2OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPB02 in MCMv32$^k$</td>
</tr>
<tr>
<td>1OH2OO $\rightarrow$ cis4OHisoprene</td>
<td>$4.8 \times 10^{13} \exp(-9203/T)^i$</td>
</tr>
<tr>
<td>Z1OH4OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPA02 in MCMv32$^k$</td>
</tr>
<tr>
<td>Z1OH4OO $\rightarrow$ cis4OHisoprene</td>
<td>$8.5 \times 10^8 \exp(-5930/T)^i$</td>
</tr>
<tr>
<td>cis4OHisoprene + O$_2$ $\rightarrow$ Z4OH1OO</td>
<td>$2.7 \times 10^{-11} \exp(390/T)^i \times 0.3 \times 0.7^i$</td>
</tr>
<tr>
<td>cis4OHisoprene + O$_2$ $\rightarrow$ 4OH3OO</td>
<td>$2.7 \times 10^{-11} \exp(390/T)^i \times 0.3 \times 0.7^i$</td>
</tr>
<tr>
<td>cis4OHisoprene + O$_2$ $\rightarrow$ 4OH3OO</td>
<td>$1.4 \times 10^{14} \exp(-3910/T) \times 7.0 \times 10^{-27} \exp(9110/T)^i$</td>
</tr>
<tr>
<td>cis4OHisoprene + O$_2$ $\rightarrow$ 4OH3OO</td>
<td>$8.3 \times 10^{14} \exp(-10220/T) \times 1.8 \times 10^{-27} \exp(10216/T)^i$</td>
</tr>
<tr>
<td>trans4OHisoprene + O$_2$ $\rightarrow$ 4OH3OO</td>
<td>$5.0 \times 10^{14} \exp(-10120/T) \times 3.1 \times 10^{-27} \exp(10116/T)^i$</td>
</tr>
<tr>
<td>trans4OHisoprene + O$_2$ $\rightarrow$ E4OH1OO</td>
<td>$5.7 \times 10^{12} \exp(-8410/T) \times 5.4 \times 10^{-26} \exp(8405/T)^i$</td>
</tr>
<tr>
<td>Z4OH1OO $\rightarrow$ cis4OHisoprene + O$_2$</td>
<td>$1.4 \times 10^{14} \exp(-9110/T)^i$</td>
</tr>
<tr>
<td>4OH3OO $\rightarrow$ cis4OHisoprene + O$_2$</td>
<td>$8.3 \times 10^{14} \exp(-10220/T)^i$</td>
</tr>
<tr>
<td>4OH3OO $\rightarrow$ cis4OHisoprene + O$_2$</td>
<td>$5.0 \times 10^{14} \exp(-10120/T)^i$</td>
</tr>
<tr>
<td>E4OH1OO $\rightarrow$ trans4OHisoprene + O$_2$</td>
<td>$5.7 \times 10^{12} \exp(-8410/T)^i$</td>
</tr>
<tr>
<td>E4OH1OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPC02 in MCMv32$^k$</td>
</tr>
<tr>
<td>E4OH1OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPDO$_2$ in MCMv32$^k$</td>
</tr>
<tr>
<td>4OH3OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPC02 in MCMv32$^k$</td>
</tr>
<tr>
<td>4OH3OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPDO$_2$ in MCMv32$^k$</td>
</tr>
<tr>
<td>4OH3OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPC02 in MCMv32$^k$</td>
</tr>
<tr>
<td>4OH3OO $\rightarrow$ MACR+HCHO+OH</td>
<td>$4.8 \times 10^{11} \exp(-9203/T)^i$</td>
</tr>
<tr>
<td>Z4OH1OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPC02 in MCMv32$^k$</td>
</tr>
<tr>
<td>Z4OH1OO + HO$_2$, RO$_2$, NO, NO$_3$</td>
<td>like ISOPC02 in MCMv32$^k$</td>
</tr>
<tr>
<td>Z4OH1OO $\rightarrow$ MACR+HCHO+OH</td>
<td>$8.5 \times 10^8 \exp(-5930/T)^i$</td>
</tr>
<tr>
<td>HPALD1 + hν $\rightarrow$ OH + PACALD1</td>
<td>$100 \times j$(MACR)$^{1,lm}$</td>
</tr>
<tr>
<td>HPALD1 + OH $\rightarrow$ OH</td>
<td>$4.6 \times 10^{-11}$</td>
</tr>
<tr>
<td>HPALD1 + hν $\rightarrow$ OH</td>
<td>$200 \times j$(MACR)$^{1,lm}$</td>
</tr>
<tr>
<td>HPALD2 + OH $\rightarrow$ OH</td>
<td>$100 \times j$(MACR)$^{1,lm}$</td>
</tr>
<tr>
<td>HPALD2 + hν $\rightarrow$ OH</td>
<td>$4.6 \times 10^{-11}$</td>
</tr>
<tr>
<td>HPALD2 + hν $\rightarrow$ OH</td>
<td>$200 \times j$(MACR)$^{1,lm}$</td>
</tr>
</tbody>
</table>

$^a$ yields adapted from Fan et al. 2004$^{29}$
$^b$ Fan et al. 2004$^{29}$
$^c$ MCMv32
$^d$ Peeters and Müller 2010$^{28}$
$^e$ Archibald et al. 2010$^{30}$
$^f$ Wolfe et al. 2012$^{31}$
$^g$ Absorption cross section and quantum yield of j(MACR) from Gierczak et al. 1997$^{25}$
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction rate constant / cm³ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIM-CS (+LIM modifications)</td>
<td></td>
</tr>
<tr>
<td>ISOPAO₂ ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>Z1OH₄OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>1OH₂OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>E1OH₄OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>ISOPCO₂ ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>Z4OH₁OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>4OH₃OOO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>E4OH₁OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>1OH₂OO ¹,₅→₅− shift MVK+HCHO+OH</td>
<td>2.38×10¹² exp(−10770/T)³</td>
</tr>
<tr>
<td>4OH₃OO ¹,₅→₅− shift MACR+HCHO+OH</td>
<td>1.27×10¹² exp(−10570/T)³</td>
</tr>
<tr>
<td>LIM-J (+LIM modifications)</td>
<td></td>
</tr>
<tr>
<td>ISOPAO₂ ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>Z1OH₄OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>1OH₂OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>E1OH₄OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>ISOPCO₂ ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>Z4OH₁OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>4OH₃OOO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>E4OH₁OO ¹,₆→₆− shift HO₂+HPALDₐ</td>
<td>1.5×0.71×KRO₂HO₂²×2.0×10²¹ exp(−9000/T)²</td>
</tr>
<tr>
<td>1OH₂OO ¹,₅→₅− shift MVK+HCHO+OH</td>
<td>15×2.38×10¹² exp(−10770/T)⁴</td>
</tr>
<tr>
<td>4OH₃OOO ¹,₅→₅− shift MVK+HCHO+OH</td>
<td>15×2.38×10¹² exp(−10770/T)⁴</td>
</tr>
</tbody>
</table>

* added to account for that HPALD yield was measured in comparison to ROOH formation in all RO₂ species in Crounse et al. 2011 ¹⁰
* KRO₂HO₂=2.91×10⁻¹³ exp(1300/T)², MMv32
* Crounse et al. 2011 ¹⁰
* da Silva et al. 2010 ¹²
* upper limit in Crounse et al. 2011 ¹⁰
* this work
* Hofzumahaus et al. 2009 ¹⁰
Table S4  Isomer specific rate-coefficients (305 K) for the 1,5-H and 1,6-H-shift reactions of isoprene peroxy radicals in the different model modifications. The value for the 1,6-H-shift in LIM-CS was calculated from the bulk rate coefficient by Crounse et al. taking the RO$_2$ partitioning from Table S5 into account.

<table>
<thead>
<tr>
<th>Model modification</th>
<th>k(1,5-H-shift, 305 K)$^a$/s$^{-1}$</th>
<th>k(1,6-H-shift, 305 K)$^a$/s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIM</td>
<td>0.038$^{+0.016}_{-0.011}$</td>
<td>3.1$^{+1.5}_{-2.5}$</td>
</tr>
<tr>
<td>LIM-CS</td>
<td>0.00111$^{+0.0285}_{-0.00105}$</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.067$^{+0.034}_{-0.034}$</td>
<td>daSilva et al.$^{32}$</td>
</tr>
<tr>
<td>LIM-J</td>
<td>0.017$^{+0.020}_{-0.011}$</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>0.10$^{b}_{-0.10}$</td>
<td>this work</td>
</tr>
</tbody>
</table>

$^a$ mean temp. during isoprene oxidation in Fig. 3

$^b$ lower limit according to the sensitivity test in Fig. S11 in this work

Table S5  Partitioning of the RO$_2$ isomers from the 1-OH and 4-OH addition reactions of isoprene in the LIM-J mechanism for conditions of the experiment shown in Fig. 3. The partitioning is approximately constant over time during the experiments and is mainly controlled by the fast equilibrium reactions between the isomers. Numbers are mean values during the isoprene oxidation phase of the experiment.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1OH4OO</td>
<td>5.9%</td>
</tr>
<tr>
<td>1OH2OO</td>
<td>58.9%</td>
</tr>
<tr>
<td>Z1OH4OO</td>
<td>4.0%</td>
</tr>
<tr>
<td>E4OH1OO</td>
<td>1.7%</td>
</tr>
<tr>
<td>4OH3OO</td>
<td>26.8%</td>
</tr>
<tr>
<td>Z4OH1OO</td>
<td>2.7%</td>
</tr>
</tbody>
</table>
Model-measurement comparison for NO

Figure S2 shows modelled NO concentrations together with measurements by the chemiluminescence instrument and measured NO$_2$ photolysis frequencies. In the chamber NO$_X$ is produced by the photolysis of HONO, which is photochemically produced in the sunlit chamber (see chamber description). The NO concentration is in a photostationary state with NO$_2$ and O$_3$, which is only little disturbed by peroxy radicals. Therefore, NO mixing ratios are reasonably well described by all models.

**Figure S2**  NO$_2$ photolysis rates and comparison of modelled and measured (black dots) NO mixing ratios for the isoprene experiment shown in Fig. 3.
**Measurement and model results for MVK and MACR**

The MVK+MACR data shown in Fig. 3 were measured as a sum by a PTR+SRI-TOF-MS instrument operated in the $\text{H}_3\text{O}^+$-mode and by a GC-FID which measured MACR and MVK concentrations separately (see above). The resulting data sets (MVK+MACR) of the two measurement methods agree well within their instrumental uncertainties and are used for the optimisation of LIM-J in addition to the radical measurements (see below). MACR was additionally measured by PTR+SRI-TOF-MS using NO$^+$ for ionization. The MACR data from PTR+SRI-TOF-MS are compared to the corresponding data from the GC-FID in Fig. S3. Here, we find a systematic deviation for MACR exceeding the combined measurement errors (Fig. S3). Thus, while the sum of MACR and MVK is in good agreement for both measurement techniques, the partitioning of both products is more uncertain than given by the measurement errors. This uncertainty has no influence on the determination of the OH regeneration following the 1,5-H-shift reactions of RO$_2$ isomers, since OH is formed as a co-product for both MVK and MACR.

The comparison of the modelled and measured MVK and MACR concentrations (Fig. S3) shows an underprediction of MVK (GC) by MCM, while MCM model results for MACR lie between the experimental data by PTR+SRI-TOF-MS (NO$^+$) and GC-FID. In case of LIM, both MVK and MACR are greatly underestimated due to the strong influence of the 1,6-H-shift which competes with the production of MVK and MACR by the 1,5-H-shift reaction. The optimised models (X and LIM-J) provide a much better fit to both MVK and MACR than LIM. Due to the unresolved discrepancy for MACR between GC and PTR+SRI-TOF-MS data, no further conclusion can be drawn with respect to the most likely partitioning of the RO$_2$ isomers in LIM which produce either MVK+OH or MACR+OH by 1,5-H-shift isomerisation (cf., Table S3).

Recently, Liu et al. 2012$^{40}$ discovered an interference from low-volatility oxidation products of isoprene in the measurements of MVK and MACR by PTR+SRI-TOF-MS, when the RO$_2$ removal was dominated by reaction with HO$_2$. In our experiment, in which the RO$_2$ removal is dominated by isomerisation and NO reactions, the concurrent measurements of MVK+MACR with an GC-FID instrument showed good agreement with those by the PTR+SRI-TOF-MS instrument, suggesting that our PTR+SRI-TOF-MS ($\text{H}_3\text{O}^+$-mode) measurements were not significantly biased by such an interference. The larger MACR measurements by PTR+SRI-TOF-MS (NO$^+$) could be a hint for an artefact in the measurements of the PTR+SRI-TOF-MS. If this artefact was the same as reported by Liu et al. 2012$^{40}$, however, one would expect to find an artificial signal in both measurement modes of the instrument, because it was also found in both measurement modes by Liu et al. 2012$^{40}$. In any case, MACR measurements by PTR+SRI-TOF-MS (NO$^+$ mode) are not needed for the estimate of the isomerisation rate constants in LIM-J, which relies on the sum of measured MVK and MACR concentrations by PTR+SRI-TOF-MS ($\text{H}_3\text{O}^+$-mode) and GC-FID. Similar to our findings, Berndt 2012$^{41}$ observed good agreement for MVK+MACR data measured by a PTR-MS and a GC-FID in an experiment studying the
photo-oxidation of isoprene in an NO-free flow-tube experiment. The reason why our and 
Berndt’s 2012 results differ from the findings of Liu et al. 2012 is not clear and may be 
due to the different experimental conditions in the experiments. Also other field campaign 
comparisons between PTR-MS and reference instruments showed good agreement\(^\text{42,43}\) 
giving no hints for interferences in PTR-MS measurements.

In the present work, yields of $39\pm3\%$ MVK and $23\pm4\%$ MACR were calculated as 
averged values of all experiments for the OH isoprene reaction using measured MACR 
and MVK concentrations (PTR+SRI-TOF-MS). The values agree with an earlier isoprene 
study by Karl et al.\(^4\) who determined yields of $41\pm3\%$ and $27\pm3\%$ for MVK and MACR, 
respectively, at similar conditions. A comparison with other laboratory studies is difficult, 
because yields depend on the concentrations of NO, HO\(_2\) and RO\(_2\) in the specific exper-
iments. As illustrated in Fig. 1, MVK and MACR can be formed by reactions of RO\(_2\) with 
NO and by the 1,5-H-shift reactions, which compete with the reaction between RO\(_2\) and 
HO\(_2\). Nearly all other studies used high concentrations of isoprene and NO, or produced 
large RO\(_2\) and HO\(_2\) concentrations, in order to investigate either MVK and MACR yields 
specifically from the RO\(_2\) plus NO reaction, or products from RO\(_2\) plus HO\(_2\) reactions. 
Reported yields are approximately 40 % and 26 % for MVK and MACR, respectively, if the 
RO\(_2\) plus NO reaction dominates\(^26\). In the absence of NO, the yields of MVK and MACR 
drop to approximately 10-15 % when large HO\(_2\) and RO\(_2\) concentrations are used in the 
experiments as shown by Navarro et al.\(^44\). Due to the large RO\(_2\) and HO\(_2\) concentrations, 
relatively slow unimolecular reactions like the 1,5-H and 1,6-H-shift played most likely a 
minor role in their work.

In two further studies, Paulot et al.\(^26\) and Crounse et al.\(^30\) (the same group) mea-
ured the formation of isoprene products from the oxidation of isoprene at low NO concen-
trations (30–60 pptv). Besides isoprene epoxides, HPALD, and ISOPOOH, small amounts 
of MVK and MACR were detected. Moreover, the ratio of measured isoprene nitrate to 
MVK+MACR concentrations was approximately 50 % smaller than at high NO conditions, 
indicating that MVK and MACR were partly formed by an unknown reaction without NO\(^30\). 
Paulot et al.\(^26\) found also indirect evidence for the formation of OH. In conclusion, they 
considered the occurence of MVK, MACR and OH to be the result of a minor (12 %) re-
action channel of isoprene peroxy radicals with HO\(_2\), similar to the reaction proposed by 
Lelieveld et al.\(^45\) as an OH source. Peeters and Müller\(^28\), however, interpreted the obser-
vation by Paulot et al. as evidence for their postulated 1,5-H-shift reaction and adjusted 
the corresponding rate coefficient in LIM to the experimental results of Paulot et al.\(^26\). The 
consistency of the two interpretations with the present study is discussed in the model 
sensitivity studies below.
Figure S3  Comparison of modelled and measured MACR and MVK concentrations for the isoprene experiment shown in Fig. 3. Measurements by PTR-SRI-TOF-MS are plotted as black and those of GC-FID as grey dots. Grey shaded areas give the 1\(\sigma\) accuracy of measurements.
Model sensitivity tests and uncertainties: Base model

For test purposes, model calculations were also done using the Regional Atmospheric Chemical Mechanism (RACM) by Stockwell et al.\textsuperscript{46} including the updated isoprene degradation mechanism RACM-MIM-GK (MIM = Mainz Isoprene Mechanism\textsuperscript{47}, G = Geiger et al.\textsuperscript{48}, K = Karl et al.\textsuperscript{4}) listed in the supplement of the paper by Lu et al.\textsuperscript{8}. This mechanism applies lumped chemical reactions in contrast to the nearly explicit mechanisms in MCM and was used for the interpretation of the HO$_X$ measurements from the PRIDE-PRD2006 campaign\textsuperscript{8,20}. There, it was shown that the model underprediction of OH is independent of the application of either one of the models. In the isoprene experiments in SAPHIR, the results are also independent of the choice of the base model as seen in Fig. S4. After isoprene addition, OH and HO$_2$ concentrations predicted by RACM-MIM-GK are slightly smaller than those predicted by MCM, but the magnitude of the discrepancy between measured and modelled OH remains essentially the same.

Additional model runs were performed to test the influence of model constraints. In the original base run (Fig. 3), the model is used to calculate concentrations of radicals and trace gases (e.g. isoprene, MVK, MACR). In the test run shown in Fig. S5, only the concentrations of radicals were calculated, while isoprene, MVK, MACR, NO, NO$_2$, O$_3$, HONO, HCHO, and CH$_3$CHO were constrained to measured values, similar to the approach used for the interpretation of the field data from the PRIDE-PRD2006 campaign. No significant difference is found between the model runs with the different constraints (red and green lines in Fig. S5). Thus, the model underprediction of OH in the presence of isoprene in the SAPHIR experiments is not caused by the chosen boundary conditions. This sensitivity run also demonstrates that nearly the same results are obtained, if isoprene is either constrained to the time series of PTR+SRI-TOF-MS measurements or calculated by the model with only modelled isoprene injections.

For model calculations the amount of isoprene that was injected into the chamber was adjusted to match the change in the OH reactivity, which is a measurement of the amount of injected isoprene. The increase in the isoprene mixing ratio measured by PTR+SRI-TOF-MS and GC-FID is consistent with the observed increase in the OH reactivity within the uncertainty of measurements. If the model is adjusted to the incremental change of isoprene measured by PTR+SRI-TOF-MS (rather than by OH reactivity), nearly the same radical concentrations are calculated (Fig. S6). Thus, the choice of this model constraint has also no significant influence on the presented results.

The role of the chemical degradation of MVK and MACR on the calculated radical concentrations was investigated in another test run. MVK and MACR are first-generation oxidation products of isoprene and can undergo further OH reactions, leading to second-generation products. In this test run, reactions of MVK and MACR with OH and ozone were turned off (Fig. S5). The small differences between this model run (blue line) and the full model (red line) demonstrates that the follow-up chemistry of MVK and MACR
was of minor importance during these experiments. Thus, uncertainties in the chemical oxidation mechanisms of MVK and MACR have no effect on the interpretation of the isoprene degradation experiments in this work.

All model calculations, especially those of OH concentrations and OH reactivity, shown here are insensitive to parameters used to describe chamber properties. The formation of RO₂ radicals from an unknown chamber source (see above) contribute an additional uncertainty in the modelled RO₂ concentrations by approximately $1 \times 10^8$ cm$^{-3}$. The chamber sources of HCHO and CH$_3$CHO, and the photochemical degradation of CH$_3$CHO to HCHO contribute significantly to the entire formaldehyde concentration that builds up during the experiments. For that reason, HCHO yields from the photochemical oxidation of isoprene can be determined only with an accuracy of approximately 30%.
Figure S4  Model-measurement comparison for OH, HO\textsubscript{2}, and k(OH) using either MCMv32 or RACM-MIM-GK for modelling. The data are from the experiment on 5 July shown in Fig. 2.
**Figure S5**  Model-measurement comparison for OH, HO₂, k(OH), and MVK+MACR for the experiment shown in Fig. 3. The experimental data were obtained by LIF (black dots in panel a, b, c), DOAS (grey dots in panel a), and PTR+SRI-TOF-MS (black dots in panel d). Three different model runs are shown. (1) red line: the entire isoprene mechanism (MCMv32), (2) green line: the entire isoprene mechanism with isoprene, MVK, MACR, NO, NO₂, O₃, HONO, HCHO, and CH₃CHO concentrations constrained to measurements, and (3) blue line: the isoprene mechanism (MCMv32) without further reactions of first-generation products MVK and MACR.
Figure S6  Comparison of modelled OH, HO$_2$, k(OH), and isoprene time series for the isoprene experiment shown in Fig. 3, if isoprene additions are adjusted to either changes in the measured k(OH) or to changes in measured isoprene concentrations.
Model sensitivity tests and uncertainties: LIM and LIM-CS

The LIM model greatly overestimates the observed OH and HO$_2$, whereas it underestimates MVK and MACR (Fig. 3, Fig. S3). The strong radical enhancement is mainly due to the 1,6-H-shift reaction, which produces HPALD+HO$_2$, followed by the photolysis of HPALD yielding additional OH. The absorption cross-section and OH quantum yield of HPALD were confirmed by laboratory studies. Thus, the rate coefficient for the 1,6-H-shift must be too large in the LIM. The uncertainty of this rate constant is in the order of a factor of 5. In order to bring modelled OH and HO$_2$ into agreement with the observations, a much larger reduction by approximately a factor of 50 is needed (LIM-CS in Fig. 3, Fig. S3). This result is consistent with the conclusion by Crounse et al., who derived the rate coefficient for the 1,6-H-shift from measurements of the HPALD formation rate. Like in the original LIM, the 1,6-H-shift remains the dominating isomerisation reaction channel.

A difference remains between calculated and measured OH and MVK+MACR concentrations in the LIM-CS. At the end of the experiment (Fig. 3), the discrepancy for MKV+MACR reaches 20%. This value is within the 2σ accuracy of instruments, so that the uncertainty in the instrumental calibration could explain a major part of the discrepancy. Another experimental reason for this discrepancy could be an unaccounted interference. Liu et al. found an artificial signal in measurements of MVK and MACR by their PTR-TOF-MS, which they assumed to be caused by other isoprene oxidation products like ROOH (see above). If we assume that isoprene ROOH in our experiment is completely converted and detected as MVK+MACR, then the gap between modelled and measured MVK+MACR mixing ratios would be closed (Fig. S7). However, the good agreement of PTR+SRI-TOF-MS and GC-FID measurements would require that also the GC-FID measurements suffered coincidentally from the same interference, which seems unlikely. Further product studies will be needed to resolve this issue.

Several other possibilities were tested in order to explore, if the gap between measured and modelled MVK+MACR could also be closed by the uncertainty of the reaction mechanism (Fig. S8). One possible error source influencing the modelled MVK+MACR value is the rate constant for the reaction of RO$_2$ with NO. Zhang et al. measured a reaction rate constant of $(9\pm 3) \times 10^{-12}$ cm$^3$s$^{-1}$ by direct observation of isoprene RO$_2$ radicals with CIMS. This value is also used in MCM. Another source of error is the rate of the 1,6-H-shift reaction which competes with the RO$_2$ reaction channels forming MVK and MACR. Crounse et al. estimated the error of the 1,6-H-shift isomerisation rate as ±50%. In sensitivity model runs, these rate constants were changed within their limits (Fig. S8). Only small changes in the modelled OH, HO$_2$, RO$_2$ concentrations and OH reactivity were obtained. Thus, the model-measurement agreement for the radicals is not affected. Although the sensitivity on the calculated MVK and MACR concentrations is larger than that on the radical concentrations, changes in MVK+MACR concentrations are small.

Further model runs were performed to investigate, if other reactions have the po-
tential to increase MVK and MACR in the model. Paulot et al.\textsuperscript{26} and Crounse et al.\textsuperscript{30} explained unexpected MVK and MACR production in their experiments by a so far unknown HO\textsubscript{2} plus RO\textsubscript{2} reaction channel yielding OH+HCHO+0.61MVK+0.39MACR with a maximum yield of (12±12) %. Model results including this potential reaction pathway in addition to the LIM-CS modification show that calculated MVK and MACR concentrations are still smaller than measurements (Fig. S9). In order to match the observations, a much larger yield of this reaction pathway of 60 % would be required (Fig. S9), contradicting the findings by Paulot et al.\textsuperscript{26}.

MVK and MACR are also produced by RO\textsubscript{2} self- and cross-reactions. The reaction rate constants for isoprene peroxy radicals were experimentally determined by Jenkin et al.\textsuperscript{50} and are within the range of $(0.8\text{-}2.9) \times 10^{-12}$ cm$^3$s$^{-1}$. These reaction rate constants are also used in MCMv32, so that MVK and MACR production from RO\textsubscript{2}+RO\textsubscript{2} reactions is accounted for in the models. Taking again the LIM-CS modifications, which would explain measured OH concentrations, a sensitivity model run (Fig. S9) shows that fifty times larger reaction rate constants would be required, in order to reproduce MVK and MACR measurements. Such a large error in the experimental rate constants seems unlikely. Also, the calculated RO\textsubscript{2} concentrations would be considerably reduced in this case, causing a mismatch between modelled and measured RO\textsubscript{2} (Fig. S9).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure_s7.png}
\caption{Comparison of the sum of measured MVK and MACR mixing ratios (black dots: PTR-TOF-MS, grey dots: GC-FID) with calculations applying LIM-CS (green lines). The gap between measured and calculated MVK+MACR would be closed, if measurements were disturbed by ROOH with a 100 % yield (dashed green line).}
\end{figure}
Figure S8  Sensitivity test of the LIM-CS model with respect to experimental uncertainties in the reaction rate constants of the RO₂+NO reaction (left panel) and the 1,6-H-shift reaction (right panel). Coloured areas show the resulting range of model values for the experiment shown in Fig. 3. Left panel: the reaction rate constant for the RO₂+NO reaction was varied within the error limits (±30%) specified by Zhang et al. Right panel: the 1,6-H-shift isomerisation rate constants were varied within the error limit of ±50% estimated by Crounse et al.
Figure S9  Potential enhancement of MVK+MACR concentrations in the LIM-CS model run by (1) RO₂+RO₂ and (2) RO₂+HO₂ reactions. (1) RO₂+RO₂ reactions can produce MVK and MACR. In order to explain the observed MVK+MACR, a very fast reaction rate constant of $5 \times 10^{-11}$ cm$^3$s$^{-1}$ would be required which exceeds the MCMv3.2 rate constant of $(0.8-2.9) \times 10^{-12}$ cm$^3$s$^{-1}$ by an order of magnitude. (2) A hypothetical reaction channel for the reaction of RO₂+HO₂ was added which produces MVK/MACR, HCHO, OH and HO₂ as suggested by Paulot et al. However, a large yield of 60% for this reaction would be required to explain the observations, whereas the 12% yield measured by these authors increases the calculated MVK and MACR concentrations only slightly.
Model sensitivity tests and uncertainties: LIM-J

In LIM-J, rate coefficients for the 1,5-H-shift and for the 1,6-H-shift are further optimised, in order to achieve the best match between observations and calculations. In LIM-CS, both, calculated OH and MVK+MACR are lower than measurements (but are still within their 2σ uncertainties). Because the 1,6-H-shift produces OH on the cost of MVK+MACR, optimisation of only the 1,6-H-shift rate could further improve the model-measurement agreement for OH, but would decrease the model-measurement agreement for MVK+MACR. In contrast, the 1,5-H-shift leads to production of OH and MVK and MACR at the same time. Therefore, this reaction pathway has the potential to explain the fast OH reformation and to resolve the underprediction of MVK+MACR found in the LIM-CS run. Fig. 3 demonstrates that simultaneous optimisation of both rates in the LIM-J modification provides a consistent description of all observed parameters including concentrations of OH, HO₂, RO₂, k(OH), isoprene, MVK+MACR. The optimised 1,5-H-shift rate coefficient for the 1-OH-2-OO and 4-OH-3-OO isomers has a value of 0.017 s⁻¹ (305 K) which is equivalent to a rate constant of 0.015 s⁻¹ for the bulk of the isoprene peroxy radicals. The upper limit of the HPALD formation rate determined by Crounse et al.³⁰ is our optimised rate coefficient for the 1,6-H-shift.

The comparison of the results of the LIM-J and LIM-CS model runs (Fig. 3) shows that modelled radical concentrations are less sensitive to the change of the 1,5-H-shift rate constant compared to modelled MVK and MACR concentrations. For this reason, the uncertainty of the adjusted 1,5-H-shift rate coefficient is mainly determined by the accuracy of the measured MVK and MACR data. Fig. S10 shows model sensitivity runs for the range of the 1,5-H-shift rate coefficients which can explain the measured MVK+MACR values within their error limits (±14%; Table S1). The resulting uncertainty of the 1,5-H-shift rate constant is approximately a factor of 2-3. The optimised value of the rate coefficient is 15 times larger than the theoretical value by da Silva et al.³² and a factor of 2.2 smaller than the value by Peeters and Müller²⁸ (Table S4). Despite the relative large differences, the experimentally determined value lies within the uncertainty range of these theoretical predictions²⁸,³² (Table S4). This value is larger than the value suggested by Crounse et al.³⁰. Although these authors state that their experiments do not allow an accurate determination of this reaction rate constant, they conclude that their observations are incompatible with the results by Peeters and Müller²⁷ and therefore they are also incompatible with the 1,5-H-shift rate in LIM-J. Because isomerisation rates in LIM-CS are adopted from experiments by Crounse et al.³⁰, reasons for the gap between measured and modelled MVK+MACR in LIM-CS (one difference between LIM-CS and LIM-J in our experiments) discussed above would also resolve this incompatibility.

Further model tests were performed to investigate the sensitivity of LIM-J results to variations of the 1,6-H-shift rate constant. In our optimisation the upper limit of the value, which was determined with an uncertainty of 50 % by Crounse et al.³⁰, is needed to match radical and MVK+MACR concentrations best. A sensitivity model run was performed
with no 1,6 H-shift isomerisation (Fig. S11). Results show only small changes of radical, isoprene, MVK and MACR concentrations, which still describe measurements within their uncertainty. Therefore, our experiments do not allow to determine an accurate 1,6-H-shift rate constant. This would require measured concentrations of HPALDs, which are exclusively formed from the 1,6-H-shift. These data, however, are not available due to lack of a calibration standard for measurements by PTR+SRI-TOF-MS.

Results achieved with the LIM-J model are insensitive how isoprene concentrations are derived. In Fig. S12, two model calculations are compared: (1) Isoprene was calculated by the model and increased at the points in time, when isoprene was injected into the chamber like done for calculations in Fig. 3. The amount of isoprene was adjusted to the change in the measured OH reactivity. (2) In the test case, the model was constrained to the measured isoprene time series (PTR+SRI-TOF-MS). Isoprene was constrained to the time series of measurements by the PTR+SRI-TOF-MS instrument. Both approaches give nearly the same radical and MVK+MACR concentrations demonstrating the insensitivity of the model results with respect to the chosen boundary conditions for isoprene.
**Figure S10**  Sensitivity of the LIM-J model results (solid line) to variations of the reaction rate constant for the 1,5-H-shift reaction. The experimental data (dots) are from the experiment shown in Fig. 3. The blue areas represent the uncertainty range of the isomerisation rate ($0.017^{+0.020}_{-0.011}$ s$^{-1}$) that can explain the measured MVK+MACR values within their error limits of 14%.
Figure S11  Sensitivity of the LIM-J model results (solid line) to variation of the reaction rate constant for the 1,6-H-shift reaction. The experimental data (dots) are from the experiment shown in Fig. 3. The blue area represent the range of the isomerisation rate from zero to the optimised value in LIM-J, which is the upper limit of the uncertainty range given by Crounse et al.³⁰.
Figure S12  Comparison of model results using different constraints for isoprene in LIM-J. The dark blue line represents the results from the standard procedure adjusting the isoprene additions to the incremental increase of k(OH). The light blue line gives the model results using the measured isoprene time series (PTR+SRI-TOF-MS) as a constraint.
Regeneration of radicals from the isoprene + OH reaction

In Fig. 1 branching ratios for reaction channels of RO$_2$ radicals from isoprene+OH as suggested by the LIM-CS and LIM-J model are given for conditions of the experiment shown in Fig. 3. In LIM-CS, 62% of RO$_2$ react with NO (100 pptv), 13% undergo 1,6-H-shift isomerisation, whereas the contribution of the 1,5-H-shift is negligibly small. In LIM-J approximately 42% reacts with NO, 28% undergoes 1,5-H-shift and 13% 1,6-H-shift isomerisation. On a minute time scale, each of these reactions regenerates one OH or HO$_2$ radical. HO$_2$ is further converted by NO to OH with a yield of 0.7 at the conditions of the experiment. Thus, in case of LIM-CS, the RO$_2$ reactions with NO and 1,5-H and 1,6-H isomerisation regenerate directly 43%, <1%, and 9%, respectively, of the OH consumed by isoprene. In case of LIM-J, the corresponding OH regeneration is 29%, 29% and 9%.

Although the branching ratio of the 1,6-H-shift channel is relatively small, the overall impact on OH is increased by the subsequent formation of additional HO$_X$ radicals by photolysis of HPALD and PACALD. The additional HO$_X$ production is delayed by 1-2 hours so that HPALD and PACALD accumulate. Approximately two thirds of HPALD undergo photolysis, while one third undergoes an OH neutral reaction. Each photolysed HPALD leads to the formation of two OH and one HO$_2$ radical. Since 70% of the HO$_2$ is converted to OH, the yield from the follow-up chemistry of each HPALD molecule is about 1.8 OH radicals. As a result, the delayed OH production from HPALD is 24% in case of LIM-CS and LIM-J for each OH radical consumed by isoprene.

The direct and delayed OH yields sum up to 33% (LIM-CS) and 62% (LIM-J) via isomerisation (1,5-H and 1,6-H shift) for each OH that has been consumed by the reaction with isoprene. Taking also the radical recycling by RO$_2$ + NO into account, 76% and 91% of the initially consumed OH is regenerated at the given experimental conditions (305 K, 100 pptv NO) in LIM-CS and LIM-J, respectively. The chemistry of HPALD is not exactly known and more OH is potentially formed than considered here (Peeters et al. 2009). This simple estimate does not consider possible leftovers of HPALD and PACALD after sunset, which could be deposited at night in the real atmosphere. Similarly, part of the HPALD/PACALD was left at the end of the SAPHIR experiments.
**Interpretation of the X mechanism**

OH, HO₂, and RO₂ are linked by radical chain reactions and constitute the radical family ROₓ (OH + HO₂ + RO₂). The abundance of ROₓ is determined by two types of processes: (1) initiation reactions which produce highly reactive, short-lived radicals from closed-shell molecules, and (2) termination reactions which deplete radicals by radical-radical recombination. To the first category belongs, for example, OH production by photodissociation of O₃ and HONO, and HO₂ formation by photolysis of formaldehyde. An example for the second category is the formation of hydroperoxides by self- and cross-reactions of HO₂ and RO₂.

Here, we assume that radical interconversion within the ROₓ family is cyclic (Fig. S13) and much faster than the processes that produce or deplete ROₓ. For this condition, a quasi-equilibrium is established between OH, HO₂, and RO₂ with fractional contributions of α, β, and γ, respectively.

\[
\begin{align*}
[RO_x] &= [OH] + [HO_2] + [RO_2] \quad (1) \\
[OH] &= \alpha \times [RO_x] \quad (2) \\
[HO_2] &= \beta \times [RO_x] \quad (3) \\
[RO_2] &= \gamma \times [RO_x] \quad (4)
\end{align*}
\]

**Figure S13** General reaction scheme illustrating radical cycling between OH, HO₂, and RO₂. Reaction 1: OH to RO₂ conversion by a VOC, e.g., isoprene. Reaction 2: RO₂ to HO₂ conversion by NO. Reaction 3: HO₂ to OH conversion by NO. Reactions 4, 5, 6: alternative conversion reactions without NO (e.g., isomerisation reactions, or reactions with X). Here, we assume that the OH to RO₂ conversion is much faster than the competing OH to HO₂ conversion by CO, HCHO etc. Therefore, OH to HO₂ conversion is not included in the scheme. The \( k \)-values denote (pseudo) first-order rate constants (s⁻¹) for the respective reactions.
We assume a VOC-rich atmosphere, in which OH is predominantly converted to \( \text{RO}_2 \) (reaction 1 in Fig. S13) and parallel conversion to \( \text{HO}_2 \) (e.g., by reaction with CO, HCHO etc.) can be neglected. The equilibrium between the \( \text{RO}_X \) species can be described by the following steady-state budget equations for OH (Eq. 5), \( \text{HO}_2 \) (Eq. 6), and \( \text{RO}_2 \) (Eq. 7).

\[
\begin{align*}
k_1[\text{OH}] & = (k_3 + k_6)[\text{HO}_2] + k_4[\text{RO}_2] & (5) \\
(k_3 + k_6)[\text{HO}_2] & = (k_2 + k_5)[\text{RO}_2] & (6) \\
k_1[\text{OH}] & = (k_2 + k_4 + k_5)[\text{RO}_2] & (7)
\end{align*}
\]

From Eqs. 5–7, the partitioning factors \( \alpha, \beta, \) and \( \gamma \) can be determined.

\[
\begin{align*}
\alpha & = \frac{1}{1 + (1 + \frac{k_2+k_5}{k_3+k_6})(\frac{k_1}{k_2+k_4+k_5})} & (8) \\
\beta & = \alpha \times \left(\frac{k_2+k_5}{k_3+k_6}\right) \left(\frac{k_1}{k_2+k_4+k_5}\right) & (9) \\
\gamma & = \alpha \times \left(\frac{k_1}{k_2+k_4+k_5}\right) & (10)
\end{align*}
\]

**Recycling by NO**

In case of recycling by NO only (i.e., \( k_4 = k_5 = k_6 = 0 \)) and considering that \( \text{HO}_2 \) and \( \text{RO}_2 \) have almost the same rate constant for their reaction with NO (i.e., \( k_2 \approx k_3 \)), Eqs. 8–10 can be simplified as follows.

\[
\begin{align*}
\alpha & \approx \frac{1}{1 + 2\frac{k_2}{k_1}} & (11) \\
\gamma & \approx \beta \approx \alpha \times \frac{k_1}{k_2} & (12)
\end{align*}
\]

For a high VOC/low NO case \( k_1 \gg k_2 \), we get:

\[
\alpha \approx 0.5 \times \frac{k_2}{k_1} \quad \text{and} \quad \gamma \approx \beta \approx 0.5 & (13)
\]

The assumptions \( k_2 \approx k_3 \) and \( k_1 \gg k_2 \) are well fulfilled for the present isoprene experiments (e.g., \( k_1=2.5 \text{ s}^{-1} \) at 1 ppbv isoprene, \( k_2=0.021 \text{ s}^{-1} \) and \( k_3=0.02 \text{ s}^{-1} \) at 100 pptv NO and 1 atm, 305 K; cf. Table S3). Eq. 13 means that \( \text{HO}_2 \) and \( \text{RO}_2 \) contribute both about half of the \( \text{RO}_X \) radicals for pure NO recycling, while the concentration of OH is smaller than that of \( \text{HO}_2 \) by about a factor \( \alpha/\beta = k_2/k_1 \) (about 1:125 for 1 ppbv isoprene and 100 pptv NO).
**Recycling by NO and X**

The X-mechanism allows for additional recycling by X, which behaves like recycling by NO, so that we can write \( k_5 = k_6 = k_X \) in Eqs. 8–10. For \( k_1 \gg k_2 \) (high VOC/low NO case) and \( k_1 \gg k_X \), we get the following partitioning of radicals:

\[
\alpha \simeq 0.5 \times \frac{k_2 + k_X}{k_1} \quad \text{and} \quad \gamma \simeq \beta \simeq 0.5 \tag{14}
\]

In case of our isoprene experiment, \( k_X \) has a value of 0.02 s\(^{-1}\), equivalent to 100 pptv NO. Thus, the OH to RO\(_X\) ratio is doubled at the expense of HO\(_2\) and RO\(_2\) which show little change.

**Recycling by NO and isomerisation reactions**

In LIM-CS and LIM-J, additional recycling occurs by isomerisation (1,5-H-shift, 1,6-H-shift) and subsequent decomposition of isoprene RO\(_2\). This case can be described by Eqs. 8–10 using \( k_4 = k_{1,5H}, k_5 = k_{1,6H}, k_6 = 0, \) and \( k_2 \simeq k_3 \). This results in the following radical partitioning:

\[
\alpha = \frac{1}{1 + (2 + \frac{k_5}{k_2})(\frac{k_1}{k_2 + k_4 + k_5})} \tag{15}
\]

\[
\beta = \alpha \times \left(1 + \frac{k_5}{k_2}\right) \left(\frac{k_1}{k_2 + k_4 + k_5}\right) \tag{16}
\]

\[
\gamma = \alpha \times \left(\frac{k_1}{k_2 + k_4 + k_5}\right) \tag{17}
\]

For \( k_1 \gg k_2 \) (high VOC/low NO case) and \( k_1 \gg k_4 + k_5 \), we get:

\[
\alpha \simeq k_2 + k_4 + k_5 \quad \frac{1}{(2 + r)k_1} \tag{18}
\]

\[
\beta \simeq \frac{1 + r}{2 + r} \tag{19}
\]

\[
\gamma \simeq \frac{1}{2 + r} \tag{20}
\]

Here, \( r = k_5/k_2 \) denotes the ratio of the rate coefficients for the 1,6-H-shift and NO reactions of isoprene RO\(_2\). With \( r \ll 2 \) and \( k_4 = k_{1,5H} \) and \( k_5 = k_{1,6H} \), the partitioning can be rewritten as:

\[
\alpha \simeq 0.5 \times \frac{k_2 + (k_{1,5H} + k_{1,6H})}{k_1} \quad \text{and} \quad \gamma \simeq \beta \simeq 0.5 \tag{21}
\]

Comparison of Eq. 14 and Eq. 21 shows that the recycling by X has the same effect on the radical distribution as the 1,5-H-shift and 1,6-H-shift reactions, i.e. \( k_X \) represents
the sum of the isomerisation rates, $k_{1,5H} + k_{1,6H}$. In the present work, $k_X$ and $k_{1,5H} + k_{1,6H}$ were determined independently, yielding values of 0.02 s$^{-1}$ (X) and (0.015+0.007) s$^{-1}$ (LIM-J), respectively, giving similar numbers. Both mechanisms, X and LIM-J, produce one MVK or MACR molecule per HO$_X$ in the additional recycling reactions (RO$_2$+X and 1,5-H-shift, respectively). Therefore, the mechanisms with X and LIM-J yield the same good description of our observations in the isoprene experiments.
References


