Chapter 5
State of the Art OH and HO_2 Radical Measurement Techniques: An Update

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Abstract The methods used for atmospheric measurements of OH and HO_2 radicals are reviewed. Focus is given to advances in the measurement technology, instrument design and calibration for OH and HO_2 measurements and a summary of results from some recent intercomparison studies, in particular, the HOxCOMP campaign are presented.

Keywords Radicals • Oxidation • Photochemistry • FAGE • CIMS • Interferences

5.1 Introduction

Free-radicals mediate virtually all of the oxidative chemistry in the atmosphere, being responsible for the transformation of primary emissions into secondary pollutants such as NO_2, O_3 and particulates. Radicals control the lifetime of climate gases (e.g. CH_4), the budget of O_3 in all parts of the atmosphere, and the production of acidic species. Understanding the behaviour of free-radicals in the atmosphere is of paramount importance in understanding the lifetime and hence spatial scales of pollutant transport. Predictive models for future air quality and climate change contain complex chemical schemes, and the measurement of free-radicals in the present atmosphere constitutes the best validation of these schemes through comparison with model predictions. The lifetime of free-radicals is short, and in general, their budgets are controlled only by *in situ* chemistry, and not by transport processes, and hence the chemistry can be studied by field-measurements at a single point in order to constrain zero-dimensional models. In summary, free-radicals are the instigators of all chemistry that impacts climate and air quality, and are ideal targets for atmospheric models. They are short-lived (seconds), and hence their concentrations are not influenced by their transport, only by the local *in situ* chemistry.

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The hydroxyl radical, OH, removes the majority of trace gases emitted into the atmosphere, including greenhouse gases and substances harmful to health, and initiates the formation of wide range of secondary species, for example ozone and secondary organic aerosol, two components of photochemical smog. The reaction of HO_2 and RO_2 radicals with NO represents the only tropospheric *in situ* source of ozone. There have now been a considerable number of field campaigns in which field measured concentrations of short-lived free-radicals have been compared with the results of zero-dimensional model simulations, highly constrained to the observed field data for longer-lived species (for older work see [15, 19] and references therein). The use of a zero-dimensional model with no spatial resolution is presumed adequate for model comparisons, since transport of such short-lived radical species does not contribute significantly to their local concentration.
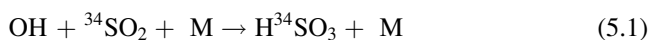
In this paper, a summary and recent developments will be presented concerning two techniques that are currently used for the measurement of tropospheric OH and HO_2 radicals, namely laser-induced fluorescence at low-pressure, known as FAGE (Fluorescence Assay by Gas Expansion), and CIMS (Chemical Ionisation Mass Spectrometry). The emphasis will be on developments concerning FAGE. FAGE detects OH directly, whereas in the CIMS method it is first converted to H_2SO_4 which is then detected by mass spectrometry. HO_2 is not detected directly by either of the techniques, rather it is converted first to OH. Other methods have been developed for the direct detection of OH and HO_2 radicals, for example Differential Optical Absorption Spectroscopy (DOAS) and Matrix Isolation Electron Spin Resonance (MIESR). However, other than for comparison in chambers these will not be considered in this paper, as they are techniques that are no longer used for field measurements. Advances in technology, instrument design and calibration will be discussed for OH and HO_2 measurements, together with a summary of results from some recent intercomparison studies, in particular the HOxCOMP campaign [10, 31] performed in the SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber) chamber at Forschungszentrum, Julich. Interferences are a potential problem shared by all field instruments, and recently there has been a reported interference for HO_2 measured using the FAGE technique [11], which will be discussed, together with potential interferences for OH which may be present under certain types of field conditions. A new method, which is able to partially speciating atmospheric peroxy radicals is also described, as detection is based on the FAGE technique following a pre-reactor which converts organic peroxy radicals into HO_2 which are then detected [8].

5.2 FAGE and CIMS Techniques Used for Field Measurement of Tropospheric OH and HO_2 Radicals

Field measurements of tropospheric OH and HO_2 radicals are extremely challenging, owing to their very low concentrations (OH ~ 10^6 molecule cm^{-3}; HO_2 ~10^8 molecule cm^{-3}), high reactivity and therefore short lifetime ($\tau(OH)$ ~0.01–1 s;

$\tau(HO_2)$ ~5–100 s), and their rapid loss rate onto surfaces of inlets. Both the FAGE and CIMS techniques have been described before (for representative references see [15]), and have enjoyed considerable success for field measurement of OH and HO$_2$. In the FAGE technique, OH radicals are measured by 308 nm laser-induced fluorescence (LIF) spectroscopy at low pressure and HO$_2$ is first converted to OH by the addition of NO prior to FAGE detection of the OH formed. Simultaneous measurements are possible *via* two independent detection cells, which depending on the design are either in series with a single sampling pinhole and the OH fluorescence cell closer to the sampling nozzle, or in parallel with two independent sampling pinholes, and allowing a different pressure in each cell. Delayed gated photon counting is used to detect fluorescence from OH and to discriminate from the more intense scattered light. Two types of high pulse-repetition frequency laser system are used, either a Nd: YAG pumped dye-laser, which is frequency doubled to generate 308 nm, or an all solid state Nd: YAG pumped titanium sapphire laser, which is frequency tripled to generate 308 nm. A typical detection limit for the FAGE technique is $(2–5) \times 10^5$ and $(5–10) \times 10^5$ molecule cm^{-3} for OH and HO$_2$, respectively, with an accuracy of ~20–30% [15].

In the CIMS technique OH is converted quantitatively to H$_2{}^{34}$SO$_4$ by the following reactions:

$$OH + {}^{34}SO_2 +\ M \rightarrow H^{34}SO_3 +\ M \qquad (5.1)$$

$$H^{34}SO_3 + O_2 \rightarrow {}^{34}SO_3 +\ HO_2 \qquad (5.2)$$

$${}^{34}SO_3 + H_2O\ +\ M \rightarrow H_2{}^{34}SO_4 +\ M \qquad (5.3)$$

and H$_2{}^{34}$SO$_4$ is chemically ionised by the reaction:

$$NO_3{}^-.HNO_3 + H_2{}^{34}SO_4 \rightarrow H^{34}SO_4{}^-.HNO_3 +\ HNO_3 \qquad (5.4)$$

The isotopically labelled ^{34}S is used to discriminate against naturally occurring H$_2{}^{32}$SO$_4$. The CIMS method is the most sensitive of all OH field instruments, with a detection limit of better than 10^5 molecule cm^{-3} [1, 7, 32].

There remains only one calibration method used in the field for the calibration of FAGE and CIMS instruments, the mercury pen-lamp photolysis of water vapour at 184.9 nm, which in the presence of air generates equal concentrations of OH and HO$_2$, which are given by:

$$[OH] = [HO_2] = [H_2O]\, \sigma_{H2O,184.9\,nm}\, \phi_{OH}\, F_{184.9\,nm}\, t \qquad (5.E1)$$

where σ is the water vapour absorption cross-section, ϕ is the photodissociation quantum yield of OH from water vapour $(=1)$, F is the photon flux of the lamp, all at 184.9 nm, and where t is the photolysis exposure time. The first three terms can be determined accurately, and there have been two approaches to measure the

product $F_{184.9 \text{ nm}}$ t. One approach measures $F_{184.9 \text{ nm}}$ directly using a calibrated phototube, and t is calculated using the known flow properties of the calibration flow tube. The other approach is to use a chemical actinometer to determine the product, rather than each individually, and two have been developed involving the production and measurement of O_3 or NO initiated from O_2 and N_2O (added to the flow) photolysis, respectively, and which give the same value within errors.

All groups active in field measurements of OH and HO_2 rely on the photolysis of water vapour to calibrate their instruments, and although there is currently no evidence that there is a bias or other problem with this method, it is a concern that reliance for all absolute concentrations is given to a single method. Intercomparisons with the DOAS method, which does not rely on a calibration (only needing knowledge of spectroscopic constants which are well established in the laboratory), either in the field [17] or in chambers [30, 31], provides confidence in the calibration method. Indirect calibration has been achieved using the decay of a hydrocarbon for which the rate coefficient k_{OH+HC} is well established in the literature, with [HC] measured using GC-FID as function of time to give:

$$[OH] \ = \frac{(-d[HC]/dt)}{k_{OH+HC} \times [HC]} \tag{5.E2}$$

Such an approach has given good agreement with [OH] measured in chambers with instruments calibrated using the water photolysis method [2]. The calibration of instruments as a function of pressure, which varies during the operation of aircraft measurements, is difficult to achieve, but recently the HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) [13] chamber, which is constructed of stainless steel, has been used to generate OH radicals at a total pressure of 220–760 Torr. OH concentrations determined by HC decays agreed with those obtained using a FAGE instrument that had been previously calibrated using the water vapour technique at atmospheric pressure, but using sampling pinholes of different diameters to reproduce the necessary pressure within the fluorescence cell [23]. The generation of OH from a reaction of an alkene giving a known yield of OH can also been used to calibrate for OH [24], but is not currently used in the field. For HO_2, observing the rate of HO_2 decay from the second order self-reaction, and knowledge of the rate coefficient and any wall loss, k_{loss} enables [HO_2] to be determined from solution of the following differential equation:

$$\frac{d[HO_2]}{dt} = -(k_{loss}[HO_2] + 2k_{HO2+HO2}[HO_2]^2) \tag{5.E3}$$

in order to calibrate instruments. This method has enjoyed success in chambers [23], but is not used in the field owing to the length of time required to observe the decay under realistic concentrations of HO_2.

5.3 HOxCOMP: A Recent Intercomparison at the SAPHIR Chamber

Intercomparisons between different field instruments measuring OH and/or HO$_2$ radicals are still uncommon, but represent one of the quality control mechanisms to probe any differences in instrument behaviour, calibration and susceptibility towards interferences [15]. The SAPHIR campaign in Julich is a highly-instrumented chamber equipped with the only operating long-path DOAS instrument with the capability of measuring atmospheric levels of OH. As DOAS requires no calibration, merely knowledge of the absorption cross-sections at the relevant temperature and pressure and the path length, it provides an absolute standard for OH. The HOxCOMP campaign, performed in 2005 [10, 31], provided both an out of chamber (ambient) and an in chamber formal-blind intercomparison for both OH and HO$_2$. One DOAS (in SAPHIR chamber only), 3 FAGE and 1 CIMS instruments from Germany and Japan were involved, and followed on from a successful previous OH intercomparison involving just the Julich group [30]. For OH the agreement is in general very good over a range of different levels of humidity, O$_3$, NO$_2$, and radiation (including under dark conditions) with gradients of the correlation plots ranging from 1.01 to 1.13. A CIMS instrument also participated in the ambient phase of the intercomparison, together with three LIF instruments, and correlation gradients of 1.06–1.69 were observed, which were sometimes outside the combined uncertainty limits.

Three FAGE instruments employing NO induced HO$_2$ $\rightarrow$ OH conversion participated in an HO$_2$ intercomparison, and here the agreement between instruments was more variable, with correlation slopes between 0.69 and 1.26 in the chamber and sometimes higher for ambient [10]. The agreement in the chamber was a function of the particular experiment, with better correlations when grouped by water vapour. There is an unknown factor related to water vapour which appears to give a bias for some instruments [10].

5.4 Partial Speciation of RO$_2$ and HO$_2$ Using a Variant of FAGE (ROxLIF)

Although one of the holy grails for atmospheric composition is the speciated field measurement of individual peroxy radicals, this has not yet been realised. The ROxLIF method is a fairly recent innovation which enables HO$_2$ and the sum of organic peroxy radicals to be measured separately [8], and with good sensitivity (~0.1 pptv detection limit in ~1 min). This provides additional information than provided by the peroxy radical chemical amplifier (PERCA) technique, although HO$_2$ and the sum of RO$_2$ has been measured separately using a CIMS detection method to measure OH via H$_2$SO$_4$ formation (ROXMAS: [14]; PerCIMS: [6]). Although upon addition of NO, conversion of RO$_2$ to RO is rapid (OH in the case of
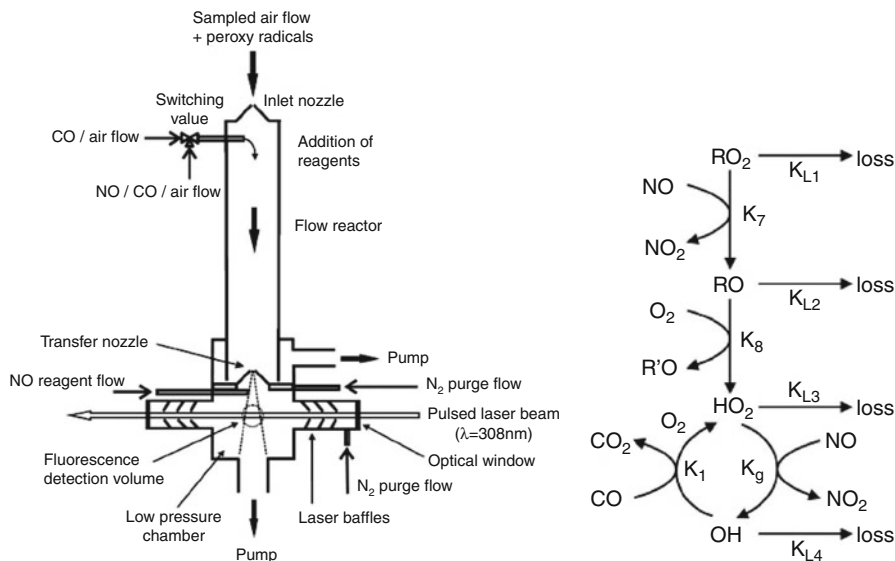
Fig. 5.1 Schematic diagram (*left*) of the ROxLIF instrument used to measure the sum of organic peroxy radicals. RO_2 is first converted to HO_2 in the flow reactor (25 hPa) through the addition of NO and CO via the chemical scheme shown on the *right hand panel*, and HO_2 is then detected in a FAGE fluorescence cell (Taken from Fuchs et al. [8])

HO_2), in a normal FAGE fluorescence cell, where the pressure is typically between 0.6 and 4 Torr, the rate of the reaction:

$$RO + O_2 \rightarrow R'CHO + HO_2 \qquad (5.5)$$

is too slow to give significant conversion prior to the laser-probe volume where OH is detected, and so RO_2 does not constitute any of the signal measured as HO_2. This assumption, however, has recently been brought into question for larger R, and also when R contains an unsaturated or oxygenated functional group, as described below. Figure 5.1 shows the apparatus developed by Fuchs et al. [8] to measure RO_2 radicals, which is a modification of FAGE with a tubular pre-reactor into which ambient air is sampled via an expansion and NO and CO are added. The pre-reactor is connected to the FAGE fluorescence cell via a large pinhole (4 mm in diameter), where air undergoes a further, but modest expansion, and OH and HO_2 are detected (the latter via a second addition of NO).

The NO converts both HO_2 to OH, and RO_2 to RO, but as the pre-reactor is held at a considerably higher pressure (~30 Torr), the rate of reaction (5) is now high enough to give good conversion of RO to HO_2. However, the HO_2 formed is rapidly converted to OH, and due to the relatively long residence time in the pre-reactor to ensure that reaction (5) is complete, wall-losses of OH will be significant, leading to a very large loss of radicals before the second expansion, and concomitant loss in sensitivity. In a manner similar to PERCA, CO is added to convert OH and HO_2, and the relative flows and hence partial pressures of NO and CO are maintained

such that the lifetime of OH by reaction with CO is very short, and the HO$_2$ to OH ratio kept high, so wall losses are minimised (HO$_2$ is much less reactive on the walls). Hence the radicals are in the form of HO$_2$ when sampled a second time into the FAGE cell for detection as HO$_2$. This method has now been adopted by other groups, and has enjoyed success both in the field and in chamber studies. Although a larger number of NO$_2$ and CO$_2$ molecules will be formed, as in PERCA, it is HO$_2$ that is detected directly using the FAGE technique with excellent sensitivity.

Speciation between, OH, HO$_2$ and the sum of other peroxy radicals is achieved in the ROxLIF method via modulation of the two NO flows and the CO flow. With no NO or CO added in the pre-reactor, HO$_2$ and RO$_2$ survive the passage to the second pinhole, and enter into the FAGE fluorescence cell, where only OH is detected in the absence of added NO. The OH signal is very low as ambient OH is chemically or physically lost on the walls during the significant residence time in the pre-reactor. With NO added in the fluorescence cell HO$_2$, but not RO$_2$, is detected due to the very low pressure (but see section below on interferences), and if CO is added to the pre-reactor, the sum of OH and HO$_2$ can be measured. Finally with NO added as well to the pre-reactor the sum of OH, HO$_2$ and RO$_2$ is measured, and RO$_2$ can be obtained by subtraction. If the pre-reactor/fluorescence cell combination is calibrated for HO$_2$, then measurement of [HO$_2$] in a separate, independent FAGE cell will enable continuous subtraction of the contribution of HO$_2$ to the observed total signal from HO$_2$ and RO$_2$ in the RO$_2$ cell. By adding the relevant hydrocarbon to the calibration flow-reactor containing water vapour, a range of RO$_2$ species can be generated and used to calibrate the instrument. Fuchs et al. measured the relative sensitivity of their ROxLIF instrument for peroxy radicals derived from methane (1.00), ethane (0.91), propane (0.96), isobutane (0.59), ethene (0.98) and isoprene (1.21), with the value in brackets being relative to CH$_3$O$_2$. A disadvantage is that ROxLIF still does not distinguish between different organic peroxy radicals, so in order to compare with a model calculation, it is necessary first to multiply the model-derived concentration for each RO$_2$ by the relevant sensitivity factor in order to compare with the field measured value. However, the ratio [ΣRO$_2$]/[HO$_2$] from the same instrument still provides important, and novel information about the mechanisms for chemical oxidation. An intercomparison between ROxLIF and the matrix isolation electron spin resonance (MIESR) technique (no longer operated by Julich) for HO$_2$ and RO$_2$ gave good agreement, with correlation slopes of 0.98 and 1.02, respectively [9]. An older field intecomparison between a PerCIMS and FAGE instrument for HO$_2$ also gave good agreement [27].

5.5 Surprising Results from the Field Which Have Raised Questions

Measurements of OH and HO$_2$ radicals in and above forested regions at low NOx have proven difficult to reconcile with the calculations of constrained box-models with embedded chemical mechanisms which can be very detailed. Carslaw et al. [3]

Fig. 5.2 Observed to
modelled ratio of [OH] taken
during INTEX-A for less than
1 km altitude (*open circles*)
and from the ground during
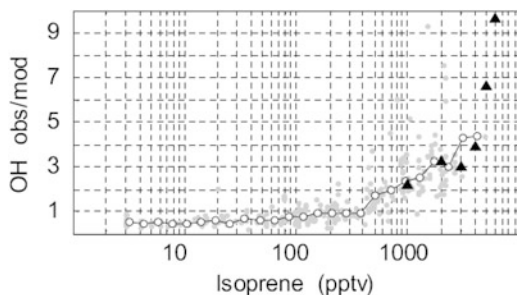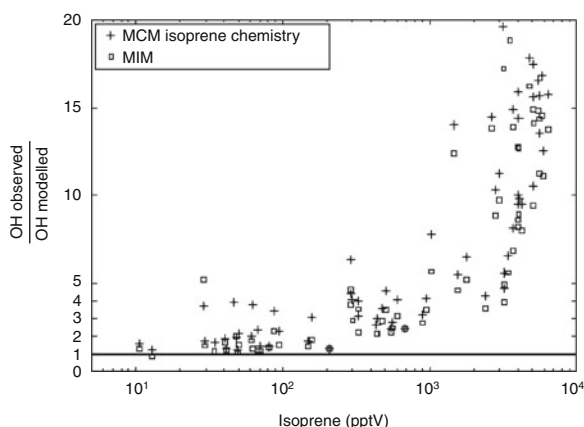PROPHET (*solid triangles*)
(Taken from Ren et al. [29])

Fig. 5.3 Observed to
modelled ratio of [OH] during
the GABRIEL campaign over
the Suriname rainforest as a
function of isoprene
concentration, for two
different models (Taken from
Kubistin et al. [20])

observed an OH_{obs}/OH_{mod} ratio of ~2 in a pine forest during the AEROBIC
campaign in Northern Greece. During INTEX-A over the continental United States
Ren et al. [29] reported OH_{obs}/OH_{mod} and $HO_{2,obs}/HO_{2,mod}$ ratios up to 8 and 5,
respectively, with the ratio scaling roughly with the concentration of isoprene, as
shown for OH in Fig. 5.2. Measurements in the boundary layer above the tropical
rainforests of Suriname during the GABRIEL campaign [20] observed similar
behaviour, with OH_{obs}/OH_{mod} as high as 15, as shown in Fig. 5.3. In these environ-
ments, which are characterised by a rich mix of biogenically derived BVOCs, it is
difficult to adequately measure all the sinks for OH. Whalley et al. [37], using field
measurements of OH reactivity to constrain the total rate of loss of OH, were able to
show in a tropical rainforest in Malaysian Borneo during the OP-3 campaign that
including all measured OH sources into a model gave a factor of ~10 underpre-
diction compared with measured [OH], as shown in Fig. 5.4. Likewise, Stone et al.
[33], using the very detailed *Master Chemical Mechanism*, reported a significant
underprediction of [OH] using currently accepted mechanisms. Finally, as shown
in Fig. 5.5, during low NOx periods near the Pearl River Delta in China during
the PRIDE-PRD campaign, Hofzumahaus et al. [18], using a similar approach with
measured [OH] and OH reactivity, reported a significant model underprediction.
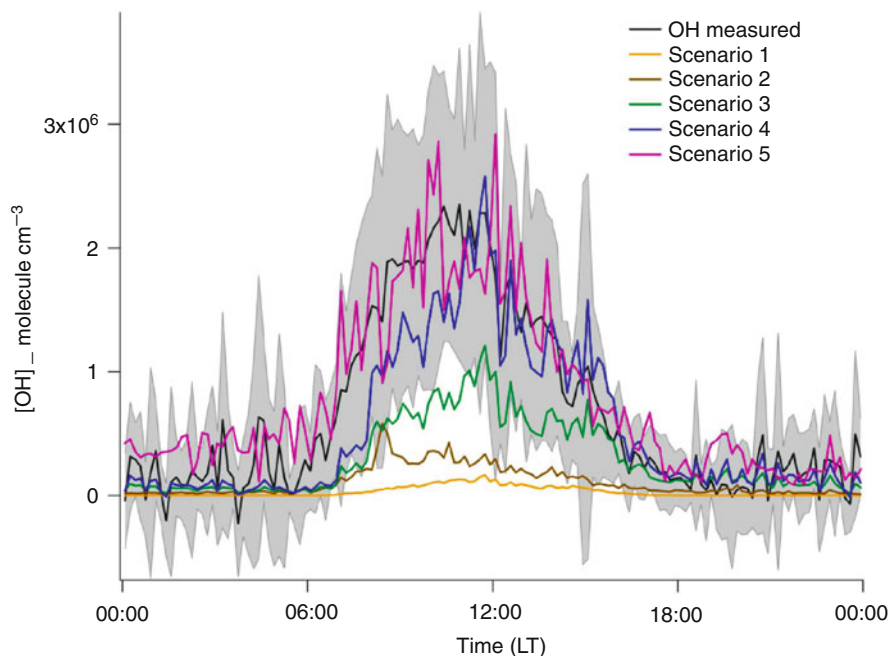
Fig. 5.4 Diurnal profile of measured OH concentrations during the OP-3 campaign in Borneo (*black line*) together with model calculations constrained by the measured OH reactivity and various source terms (Scenarios 1–5). Unless a significant OH recycling term during the oxidation of isoprene is included, the measured/modelled ratio of [OH] is high (Taken from Whalley et al. [37])
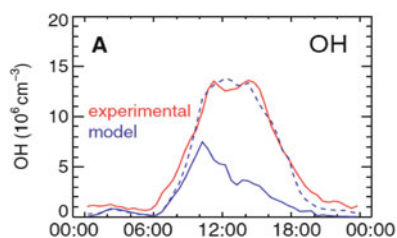

Fig. 5.5 Comparison of measured and modelled mean diurnal profiles of OH radicals during the Pearl River Campaign, China. The model used was the RACM, with the *dotted line* representing an extended RACM model with additional HO$_2$ and RO$_2$ recycling (Modified from Hofzumahaus et al. [18])

Recently, attention has been given to the photo-oxidation of hydroperoxy-aldehydes (HPALDS), a product of isoprene oxidation, which upon photolysis leads to the formation of OH, and which also reacts with OH, and inclusion of this chemistry buffering OH concentrations improves agreement between measurements and model calculations [35].

All of these results suggest a lack of understanding in our description of the chemistry taking place at these locations. There have been a number of theoretical, laboratory and chamber studies which have suggested new sources of OH from the oxidation of isoprene, and which can partially explain these findings. Discussion of this new chemistry is beyond the scope of this paper, yet remains a controversial topic with several groups striving to measure the rates of key reactions in the laboratory. Some aspects of this are covered in, for example, Taraborrelli et al. [35], Stone et al. [33], Peeters et al. [26], Crounse et al. [5] and papers therein.

5.6 HO_2 Interference from Alkene-Derived RO_2 Radicals

Ambient measurements of HO_2 have almost exclusively been made by chemical titration of HO_2 to OH by NO and the subsequent detection by FAGE of the OH radical using laser induced fluorescence (LIF) at low pressures (~1 Torr) [15]. Until recently it was assumed that higher peroxy radicals (RO_2) could not act as an HO_2 interference in LIF because although these species also react with NO to form an alkoxy radical (RO) at 1 Torr the subsequent reaction $RO + O_2$ to give HO_2 is too slow. Independent laboratory studies conducted at the University of Leeds, UK [16] and at the Forschungzentrum, Julich, Germany [11], however, have revealed that alkene-derived RO_2 radicals, longer chain alkane-derived RO_2 (>C3) and also RO_2 from methanol and aromatic species can be converted to HO_2 in the presence of NO in a LIF detection cell, via the mechanisms shown in Fig. 5.6 [11]. Heard et al. [16] showed that if allowed to proceed to completion by ensuring a long enough reaction time, the yields of HO_2 were found in the most part to agree with yields calculated using the *Master Chemical Mechanism* (http://mcm.leeds.ac.uk/ MCM/) [16]. For ethene and isoprene derived RO_2 species, the relative sensitivity was found to be close to 100% with respect to that for HO_2. Ironically, it was during experiments designed to measure the HO_2 yield following the oxidation of OH by isoprene, that the interference in the detection of HO_2 due to alkene-derived RO_2 was discovered, as the reaction of OH with ethene appeared to generate HO_2, which it should not in the absence of NO [16]. Given these results, and the agreement with the MCM, it is perhaps surprising that it has taken the radical measurement community so long to appreciate that some RO_2 species may contribute some of the signal that has previously been assigned to HO_2, particularly in urban or forested environments. Using a clever isotope experiment, it was also demonstrated that the photolysis of water vapour at 185 nm generated equal concentrations of OH and HO_2, a critical assumption made by groups using this calibration method, but never explicitly demonstrated [11].

However, the interference will only be significant for field reported concentrations of HO_2 if the experimental configuration of the FAGE instrument being used is conductive to any conversion of RO_2 into HO_2 in the presence of NO. Experimental variables which vary considerably between different field instruments include the fluorescence cell pressure, the residence time of the sampled
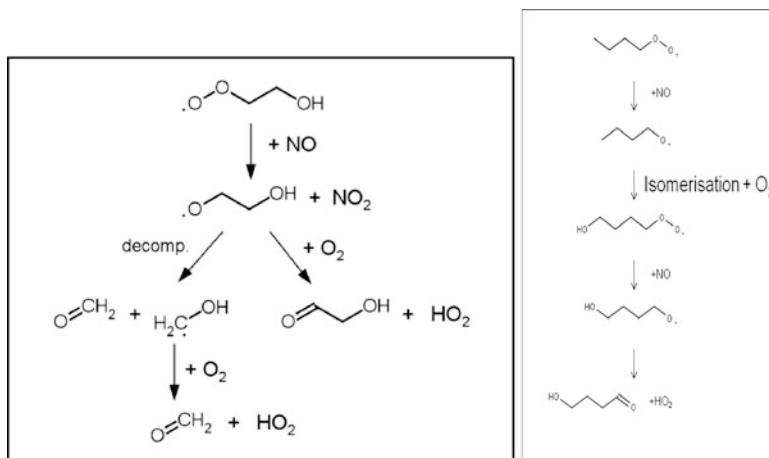
Fig. 5.6 Reaction scheme (*left*) which converts β-hydroxyalkyl peroxy radicals to HO$_2$ in the presence of NO (shown here for the ethene RO$_2$ radical) (Taken from Fuchs et al. [11]). The *right hand panel* shows how a C$_4$ alkoxy radical can isomerise and react with O$_2$ and eventually reform HO$_2$ (diagram courtesy of Dr. L. Whalley)

air in the fluorescence cell prior to laser excitation of OH (related to the pumping speed and geometry of the cell), the concentration of NO added to convert HO$_2$, details of the supersonic expansion which will determine the degree of mixing of NO into the ambient jet, the proximity of the walls to the sampled flow, and the volume from which fluorescence is imaged on to the detector (determined by whether a single or multi-pass laser excitation scheme is used). The percentage conversion of RO$_2$ into HO$_2$ will be influenced by these parameters. Fuchs et al. [11] demonstrated that by changing the inlet configuration of the FAGE cell (diameter of the sampling pinhole which changed the sample flow rate and hence the conversion reaction time), the interference was changed considerably.

Under the field operating conditions employed during the 2008 OP3 campaign that took place in the Borneo rainforest, the University of Leeds ground-based LIF instrument for HO$_2$ was not sensitive to detection of these RO$_2$ species, despite the presence of high concentrations of isoprene [16]. The large cell, low pressure and short residence time (due to large capacity pumps), coupled with relatively poor mixing of NO into the ambient air-stream for the titration of HO$_2$ to OH, minimised this potential interference, and <10% of [HO$_2$] may be attributed to any interference from isoprene derived RO$_2$ for this setup. For the Leeds aircraft instrument [4], which utilises smaller fluorescence cells and a longer residence time, the interference was higher (40% for ethene compared to 12% for the ground configuration). Furthermore, the degree of interference could be reduced using a lower concentration of NO in the cell, as predicted using the model, and consistent with the results of Fuchs et al. [11]. Equipped with knowledge of this interference for HO$_2$ and the controlling parameters, it will be possible for practitioning groups to design the configuration and geometry of their FAGE sampling systems and cells to

minimise interferences from RO_2. Also, a cell that is not subject to interference from isoprene derived RO_2 species can be used to determine the yield of HO_2 radicals from the OH initiated oxidation of isoprene. Using the Leeds ground-based LIF detection cell coupled to a flow-tube, experiments to determine the time resolved yield of HO_2 radicals during the OH-initiated oxidation of isoprene have been conducted. OH was generated by photolysis of t-butyl-hydro-peroxide by 254 nm radiation from a Hg lamp in a dry air flow at variable positions along the flow-tube. Isoprene was then added downstream of the lamp. However, no HO_2 was observed on a ~1 s timescale, consistent with a smaller value of the isomerisation rate of the isoprene-RO_2 radical to generate HO_x reported by Crounse et al. [5], but not with the larger rate calculated by Peeters et al. [26].

5.7   Is There an Interference for OH Radicals During Field Measurements Using FAGE?

Earlier experiments performed in the laboratory by Ren et al. [28] reported negligible interferences for the detection of OH for a range of species, including H_2O_2, SO_2, HONO, HCHO and a range of VOCs with difference functional groups (alkanes, alkenes, alcohols, including isoprene). A small interference scaling with ozone and water vapour was observed, as reported by some other groups, but which can be corrected for. The usual method to determine the background signal in a FAGE instrument is to exploit the narrow spectral profile of a single rotational transition of OH, and move the laser wavelength away from the OH line and measure the sum of solar, cell-induced and Mie scattered light. However, in the recent BEARPEX study in a California forest using a FAGE instrument, Mao et al. [25] used an alternative method to determine the background, which does not involve changing the wavelength, rather injecting C_3F_6 into the sampled ambient air stream to remove ambient OH before it enters the instrument. Any remaining signal is the background, although a complication was that the addition of C_3F_6 just outside the sampling inlet also removed some of the additional OH generated inside the cell. Mao et al. found that the background using this method was considerably higher than using the spectral method, and showed that the additional background was due to OH radicals, and postulated that the OH was generated within the instrument from oxidation of an unidentified biogenic VOC. Evidence was provided to rule out laser-generation of OH within the cell. Allowing for this increased background gave measured OH concentrations that were ~40–50% of those determined using the spectral background method, and which agreed better with the calculations of a constrained box model [25].

The field site was within a Ponderosa pine plantation, and a key question is whether this type of interference has been seen previously by this and other FAGE instruments operating in other forested environments. For HO_2, the degree of interference was shown to be dependent upon instrument design [11, 16], and the
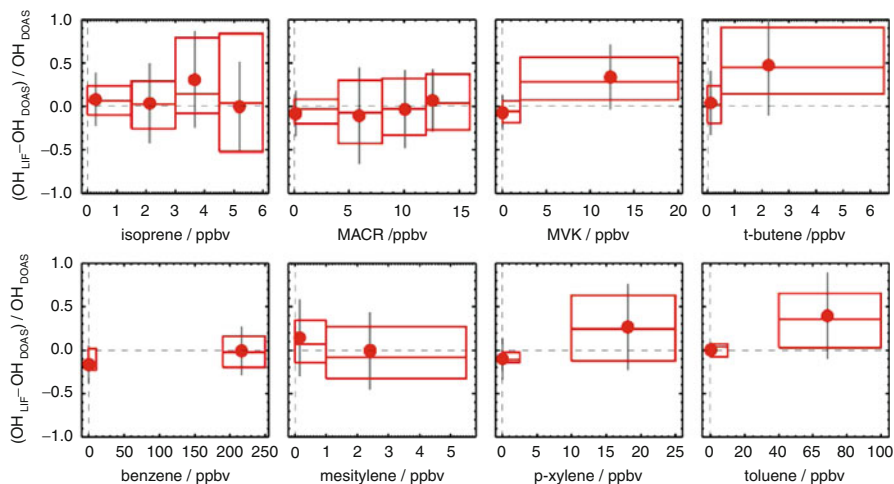
Fig. 5.7 Relative differences between DOAS and FAGE measured OH concentrations in the SAPHIR chamber as a function of various VOC concentrations. The *dots* are mean values (Taken from Fuchs et al. [12])

same may be true for any potential OH interferences. All FAGE groups should adopt the addition of C$_3$F$_6$ for some periods during fieldwork in all environments to determine the background, and compare this with the traditional spectral method, to see if there is an interference as reported by Mao et al. [25]. Laboratory experiments are also required which add a range of biogenic species and their oxidation products in order to try to observe a FAGE interference and identify its source. There is of course, no guarantee that the smoking-gun species is discovered.

A recent experiment utilising the SAPHIR chamber has compared OH concentrations measured by DOAS and FAGE under conditions of low NOx and in which significant concentrations of isoprene, methyl vinyl ketone (MVK), methacrolein (MACR) and aromatic compounds were added and were photochemically oxidised [12]. Conditions were chosen to replicate those in which significantly higher OH concentrations were measured in China compared with model predictions [18]. Over the entire set of experiments over 20 days, the linear regression of OH concentrations measured by FAGE compared to DOAS gave a slope of 1.02 ± 0.01 and an intercept of $(1.0 \pm 0.3) \times 10^5$ molecule cm^{-3}. These experiments provide strong evidence that the FAGE calibration is accurate, and as shown in Fig. 5.7, there are no significant interferences for isoprene, MACR and aromatics, although a small bias (with large uncertainties) was observed for MVK and toluene. Any differences between DOAS and LIF are far too small to explain the unexpectedly high OH concentrations seen in China [18]. Further evidence in support of the higher OH concentrations in a rainforest environment come from field measurements of HCHO using DOAS in Borneo during OP3, which can only be reproduced in a model using the measured OH levels, but not using modelled levels which are a factor of 10 lower [22].

5.8   Interferences for CIMS Instruments

In the case of CIMS, studies regarding interferences [34] have been much less studied compared to FAGE instruments. Tests include reactions that could compete with the reaction of SO_3 with H_2O (reaction (3)), the effect of H_2O vapour on the ion molecule chemistry involving NO_3^-/HNO_3/H_2SO_4 and potential wall losses. Excess propane is periodically added at the inlet (at the same injection point where SO_2 is added) in order to rapidly remove ambient OH (on a timescale that is much shorter than removal by SO_2) and enable a background signal to be determined. Also, the chemistry which generates H_2SO_4 from OH generates HO_2 in reaction (2), and this together with any HO_2 present in the ambient sample (typically HO_2 is 10–100 times more abundant than OH), could be recycled to HO_2, for example by reaction with NO or O_3 and lead to a positive bias for OH [1, 7]. Any OH produced by recycling from HO_2 (or indeed from any other mechanism) is prevented from reacting with SO_2 (and hence being detected) through removal by the addition of excess propane downstream of the injection position for SO_2 (sufficiently downstream so that all ambient OH reacts with SO_2 before it encounters propane). However, any species which can oxidise SO_2 to SO_3, but which is not removed by reaction with propane, will be detected as H_2SO_4, and will cause a positive bias to the OH measurements. Recently, Welz et al. [36] showed that the simplest Criegee intermediate, CH_2OO, reacts quickly with SO_2, and hence this is one candidate to give such an interference. A negative bias in the measured OH concentration could result from species present in ambient air reacting with OH once the air has been sampled by the CIMS inlet but before the SO_2 injection point – as these species will not be present in the calibration gas. As the transit time is short compared with the atmospheric lifetime of OH, only a small fraction of the OH would be lost in way, although this assumption may not be true if the OH reactivity is very high.

5.9   Implications for the Interpretation of Past Field Data and Future Outlook

In the case of HO_2, it is possible to provide a correction and account for the additional HO_2 concentration that derives from RO_2 radicals, using the following expression:

$$[HO_2{}^*] = [HO_2] + \sum {}_i(\alpha_{RO2,i} \times [RO_2]_i) \tag{5.E4}$$

where $[HO_2{}^*]$ is the HO_2 concentration in ambient air plus contribution from RO_2 interferences (the total measured quantity), $[HO_2]$ is the HO_2 concentration in ambient air (the desired quantity), $\alpha_{RO2,i}$ is the fraction of a given RO_2 species converted to HO_2, and subsequently OH in the detection cell, determined for the FAGE instrument in the laboratory, and $[RO_2]_i$ is the concentration of a given RO_2 in ambient air calculated using a box-model [21]. A significant disadvantage of this

method is that is relies on a model calculation for RO$_2$, as there are no field measurements of individual RO$_2$ species. However, this method does allow investigation of the difference between HO$_2$* and HO$_2$, which will depend on the mix of RO$_2$ at a particular location. For the Leeds aircraft FAGE instrument, which utilises smaller cells and for which α has been measured to be significant for some RO$_2$, the ratio [HO$_2$*]/[HO$_2$] was determined to only be 1.23 on average for the OP3 campaign over the Borneo rainforest, despite high concentrations of isoprene [33]. For other campaigns, for example AMMA [4], the value is much lower, 1.065. The correction to HO$_2$ is not likely here to change significantly any conclusions regarding the ability of the model to reproduce [HO$_2$], although this has not been tested for urban environments. However, a far better strategy is to make sure that any future measurements of HO$_2$ are not subject to this interference, through judicious design of the instrument.

For OH, it is important for the community to know whether measurements reported in previous field campaigns are accurate, for example the unexpectedly high concentrations of OH observed mainly, but not exclusively, in forested environments. The implementation of any new chemistry that is developed to explain these findings may lead to erroneous results, for example in the calculation of the lifetime of CH$_4$ (an important greenhouse gas), if the field data upon which the development of the new chemistry is based, are wrong. Mao et al. [25] developed a different measurement strategy utilising a chemical background in order to examine interferences in their instrument set-up for a forest in California, but it is difficult to know if previous measurements during other campaigns are subject to the same type of interference. All groups should perform agreed laboratory experiments to investigate the presence or not of interferences, which may allow some understanding of whether corrections to previous data are required or not. However, if an interference is revealed, the concentration of the guilty species may not have been measured, but it may be possible to use a model to calculate its concentration. Certainly groups should adopt instrument designs and sampling procedures (for example to determine the background) which minimise the possibility of interferences. In addition, there need to be further intercomparisons for OH and HO$_2$ using different methods, for example FAGE and CIMS, under field conditions in environments that provide a range of potentially interfering species.

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