**Atmospheric
Measurement
Techniques**

Intercomparison of peroxy radical measurements obtained at atmospheric conditions by laser-induced fluorescence and electron spin resonance spectroscopy

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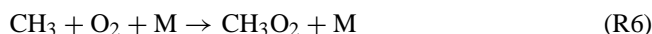
Abstract. Measurements of hydroperoxy radical (HO_2) and organic peroxy radical (RO_2) concentrations were performed by two different techniques in the atmospheric simulation chamber SAPHIR in Jülich, Germany. The first technique was the well-established Matrix Isolation Electron Spin Resonance (MIESR), which provides absolute measurements with a time resolution of 30 min and high accuracy (10%, 2σ). The other technique, ROxLIF, has been newly developed. It is based on the selective chemical conversion of RO_x radicals (HO_2 and RO_2) to OH, which is detected with high sensitivity by laser-induced fluorescence (LIF). ROxLIF is calibrated by quantitative photolysis of water vapor at 185 nm and provides ambient measurements at a temporal resolution of 1 min and accuracy of 20% (2σ). The measurements of HO_2 and RO_2 obtained by the two techniques were compared for two types of atmospheric simulation experiments. In one experiment, HO_2 and CH_3O_2 radicals were produced by photooxidation of methane in air at tropospheric conditions. In the second experiment, HO_2 and $C_2H_5O_2$ were produced by ozonolysis of 1-butene in air at dark conditions. The radical concentrations were within the range of 16 to 100 pptv for HO_2 and 12 to 45 pptv for RO_2. Good agreement was found in the comparison of the ROxLIF and MIESR measurements within their combined experimental uncertainties. Linear regressions to the combined data set yield slopes of 1.02 ± 0.13 (1σ) for RO_2 and 0.98 ± 0.08 (1σ) for HO_2 without significant offsets. The results confirm the calibration of the ROxLIF instrument and demonstrate that it can be applied with good accuracy for measurements of atmospheric peroxy radical concentrations.

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1 Introduction

Peroxy radicals play an important role in the photochemistry of the troposphere (e.g., Finlayson-Pitts and Pitts, Jr., 2000). The major source of HO_2 and RO_2 (R = alkyl group) at daytime is the reaction of photochemically formed OH radicals with carbon monoxide and hydrocarbons (RH), respectively:

$$CO + OH \rightarrow H + CO_2 \tag{R1}$$
$$H + O_2 + M \rightarrow HO_2 + M \tag{R2}$$
$$RH + OH \rightarrow R + H_2O \tag{R3}$$
$$R + O_2 + M \rightarrow RO_2 + M \tag{R4}$$

Another source of peroxy radicals is the photolysis of organic carbonyl compounds, for example, of acetaldehyde:

$$CH_3CHO + h\nu \rightarrow CH_3 + HCO \tag{R5}$$
$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{R6}$$
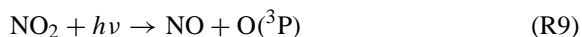$$HCO + O_2 \rightarrow HO_2 + CO \tag{R7}$$

At night many atmospheric hydrocarbons can be oxidized by photolabile nitrate radicals (NO_3), leading to alkyl radicals and subsequently RO_2 (Atkinson and Arey, 2003). Peroxy radicals are also formed in the oxidation of olefins by their reaction with ozone, which can be another significant nighttime source of RO_2 and HO_2 (e.g., Geyer et al., 2003; Kanaya et al., 2007).

One reason for the importance of peroxy radicals is their ability to produce tropospheric ozone. In an NO_x (= $NO + NO_2$) rich environment, ozone is mainly destroyed and produced by photochemical cycling of NO and NO_2 without a net change of O_3 once steady state is achieved.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R8}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{R9}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \tag{R10}$$

However, if NO is oxidized by peroxy radicals, the subsequent NO$_2$ photolysis (R9) results in a net production of tropospheric ozone:

$$RO_2 + NO \rightarrow NO_2 + RO \tag{R11}$$

$$RO + O_2 \rightarrow R'O + HO_2 \tag{R12}$$

$$HO_2 + NO \rightarrow NO_2 + OH. \tag{R13}$$

Furthermore, the peroxy radical Reactions (R11)–(R13) constitute an important source of OH in the atmosphere. For these reasons, peroxy radical concentration measurements are essential for quantifying (1) photochemical ozone production rates, and (2) radical budgets of OH, HO$_2$ and RO$_2$ in field studies.

Atmospheric measurements of peroxy radicals are a challenging task. Owing to their high reactivity, their maximum mixing ratios are small in the troposphere, on the order of 10 pptv during daytime (e.g., Monks, 2005). Thus, measurement instruments must have a high detection sensitivity. Reliable measurements are further complicated by the fact that the short-lived radicals can be lost by surface reactions in inlet systems of instruments. Lastly, calibrations of the instruments are difficult, because no permanently stable calibration mixtures exist for atmospheric peroxy radicals. If required, quantitative amounts of radicals must be prepared in specially designed flow reactors at the time of calibration.

Various techniques have been reported for the measurement of RO$_2$ and HO$_2$: (1) matrix isolation and electron spin resonance spectroscopy, MIESR (Mihelcic et al., 1985, 1990), (2) peroxy radical chemical amplification, PERCA (Cantrell et al., 1984; Hastie et al., 1991; Burkert et al., 2001; Green et al., 2006) and (3) chemical ionization mass spectrometry, ROxMas (Reiner et al., 1997) and PerCIMS (Edwards et al., 2003). These techniques differ from each other with respect to the chemical speciation of the measured radicals. MIESR is most versatile, because it can distinguish between NO, NO$_2$, HO$_2$, CH$_3$C(O)O$_2$ and RO$_2$. The latter represents the sum of alkyl peroxy radicals, RO$_2 = \sum_i RO_2^{(i)}$, where i denotes different organic peroxy radical species. PERCAs measure RO$_x$ (= RO$_2$ + RO + HO$_2$ + OH), which is a good proxy for RO$_2$ + HO$_2$, while OH and RO make a negligible contribution to RO$_x$ at atmospheric conditions. The CIMS based techniques measure RO$_x$ and distinguish the contributions of RO$_2$ and HO$_2$ by chemical modulation.

Another class of instruments applies laser-induced fluorescence (LIF) for measurement of OH and HO$_2$ (Hard et al., 1984; Hofzumahaus and Holland, 1993; Stevens et al., 1994; Brune et al., 1995; Kanaya et al., 2001; Creasey et al., 2003; Dusanter et al., 2008; Butler et al., 2008). These instruments sample ambient air by expansion into a low pressure volume, where OH is detected spectroscopically by laser excited fluorescence at 308 nm. This concept is also known as fluorescence assay with gas expansion, FAGE (Hard et al., 1984).

The detection of HO$_2$ in a FAGE instrument involves chemical conversion of HO$_2$ to OH by reaction with NO, with subsequent LIF detection of the OH product molecules.

Recently, we have further developed our LIF technique at Forschungszentrum Jülich to enable separate measurements of OH, HO$_2$ and RO$_2$ concentrations with one instrument (Fuchs et al., 2008). The setup involves one measurement channel for the specific detection of OH, while a second measurement channel (ROxLIF) is used for detection of RO$_x$. The ROxLIF concept involves a two-stage chemical conversion of RO$_x$ into OH, which is then detected by laser induced fluorescence. Modulation of the chemical conversion conditions allows the distinction between HO$_2$ and RO$_2$.

In this study, we have tested the performance and calibration of the new ROxLIF instrument by a measurement comparison against the MIESR technique. The latter was chosen as a reference, because MIESR can distinguish between HO$_2$ and RO$_2$ radicals, and yields absolute measurements with high accuracy (Mihelcic et al., 1985, 1990). The intercomparison was performed in the atmospheric simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction chamber) in Jülich. It provides a large volume of homogeneously mixed air, to which trace gases can be added at tropospheric concentration levels. For instrumental comparisons, it ensures that the instruments sample air of the same composition and at natural conditions, as was demonstrated for OH (Schlosser et al., 2007) and oxygenated volatile organic compounds (Apel et al., 2008). A further advantage of the use of a chamber is that experiments can be carried out at controlled conditions, allowing, for example, to keep radical concentrations constant at different levels. In this paper, we report the results of the measurement comparison between ROxLIF and MIESR for two sets of simulation experiments: (1) photochemical oxidation of methane by OH as an example for daytime production of peroxy radicals, and (2) ozonolysis of 1-butene as an example for a nighttime source of peroxy radicals.

2 Instrumental description

2.1 SAPHIR chamber and instrumentation

SAPHIR is designed to investigate photochemical processes under ambient conditions with atmospheric concentrations of traces gases. Detailed descriptions, focussing on particular experiments in SAPHIR, were given in the papers by Bohn and Zilken (2005), Rohrer et al. (2005), and Wegener et al. (2007). Therefore, only a short description is given here.

The reaction chamber consists of a double-walled FEP film of 125 μm to 250 μm thickness arranged in a cylindrical shape (inner diameter 5 m, length 20 m, volume 270 m^3). The film is chemically inert and it has an acceptable light transmission over the whole wavelength range of ultraviolet and visible sunlight that reaches the ground. The chamber

can be exposed to sunlight or can be kept dark by employing a fast shutter system.

The space between both films of the chamber wall is flushed permanently with clean nitrogen to avoid uncontrolled diffusion of ambient trace gases into the inner volume of the chamber. SAPHIR is operated at ambient temperature and at a pressure which is slightly (30–50 hPa) above ambient pressure. Before experiments take place, the gas inside the chamber is exchanged by clean synthetic air at a maximum flow rate of $500\,m^3/h$ until the concentrations of trace gases are below the detection limits of the attached measurement instruments. Trace gases can be injected into the chamber and are mixed to the chamber air by a fan within a few minutes. Air which is consumed by measurement devices or is lost by chamber leakages is constantly replaced with clean synthetic air, in this study at a rate of approximately $7\,m^3/h$.

If the reaction chamber is exposed to sunlight, two chemical compounds, nitrous acid (HONO) and formaldehyde (HCHO) are produced photolytically on the surface of the Teflon film (Rohrer et al., 2005; Karl et al., 2004). Although the detailed mechanism of these processes is not known, the source strengths of HONO and HCHO emissions into the chamber are well characterized by previous experiments. The quantification of these processes is important, because the following photolysis of HONO and HCHO in the gas phase constitutes a source of OH and HO_2, respectively.

In this work, parameters like temperature, pressure, relative humidity and experimental flows in the chamber were routinely monitored during all experiments. The solar actinic flux was measured by a spectroradiometer and used for the calculation of photolysis frequencies (Bohn and Zilken, 2005). NO, NO_2, and O_3 concentrations were measured by chemiluminescence detectors (Eco Physics, CLD 780TR). A gas chromatograph (Chrompack, Chrompack VOCAir) measured the concentrations of non-methane hydrocarbons. In one set of experiments, 1-butene was ozonolyzed for peroxy radical generation in the chamber. Here, 1-butene was measured by the GC instrument and simultaneously monitored by the NO chemiluminescence detector in the so called "zero mode", which serves to quantify and subtract interference signals from the reaction of alkenes with ozone. The interference signal of the chemiluminescence detector was calibrated against the GC measurements and provided a quasi-continuous measurement of 1-butene, while the time resolution of the GC was about 20 min.

2.2 ROxLIF technique

The LIF instrument applies one measurement channel for OH (Holland et al., 2003) and a second channel (ROxLIF) for the measurement of RO_2 and HO_2. ROxLIF is a newly developed technique, which has been described in detail elsewhere (Fuchs et al., 2008). It applies chemical conversion in combination with LIF for radical detection and can be operated in two chemical modes (ROx and HOx mode).

In brief, ambient air is sampled through an orifice (1 mm diameter) into a differentially pumped flow reactor, which is kept at a reduced pressure of 25 hPa. In the ROx mode, NO and CO are added as reagents to the sampled air, in order to convert atmospheric RO_x to HO_2. NO (0.7 ppmv) is responsible for the successive conversion of atmospheric RO_2 to HO_2 and HO_2 to OH (Reactions R11–R13). In contrast to previous detection of HO_2 by LIF, where RO_2 conversion was limited by the short reaction time and dilution of oxygen required in Reaction (R12), the reaction time of 0.6 s is long enough and the oxygen concentration high enough for quantitative conversion. The large amount of CO (0.17%) ensures that all HO_x (=HO_2+OH), from ambient air and from RO_2 conversion, becomes HO_2 (Reactions R1 and R2). This has the advantage that potential HO_x loss by reactions of the highly reactive OH becomes negligible in the reactor. In the HOx mode, the NO reagent is turned off and only CO is added. At this condition, only atmospheric HO_x is converted to HO_2. The alternating measurement in the HO_x and RO_x mode allows to distinguish between HO_x and RO_2 radical concentrations.

At the exit of the reactor, the central gas flow is transferred through a nozzle into a detection chamber at even lower pressure (3.5 hPa). Here, additional NO is injected into the sampled gas, causing nearly complete chemical conversion of HO_2 to OH (Reaction R13), which is detected by LIF. A pulsed narrow-bandwidth UV laser (308 nm) is used to excite the OH radicals at the rovibronic line $Q_1(3)$ of the $A^2\Sigma^+$ v'=0–$X^2\Pi$ v''=0 transition, and the resulting resonance fluorescence is measured by gated photon counting. The laser is tuned periodically on and off resonance to distinguish the OH fluorescence signal from non-resonant background signals.

The calibration of the ROxLIF measurements is based on the quantitative photolysis of water vapor in air at a wavelength of 185 nm. The photolysis produces equal concentrations of OH and HO_2 and is widely applied for calibration of HO_x instruments (Aschmutat et al., 1994; Schultz et al., 1995; Heard and Pilling, 2003). In the present work, a modified concept is used for peroxy radicals (Schultz et al., 1995; Hanke et al., 2002; Qi et al., 2006; Fuchs et al., 2008). The photolytically generated OH is completely converted to HO_2 by adding excess CO (Reactions R1 and R2) in order to determine the HO_2 sensitivity. To calibrate the ROxLIF instrument for RO_2, a corresponding hydrocarbon (RH) is added to the calibration gas, resulting in the complete conversion of OH to RO_2 (Reactions R3 and R4). In the present work only methane was used for RO_2 calibrations. This simplified procedure is justified as the ROxLIF detection sensitivity is essentially the same for the two radical species (CH_3O_2 and $C_2H_5O_2$), which were generated in the SAPHIR experiments reported below (Fuchs et al., 2008). The similar detectivity is plausible, since alkyl peroxy radicals show similar reaction rate constants towards their reaction with NO (Atkinson and Arey, 2003), which is the rate limiting step in

the RO_2 to HO_2 conversion in the flow reactor of the instrument. The estimated accuracy of calibration is approximately 20% (2σ) limiting the accuracy of ROxLIF measurements. The sensitivity of the instrument is corrected for fluorescence quenching by water vapor, but there is no chemical interference from water vapor as observed in PERCA instruments (Mihele and Hastie, 1998). If sampling highly polluted air, interferences such as thermal decomposition of atmospheric peroxy nitrates could reduce the accuracy, but such conditions were not encountered in the current experiments. The detection limits (SNR=2) are 0.1 pptv for both HO_2 and RO_2 at a time resolution of 1 min (Fuchs et al., 2008).

In the reported experiments, the flow reactor of the instrument extended into the SAPHIR chamber. The sampling point was 87 cm above the floor of the chamber. The outer surfaces of the reactor (except the inlet region) were covered with a Teflon bag in order to minimize possible radical losses on instrumental surfaces close to the inlet.

2.3 MIESR technique

MIESR was developed as a measurement technique for atmospheric peroxy radicals at the Forschungszentrum Jülich by Mihelcic et al. (1985, 1990) and is the only one of its kind. It has the capability to measure simultaneously the concentrations of HO_2, RO_2, $CH_3C(O)O_2$, NO_3 and NO_2 in the same sample of air.

The MIESR technique is an offline method. Ambient air is collected by gas expansion through a nozzle into a vacuum chamber. The radicals are trapped from the gas jet in a polycrystalline D_2O matrix which is formed in situ on a cold finger at a temperature of 77 K. The collection time for an air sample is 30 min. The samples are stored and measured under vacuum at 77 K. At this condition, the ice matrix prevents chemical interactions between reactive molecules and allows to store the sample up to several weeks without loss of radicals. Speciation and quantification of the trapped radicals are achieved in the laboratory by electron spin resonance spectroscopy. The spectra are analyzed by a nonlinear fitting procedure (Mihelcic et al., 1990). HO_2, $CH_3C(O)O_2$, NO_3 and NO_2 can be individually measured, whereas the spectra of organic peroxy radicals overlap and provide a measure of RO_2. The MIESR technique is an absolute technique and achieves a detection limit of 2 pptv for peroxy radicals at a time resolution of 30 min (Mihelcic et al., 2003). The main advantage of this method is that no calibration of the instrument is required, making it useful as a reference method for other atmospheric RO_x measurement techniques (Platt et al., 2002). The accuracy of measurements is 5%.

In the reported experiments, the MIESR sampling unit was mounted in a flange at the bottom of the SAPHIR chamber. In this setup, the upward oriented inlet nozzle of the sampling unit was about 2 cm above the chamber floor, which consists of a Teflon film. The horizontal distance between the MIESR sampling unit and the ROxLIF reactor was approximately

3 m. Turbulent mixing of the chamber air ensures that the relatively short distance between sampling point and chamber surface does not lead to gradients in the radical concentrations, which would affect the intercomparison (Schlosser et al., 2007).

3 Results

Two types of experiments were carried out in SAPHIR which provided atmospheric radical concentrations. The first experiment was performed at daylight and involved the photochemical oxidation of methane, while the second experiment involved ozonolysis of 1-butene at dark conditions. Raw data were evaluated independently by the operators of the two instruments without communicating results before final data were exchanged.

3.1 Methane photooxidation experiment

After purging the chamber with dry synthetic air overnight, water vapor was introduced into the dark chamber in the morning. High purity water was provided by a Milli-Q-water device (Millipore Corp., Milli-Q Gradient A10), vaporized and flushed into the chamber together with a high flow of synthetic air, until a water vapor mixing ratio of about 0.7% by volume (relative humidity: 50%) was achieved. Methane (Air Liquide, purity 5.5) was introduced into the chamber, resulting in an initial large mixing ratio of approximately 0.5% by volume. Fast mixing in the chamber was achieved by a fan, which was operated for the entire duration of the experiment. After the gas addition, the shutter system of the chamber was opened at 08:00 UTC for a duration of 5.5 h. The experiment was stopped at 14:30 UTC. The ROxLIF instrument was running continuously during the whole period, while the MIESR instrument took three air samples of 30 min integration time, starting at 09:00, 10:00 and 11:00 UTC.

The peroxy radical measurements of the ROxLIF and MIESR instrument are shown in Fig. 1, together with the HONO photolysis frequency, $j(HONO)$, and the mixing ratio of NO. Dashed vertical lines indicate the opening and closing of the shutter system. As soon as the shutter was opened and sunlight entered the chamber, HO_2 and RO_2 concentrations measured by ROxLIF increased during the first minutes up to 15–20 pptv. Both, HO_2 and RO_2, showed similar diurnal variations and reached approximately the same peak concentrations of 40 pptv at 12:30 UTC. The concentrations measured by ROxLIF agree very well with the simultaneous measurements by MIESR during the time of measurement overlap (9:00–11:30 UTC). Short-term fluctuations of the radical concentrations measured by ROxLIF were mainly correlated with variations of the solar UV radiation represented by $j(HONO)$. The OH radical concentration (not shown here) remained always below the detection limit ($<1\times10^6$ cm^{-3}) of the LIF instrument. After the shutter of
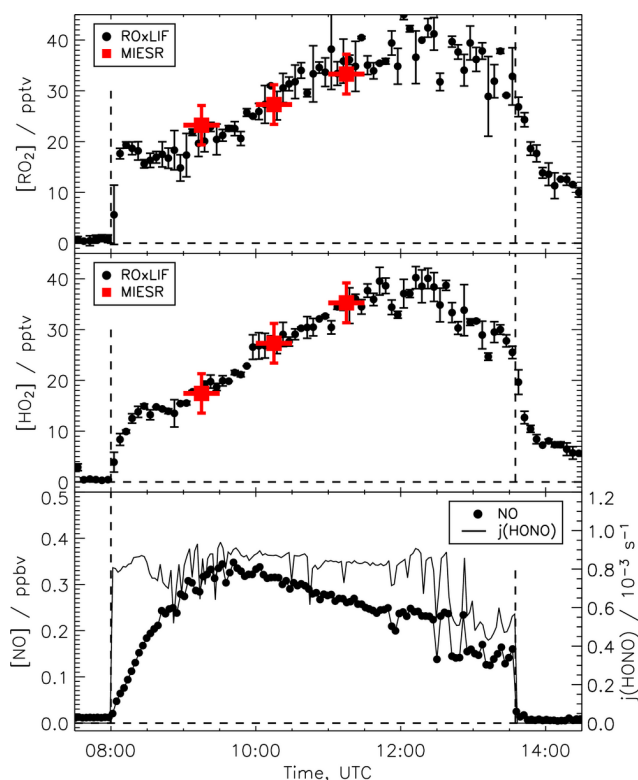
Fig. 1. Comparison of peroxy radical concentrations measured simultaneously by ROxLIF (5 min average values) and MIESR during the methane photooxidation experiment (upper panel: RO$_2$, middle panel: HO$_2$). Vertical error bars represent the 1 σ precisions of the measurements. Horizontal bars denote the 30 min sampling time intervals of the MIESR measurements. The bottom panel shows mixing ratios of NO measured by chemiluminescence and the HONO photolysis frequency measured by a spectroradiometer. Dashed vertical lines indicate the opening and closing of the shutter system of the chamber.

Fig. 2. Comparison of peroxy radical concentrations measured by ROxLIF (5 min average values) and MIESR during the 1-butene ozonolysis experiments on 24 May 2006 and 17 May 2006, respectively (upper panel: RO$_2$, middle panel: HO$_2$). Vertical error bars represent the 1 σ precisions of the measurements. Horizontal bars denote the 30 min sampling time intervals of the MIESR measurements. The bottom panel shows the corresponding concentrations of ozone and 1-butene during the two experimental runs.

the chamber had been closed, the photolytic radical production stopped, followed by a decay of the radical concentrations. The mixing ratios of NO$_x$ and O$_3$ (not shown here) increased continuously over the course of the experiment, starting at zero concentrations at 08:00 UTC and reached maximum values of 2.8 ppbv and 65 ppbv at 13:30 UTC, respectively.

3.2 1-butene ozonolysis experiment

The ozonolysis experiment was performed at dark conditions, keeping the shutter system of the chamber closed all the time. After purging the chamber overnight with clean synthetic air, ozone was generated by a silent discharge ozonizer and introduced into the chamber. The amount of added O$_3$ was accurately controlled by a magnetic valve in the inlet line, which was opened and closed by an electronic timer. The ozone mixing ratio was increased in four steps
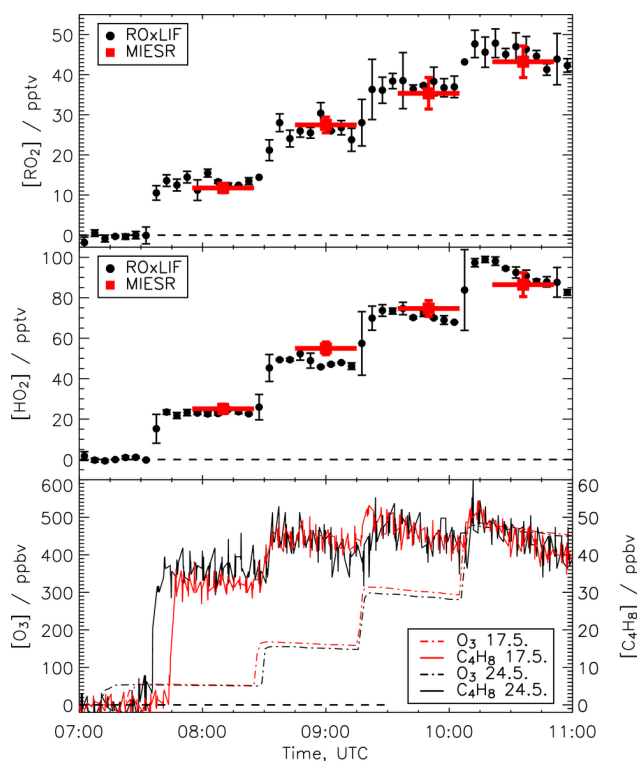
from 50 ppbv to a maximum of nearly 500 ppbv (Fig. 2). The water vapor mixing ratio was about 0.04% by volume all the time. In addition, 480 ppmv CO were initially introduced to the chamber, serving as a scavenger for OH and stabilized Criegee radicals. After the first addition of ozone, 1-butene (Linde AG, purity 3.5) was injected into the chamber, yielding an initial concentration of 36 ppbv. The slow decrease of 1-butene during the following experiment was balanced by further additions of 1-butene (each corresponding to an incremental increase of 12 ppbv), added at the same time when the ozone concentration was increased. The complete experiment was performed twice, once on 17 May 2006 and a second time on 24 May 2006, at nearly the same chemical conditions (see bottom panel of Fig. 2).

Nearly constant mixing ratios of HO$_2$ and RO$_2$ were produced in the chamber at five different concentration levels reaching from zero to a maximum of 100 pptv of HO$_2$ and 45 pptv of RO$_2$. The stepwise increase of concentrations was caused by the incremental additions of O$_3$ and 1-butene. In the first experimental run (17 May 2006), the

MIESR instrument collected four samples, each at a different level of peroxy radical concentrations for 30 min. The sampling was started approximately 15 min after each addition of O$_3$ and 1-butene, in order to ensure that the air in the chamber was homogeneously mixed and the chemical system was equilibrated. The ROxLIF instrument was running in parallel, but due to a technical failure of its flow reactor, measurements became flawed and had to be discarded. The ROxLIF measurements were repeated in the second experimental run on 24 May 2006, where the chemical conditions from 17 May 2006 were closely reproduced. This time the ROxLIF system worked properly, however, the MIESR sampler was no longer available, because it had been moved to the laboratory for analysis of the previously taken samples. Thus, the ROxLIF and MIESR data shown in Fig. 2 were not obtained simultaneously. However, as the chemical conditions were nearly the same, a comparison of the two data sets is possible (see discussion below). Based on this assumption, the results demonstrate a good agreement between the ROxLIF and MIESR technique for measurement of both HO$_2$ and RO$_2$ in the ozonolysis experiments.

4 Discussion

4.1 Peroxy radical production by methane oxidation

The chamber experiments were designed to produce HO$_2$ and one particular RO$_2$ species in each type of experiment. In the methane photooxidation experiment, traces of methane and water vapor were exposed to solar radiation in synthetic air at ambient temperature and pressure. It is expected that this mixture produces CH$_3$O$_2$ and HO$_2$ as the only peroxy radicals in the SAPHIR chamber at the given conditions. As soon as sunlight enters the chamber, i.e. when the shutter system is opened, production of OH is started by photolysis of HONO, which is formed heterogeneously at the sunlit chamber walls (see Sect. 2.1). The HONO photolysis is also a source for NO in the gas phase, which starts to built up when the chamber is illuminated. The high concentration of methane (0.5%) ensures that OH reacts quickly and exclusively to CH$_3$O$_2$, which is further converted by the available NO to HO$_2$. Recycled OH from the reaction of HO$_2$ and NO is immediately consumed by methane again. This sequence of radical reactions explains why the observed concentrations of CH$_3$O$_2$ and HO$_2$ exhibit a similar time dependence and show similar concentrations during the course of the experiment. HO$_2$ is formed predominantly from CH$_3$O$_2$, and both, HO$_2$ and CH$_3$O$_2$, are depleted mainly by reaction with NO, which has nearly the same rate constant for both radical species (Sander et al., 2006). Thus, approximately equal steady-state concentrations are expected for both radical species.

The high methane concentration in the chamber led to a reduction in the ROxLIF sensitivity, because OH radicals pro-

duced in the conversion reactor partly regenerated CH$_3$O$_2$ radicals. Model calculations of the reaction kinetics in the reactor show a reduction of the sensitivity of 4% for RO$_2$ and 9% for HO$_2$ for a methane mixing ratio of 0.5%. Since methane was not measured during this experiment and the initial mixing ratio was only estimated from its addition before the experiment started, this effect was not taken into account in the data evaluation and adds to the uncertainty in the ROxLIF measurements.

4.2 Peroxy radical production by 1-butene ozonolysis

In the dark ozonolysis experiments, ozone and 1-butene were mixed in 1 atm of dry synthetic air, which was additionally loaded with CO as an OH scavenger. The ozonolysis involves a complex system of chemical reactions, which yield various products (Grosjean et al., 1996; Grosjean and Grosjean, 1997; Olzman et al., 1997; Hasson et al., 2001; Wegener et al., 2007). In the first step, ozone is cycloadded to the alkene and forms an ozonide, which rapidly decomposes to either formaldehyde or propanal and a corresponding excited Criegee intermediate, C$_2$H$_5$CHOO* or HCHOO*, respectively. The two types of Criegee intermediates undergo fast decomposition reactions, yielding OH, HO$_2$ and C$_2$H$_5$O$_2$ radicals and stable byproducts (e.g., C$_2$H$_6$, CO, CO$_2$) or can be stabilized by collisions. The stabilized Criegee intermediates react with the large excess of CO initially injected into the chamber to corresponding aldehydes and CO$_2$ (Atkinson, 1997; Hatakeyama et al., 1994). The large amount of CO also converts OH completely to HO$_2$ and prevents possible reactions of OH with 1-butene and its ozonolysis products. Thus, the chemical system is expected to produce C$_2$H$_5$O$_2$ and HO$_2$ as the only peroxy radicals in the chamber.

Interferences of the ROxLIF measurement from Criegee intermediates are not expected in these experiments. The excited Criegee radicals from the ozonolysis reactions are short-lived intermediates in the formation process of the peroxy radicals, and as their chemical lifetime is very much shorter, their concentrations are negligible compared to those of the peroxy radicals (Jenkin et al., 1997). Stabilized Criegee radicals also do not play a role, because they are efficiently scavenged and converted to non-radical products by the high concentration of CO in the SAPHIR chamber and in the ROxLIF converter (Atkinson, 1997; Hatakeyama et al., 1994).

Peroxy radical concentrations are controlled by the concentrations of the precursors ozone and 1-butene, which slowly react with each other on a time scale of several hours, at a rate constant of $\sim 1 \times 10^{-17}$ cm^{-3}s^{-1} (Atkinson and Arey, 2003). While the radical production is rate limited by this reaction, the radical destruction in the absence of NO is determined by the much faster recombination reactions of the peroxy radicals (HO$_2$+HO$_2$, HO$_2$+RO$_2$, and RO$_2$+RO$_2$). The overall reaction kinetics has two interesting consequences. First, as 1-butene and ozone are depleted

slowly, the resulting steady-state concentrations of the peroxy radicals stay nearly constant over the 1 h observation periods applied in the ozonolysis experiments (Fig. 2). Second, the radical concentrations can be easily reproduced by adjustment of the ozone and alkene concentrations.

The chemical behavior of the reaction system and the fact that the two ozonolysis experiments (17 and 24 May 2006) were performed in clean synthetic air and at dark conditions, avoiding variable photolytic radical production, is the basis for the reproducibility of the experiments. In fact, the amount of reagents for radical production and the timing of their incremental additions were almost the same during both runs (see Fig. 2, bottom panel). The maximum difference in the measured ozone concentrations was 3% during the time intervals, where MIESR and ROxLIF measurements are compared. The corresponding concentrations of 1-butene differed by 12% after the first addition, but were equal for the following concentration levels of the experiments within the precision of the 1-butene measurement. For these reasons, it can be assumed that the time series of the relevant peroxy radical concentrations were essentially the same during both runs. Based on this assumption, it is justified to compare the measurements by ROxLIF and MIESR for both HO$_2$ and RO$_2$ in the ozonolysis experiments.

4.3 Measurement intercomparison

For quantitative analysis, the ROxLIF measurements are averaged over the sampling time period of the MIESR instrument and are compared in scatter plots versus the MIESR measurements in Fig. 3.

The HO$_2$ data in the right panel show a linear relationship with little scatter and follow closely a 1:1 line. A linear fit, which takes into account the statistical errors of both instruments ("FitExy" procedure in Press et al. (1992)), yields a slope of 0.98 ± 0.08, an intercept of (-1.2 ± 3.8) pptv and a linear correlation coefficient R^2 of 0.98. The scatter of the individual data points around the regression line can be explained by their statistical precision. This is confirmed by the goodness-of-fit probability q of 0.65. This fitting parameter indicates a linear relationship of the data within their statistical errors, if $q > 0.1$ (Press et al., 1992). The intercept of the regression line is not significant and can be explained by its statistical error.

The scatter plot for RO$_2$ in the left panel of Fig. 3 shows a similar good correlation as for HO$_2$. The data follow a linear relationship of nearly unity slope and exhibit a correlation coefficient $R^2 = 0.97$. No significant difference can be seen between the data points from the methane photooxidation and 1-butene ozonolysis experiments. This confirms that the ROxLIF instrument, which was calibrated for CH$_3$O$_2$ (see Sect. 2.2), is equally sensitive to CH$_3$O$_2$ and C$_2$H$_5$O$_2$. The regression line for the combined RO$_2$ data exhibits a slope of 1.02 ± 0.13, an intercept of (0.5 ± 4.0) pptv and a parameter q of 0.93. As for HO$_2$, no significant offset is observed.
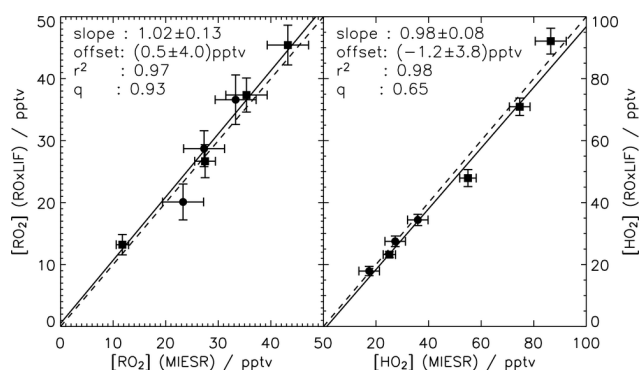

Fig. 3. Correlation of peroxy radical data measured by ROxLIF and MIESR (left panel: RO$_2$, right panel: HO$_2$). Square symbols represent data from the ozonolysis experiments and circles from the methane photooxidation experiment. For these presentations the ROxLIF data were averaged over the sampling time interval of MIESR. Error bars are 1 σ standard deviations of average ROxLIF values or 1 σ measurement errors of MIESR. The black lines represent linear fits that take into account the errors of both measurement instruments (Press et al., 1992). The corresponding fitting parameters (slope and offset, correlation coefficient r^2 and q as the probability for a linear fit) are given with their 1 σ errors in the legends. The dashed lines represent 1:1 lines.

The slopes of the regression lines for HO$_2$ and RO$_2$ indicate very good agreement of the two measurement techniques within their combined uncertainties. The uncertainties are determined by the calibration accuracy of 20% (2σ) of the ROxLIF instrument (Fuchs et al., 2008) and the 10% (2σ) measurement error of MIESR (Mihelcic et al., 2003). As a result, the measurement comparison confirms the calibration of the ROxLIF technique, here demonstrated for HO$_2$, CH$_3$O$_2$ and C$_2$H$_5$O$_2$.

The present work is the first, in which two measurement instruments have been compared for speciated peroxy radicals at atmospheric conditions. Earlier studies have either compared measurements of atmospheric HO$_2$ or total peroxy radicals. HO$_2$ measurements were first compared between LIF and MIESR during the BERLIOZ field campaign (Platt et al., 2002; Mihelcic et al., 2003). Good agreement was observed as indicated by a slope of 1.03 ± 0.08 and a correlation coefficient R^2 of 0.88 (Platt et al., 2002). The same campaign offered also an opportunity to compare RO$_x$ measurements by a PERCA instrument and MIESR. A regression line with a slope of 1.07 and a correlation coefficient $R^2 = 0.91$ demonstrated good agreement for these measurements (Platt et al., 2002). In another more recent study, HO$_2$ measurements were compared between a PerCIMS and LIF instrument in two phases: 1. by mutual exchange of calibration sources, 2. by ambient air measurements (Ren et al., 2003). In the calibration intercomparison, very good agreement was found within 2% for PerCIMS sampling from the LIF calibration

source and within 4% for LIF sampling from the PerCIMS calibration source. Good agreement was also obtained in a side-by-side intercomparison of the ambient HO$_2$ measurements. Here, the regression line yielded a slope of 0.96 and a correlation coefficient R^2=0.85. It is noteworthy that the calibrations of both techniques applied water vapor photolysis at 185 nm, which is also the basis for the ROxLIF calibration in the present work. MIESR, however, which was used as a reference in the present and previous intercomparisons, is an independent technique requiring no calibration. The result of the present intercomparison is therefore important support for the general concept of water photolysis as a tool for peroxy radical calibrations.

5 Conclusions

An intercomparison of speciated measurements of concentrations of HO$_2$ and two alkyl peroxy radicals, CH$_3$O$_2$ and C$_2$H$_5$O$_2$, has been performed successfully between the fundamentally different ROxLIF and MIESR techniques. Very good agreement of the two instruments was observed during two types of simulation experiments carried out in the atmosphere simulation chamber SAPHIR. This facility ensured that both instruments sampled well mixed air of the same chemical composition and allowed the design of experiments, in which only one specific type of RO$_2$ radical is produced together with HO$_2$. In the photooxidation of methane, concentrations of CH$_3$O$_2$ and HO$_2$ were prepared, which were dependent on the strength of the natural sunlight. In the 1-butene ozonolysis experiments, nearly constant radical concentrations of C$_2$H$_5$O$_2$ and HO$_2$ were generated, which were entirely controlled by the chosen concentrations of the reactants ozone and 1-butene.

The good agreement of the measurements by the newly developed ROxLIF and the well established MIESR technique strengthens the confidence in the measurement and calibration of the new instrument. The ROxLIF technique has advantages over the MIESR technique by offering a higher time resolution and a better detection sensitivity. The SAPHIR chamber offers the potential to serve as a reference standard for peroxy radical concentrations. As has been demonstrated in this work, the ozonolysis of 1-butene allows the controlled production of HO$_2$ and C$_2$H$_5$O$_2$ at dark conditions. The capability to create constant radical concentrations is of advantage for intercomparison of instruments, which need a relative long sampling time. The peroxy radical concentrations obtained from the 1-butene ozonolysis have been quantified in this work and can be reproduced at any time in the chamber for future quality assurance tests.

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