The oxidation capacity of the atmosphere
#
OH and $\mathrm{HO_2}$ radical measurements in a boreal forest environment using laser induced fluorescence spectroscopy

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Abstract

The main oxidant in the degradation process of volatile organic compounds (VOCs) in the atmosphere is the hydroxyl radical (OH), which is in fast equilibrium with the hydroperoxyl radical (HO_2). Previous observation and model comparison of these radical species in forest ecosystems have unveiled a significant gap in understanding of the underlying processes.

Within the framework of this PhD thesis, OH and HO_2 were measured using laser-induced fluorescence (LIF) in a pine dominated forest in Southern Finland during the HUMPPA–COPEC–2010 (Hyytiälä United Measurements of Photochemistry and Particles in Air – Comprehensive Organic Precursor Emission and Concentration study) field campaign in summer 2010. Different components of the LIF instrument were optimized and a modified background signal detection method (Inlet$P$re$I$njector technique) was integrated and applied for the first time. Simultaneous side-by-side measurements of hydroxyl radicals were conducted with two instruments using chemical ionization mass spectrometry (CIMS) and LIF, showing good agreement. The instrument intercomparison proves the ability and performance of the modified LIF instrument to measure atmospheric OH concentrations accurately. Subsequently, the LIF instrument was moved to the top of a 20 m tower, above the canopy, to investigate the radical chemistry at the ecosystem-atmosphere interface. Comprehensive measurements including observations of the total OH reactivity were conducted and analysed using steady-state calculations as well as an observationally constrained box model.

Production rates of OH calculated from measured OH precursors, are under conditions of moderate OH reactivity ($k'_{OH} \leq 15\,s^{-1}$), consistent with those derived from the steady state assumption and measured total OH loss. The primary photolytic sources of OH contribute up to one third of the total OH production. It was shown that under conditions of moderate OH reactivity hydroxyl recycling occurs mainly by HO_2 reacting with NO and O_3. In periods when high total OH reactivity ($k'_{OH} > 15\,s^{-1}$) was observed, additional recycling pathways, forming OH directly, not via reaction of HO_2 with NO or O_3 were identified.

Box model simulations agree with measurements for atmospheric hydroxyl radicals ($OH_{mod.}/OH_{obs.}$=1.04 $\pm$ 0.16), while HO_2 mixing ratios are significantly underpredicted ($HO_2{}^{mod.}/HO_2{}^{obs.}$=0.3 $\pm$ 0.2) and simulated OH reactivity does not match the observed OH reactivity. The simultaneous underprediction of HO_2 and OH reactivity in periods in which OH concentrations were simulated well, suggests that the missing OH reactivity is an unaccounted source of HO_2. Additional RO_2/HO_2 sources that are independent of OH, such as the thermal decomposition of transported peroxyalcyl nitrates (PAN) and the photolysis of glyoxal, are indicated.

Zusammenfassung

Das wichtigste Oxidationsmittel für den Abbau flüchtiger Kohlenwasserstoffverbindungen (*VOC, engl.: volatile organic compounds*) in der Atmosphäre ist das Hydroxylradikal (OH), welches sich in einem schnellen chemischen Gleichgewicht mit dem Hydroperoxylradikal (HO$_2$) befindet. Bisherige Messungen und Modellvergleiche dieser Radikalspezies in Waldgebieten haben signifikante Lücken im Verständnis der zugrundeliegenden Prozesse aufgezeigt.

Im Rahmen dieser Doktorarbeit wurden Messungen von OH- und HO$_2$-Radikalen mittels laserinduzierten Fluoreszensmesstechnik (*LIF, engl.: laser-induced fluorescence*) in einem Nadelwald in Süd-Finnland während der Messkampagne HUMPPA–COPEC–2010 (*H*yytiälä *U*nited *M*easurements of *P*hotochemistry and *P*articles in *A*ir – *C*omprehensive *O*rganic *P*recursor *E*mission and *C*oncentration study) im Sommer 2010 durchgeführt. Unterschiedliche Komponenten des LIF-Instruments wurden verbessert. Eine modifizierte Methode zur Bestimmung des Hintergrundsignals (engl.: *I*nlet*P*re*I*njector technique) wurde in den Messaufbau integriert und erstmals zur Messung von atmosphärischem OH verwendet. Vergleichsmessungen zweier Instrumente basierend auf unterschiedlichen Methoden zur Messung von OH-Radikalen, chemische Ionisationsmassenspektrometrie (*CIMS - engl.: chemical ionization mass spectrometry*) und LIF-Technik, zeigten eine gute Übereinstimmung. Die Vergleichsmessungen belegen das Vermögen und die Leistungsfähigkeit des modifizierten LIF-Instruments atmosphärische OH Konzentrationen akkurat zu messen. Nachfolgend wurde das LIF-Instrument auf der obersten Plattform eines 20 m hohen Turmes positioniert, um knapp oberhalb der Baumkronen die Radikal-Chemie an der Schnittstelle zwischen Ökosystem und Atmosphäre zu untersuchen. Umfangreiche Messungen - dies beinhaltet Messungen der totalen OH-Reaktivität - wurden durchgeführt und unter Verwendung von Gleichgewichtszustandsberechnungen und einem Boxmodell, in welches die gemessenen Daten als Randbedingungen eingehen, analysiert. Wenn moderate OH-Reaktivitäten ($k'_{\mathrm{OH}} \leq 15\,\mathrm{s}^{-1}$) vorlagen, sind OH-Produktionsraten, die aus gemessenen Konzentrationen von OH-Vorläuferspezies berechnet wurden, konsistent mit Produktionsraten, die unter der Gleichgewichtsannahme von Messungen des totalen OH Verlustes abgeleitet wurden. Die primären photolytischen OH-Quellen tragen mit einem Anteil von bis zu einem Drittel zur Gesamt-OH-Produktion bei. Es wurde gezeigt, dass OH-Rezyklierung unter Bedingungen moderater OH-Reaktivität hauptsächlich durch die Reaktionen von HO$_2$ mit NO oder O$_3$ bestimmt ist. Während Zeiten hoher OH-Reaktivität ($k'_{\mathrm{OH}} > 15\,\mathrm{s}^{-1}$) wurden zusätzliche Rezyklierungspfade, die nicht über die Reaktionen von HO$_2$ mit NO oder O$_3$, sondern direkt OH bilden, aufgezeigt.

Für Hydroxylradikale stimmen Boxmodell-Simulationen und Messungen gut überein (OH$_{mod.}$/OH$_{obs.}$=1.04 ± 0.16), während HO$_2$-Mischungsverhältnisse in der Simulation signifikant unterschätzt werden (HO$_2{}^{mod.}$/HO$_2{}^{obs.}$=0.3 ± 0.2) und die simulierte OH-Reaktivität nicht mit der gemessenen OH-Reaktivität übereinstimmt. Die gleichzeitige Unterschätzung der HO$_2$-Mischungsverhältnisse und der OH-Reaktivität, während OH-Konzentrationen von

der Simulation gut beschrieben werden, legt nahe, dass die fehlende OH-Reaktivität in der Simulation eine noch unberücksichtigte HO_2-Quelle darstellt. Zusätzliche, OH-unabhängige RO_2/HO_2-Quellen, wie z.B. der thermische Zerfall von herantransportiertem Peroxyacetyl-nitrat (PAN) und die Photolyse von Glyoxal sind indiziert.

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1. The oxidation capacity of the atmosphere

The gaseous envelope surrounding the earth - the atmosphere of earth - mainly consists of nitrogen ($\sim$ 78 % by vol.), oxygen ($\sim$ 21 % by vol.), argon ($\sim$ 0.93 % by vol.), and a variable fraction of water ($\sim$ 0-2 % by vol.). Beside those main constituents, trace gases, such as the greenhouse gases and numerous volatile organic compounds (VOCs), are significantly influencing physical and chemical properties of the earth's atmosphere. Chemical compounds are continuously emitted into the atmosphere by geological, biogenic, and anthropogenic processes (Seinfeld and Pandis, 2006; Guenther et al., 1995, and ref. therein) including substances harmful to health. Thus, environmental pollution by emissions and the capability of the atmosphere to remove pollutants strongly affects the quality of life. This fact led to an enhanced interest in understanding the underlying processes within the last decades.

Removal of pollutants and trace gases from the atmosphere is mostly initiated by oxidation processes. Products like carbon dioxide (CO_2), water (H_2O), and water soluble compounds, that can be subsequently removed from atmosphere by wet and dry deposition, are formed. Only a few species are not affected by tropospheric oxidation chemistry, such as N_2O and chlorofluorocarbons (CFCs), which reach the stratosphere by vertical transport where they finally degrade.

The most important oxidant in the troposphere during daytime is the hydroxyl radical (OH). Furthermore, the OH radical is initiating the formation of a wide variety of secondary species, e.g. ozone and secondary organic aerosol. Ozone (O_3) and hydrogen peroxide (H_2O_2) in the case of oxidation within cloud droplets are also contributing to the oxidation capacity of the atmosphere. The photolabile nitrate radical (NO_3) can be an important nighttime oxidant in the polluted atmosphere. Though, due to its outstanding reactivity the OH radical dominates the cleansing capacity of the atmosphere.

The oxidation capacity in turn defines the atmospheric lifetime and consequently affects the abundance of most trace gases. An overview of typical lifetimes and associated transport ranges for important atmospheric trace gas species is given in Figure 1.1.

Environmental changes, like increasing anthropogenic emissions, enhanced energy consumption, change in landuse, such as urbanisation and deforestation influence the physical and chemical properties of the atmosphere, leading to a continuous change of the atmospheric composition. Nonetheless, the global OH concentration remained almost constant in the past (Lelieveld et al., 2002). This indicates that the atmospheric oxidation capacity is to some extent a buffered system with respect to changes in atmospheric trace gas concentrations. OH radicals are not necessarily removed from the system by oxidation processes. In

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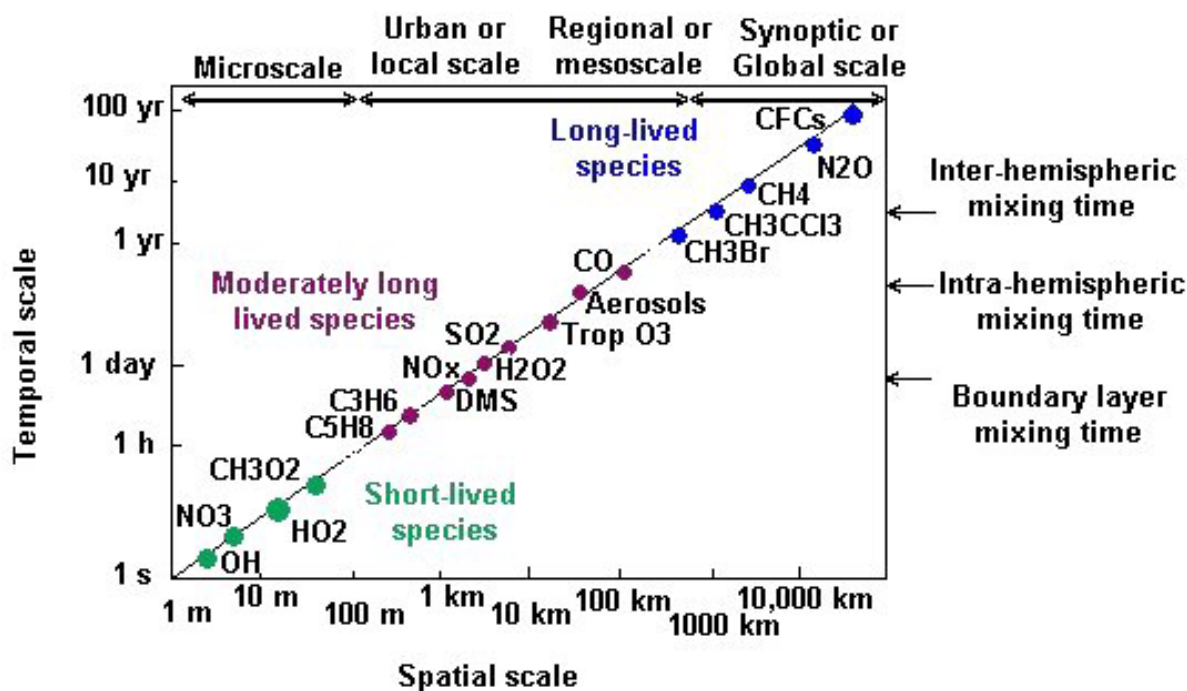
Abbildung 1.1.: Spatial and temporal scales of variability for atmospheric constituents (Taken from Seinfeld and Pandis, 2006).

fact, they are efficiently recycled, for example via the strongly linked hydroperoxyl radical (HO_2), which forms back OH in presence of nitrogen oxide (NO). Such buffering mechanisms are crucial to preserve the oxidation capacity and to prevent from catastrophic conditions, when toxic gases and gases relevant to climate would accumulate to harmful levels.

Relevance of forest ecosystems

Forests cover about one third of the earth's total land surface (FAO, 2010). They are known to be an important global source of biogenic volatile organic compounds (BVOCs) that are very reactive towards OH (Williams, 2004). A major contribution to BVOCs, such as isoprene, monoterpenes (e.g. $\alpha-$pinene), and sesquiterpenes (e.g. farnesene), is emission by vegetation (Fehsenfeld et al., 1992; Guenther et al., 1995; Kesselmeier and Staudt, 1999). Therefore, forest emissions are expected to significantly influence the oxidation capacity of the atmosphere. Measurement of OH and HO_2 radicals in forest environments, however,

unveils serious deficits in our understanding of the underlying processes. Different types of forests are known to emit various characteristic BVOCs influencing the oxidation chemistry. Several studies in and above isoprene-rich forest environments have been conducted in the past. Aircraft measurements of atmospheric trace gases performed over the pristine Amazon rainforest during the GABRIEL[1] campaign (Lelieveld et al., 2008; Kubistin et al., 2010) unexpectedly showed higher OH concentrations than predicted from box and global models. Furthermore, Kubistin et al. (2010) reported that isoprene acts as a buffer for the hydroxyl radicals, which is related to an increased HO_x recycling in the oxidation mechanism of BVOCs at low NO_x conditions, when the OH recycling reaction of HO_2 with NO is inhibited. Similarly, other studies from tropical forest regions (Stone et al., 2011; Whalley et al., 2011) reported that increased recycling would be necessary to explain the measured HO_x values. An increase of the deposition rates for OH reactants, like methyl vinyl ketone (MVK) and methacrolein (MACR), can help explain the measurement results for ground-based observations during the OP3[2] campaign in Borneo (Pugh et al., 2010a). It is unclear if measurements of the total OH reactivity are available as the observations are not compared with observations of the reactivity in the latter study. The authors conclude that the inadequacies apparent in the model are related to the representation of detailed physical and micrometeorological effects rather than errors in the chemical scheme. Measurements conducted in a deciduous forest (Tan et al., 2001) also showed an underestimation of observed OH concentrations from box model simulations. Although two follow up studies at the same site showed model predicted OH generally being in reasonable agreement with the measured OH, the model did underestimate the OH concentrations observed by a factor of about three in the afternoon during warmer periods (Griffith et al., 2013). It remains unclear if higher biogenic VOC emissions within those periods caused an instrumental interference as recently suggested by Mao et al. (2012).

Further, Kim et al. (2013) reported reasonable agreement between observed OH and that from steady-state calculations using observations, particularly measurements of HO_2, in a monoterpene dominated forest environment. Constrained box model calculations underpredicted the observed HO_2 by as much as a factor of eight and underestimated the observed OH by a factor of four. The authors conclude that the OH recycling occurs mainly via the reaction of HO_2 with NO in this forest, which is characterized by high 2-methyl-3-buten-2-ol (MBO) and monoterpene emissions (Kim et al., 2013).

Studies on oxidation processes in monoterpene dominated environments are rare. Direct OH reactivity measurements in a boreal forest, conducted by Sinha et al. (2008) and a box model study investigating the OH reactivity budget (Mogensen et al., 2011), revealed a significant fraction of "unknown OH reactivity". Comprehensive measurements in the same boreal forest were conducted during the HUMPPA–COPEC–2010 campaign (*H*yytiälä *U*nited *M*easurements of *P*hotochemistry and *P*articles in *A*ir – *C*omprehensive

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[1] *Guyanas Atmosphere-Biosphere Exchange and Radicals Intensive Experiment with the Learjet*
[2] OP3 - *O*xidant and *P*article photochemical processes above a South-East Asian tropical rain forest project

*O*rganic *P*recursor *E*mission and *C*oncentration study) (Williams et al., 2011). HUMPPA–COPEC–2010 included observations of many VOCs, HO_x and the total OH reactivity to increase our understanding of atmospheric oxidation processes based on detailed analysis of production and loss processes of the hydroxyl radical and exploring the HO_x budget in a coniferous forest, using direct calculations from measured species as well as an observationally constrained chemical box model in steady state.

The "Mainz Isoprene Mechanisms," a set of reduced chemical reaction schemes considering only isoprene as the predominant primary BVOC (Taraborrelli et al., 2009 based on Pöschl et al., 2000; Taraborrelli et al., 2012), is compared to a preliminary terpene mechanism, also taking the most abundant terpenes measured during HUMPPA–COPEC–2010 (e.g. $\alpha-$pinene, $\beta-$pinene, $\beta-$myrcene, farnesene, and Δ^3-carene) and their oxidation products into account. The modification of the chemical mechanism is analysed and discussed.

2. HO_x photochemistry in the troposphere

In the lower troposphere, the main primary source of OH on a global scale is the photolysis of ozone (O_3) and the subsequent reaction of the excited oxygen atom with water vapour (Levy II, 1971):

$$O_3 + h\nu \rightarrow O_2 + O(^1D), \qquad \lambda < 320\,nm,$$
$$O(^1D) + H_2O \rightarrow 2\,OH. \qquad\qquad\qquad (R2.1)$$
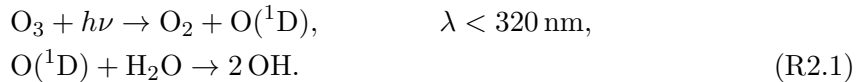
Other sources of OH, e.g. photolysis of peroxides or ozonolysis of alkenes, are known as well and were described elsewhere (Jaegle et al., 2000; Ren et al., 2008, and references therein). Once formed, OH reacts rapidly - within a typical lifetime of less than one second - with many atmospheric compounds (e.g. CO or O_3) producing hydroperoxyl radicals (HO_2). The oxidation of hydrocarbons by OH leads to the formation of peroxy radicals ($RO_x = RO_2 + HO_2$). In the presence of nitric oxide (NO) the RO_2 is converted to HO_2, which reacts with O_3 or NO forming OH (e.g. Martinez et al., 2003). Under atmospheric background conditions the HO_2 radical occurs typically at about 100 times higher concentrations compared to OH with atmospheric lifetimes in the order of $\tau_{HO_2} \approx 100\,s$, acting as a buffer for the OH radical in catalytic cycles (Weinstock, 1969; Levy II, 1971; Crutzen, 1973). The main HO_x sinks are self reactions with radicals and the formation of acids. A schematic overview of the basic HO_x chemistry is shown in Figure 2.1.

The spatial and temporal variability of HO_x radicals is typically large. Due to the short atmospheric lifetime the radicals are produced and recycled or consumed locally, depending on solar radiation, atmospheric ozone column, absolute humidity, and various trace gas concentrations. Typical OH concentrations in the lower troposphere during daytime are in the order of $[OH] \approx 10^6\,molec.\,cm^{-3}$ (equivalent to mixing ratios in the sub-ppt$_V$ range), while HO_2 concentrations are in the order of $[HO_2] \approx 10^8\,molec.\,cm^{-3}$ (equivalent to mixing ratios in the lower ppt$_V$ range).

The most relevant production, loss, and recycling pathways of HO_x will be treated in detail in the following sections.

2.1. HO_x production

Ozone molecules absorbing a photon with a wavelength $\lambda < 320\,nm$ dissociate into molecular oxygen and an excited oxygen atom, $O(^1D)$. This oxygen atom loses its excitation energy
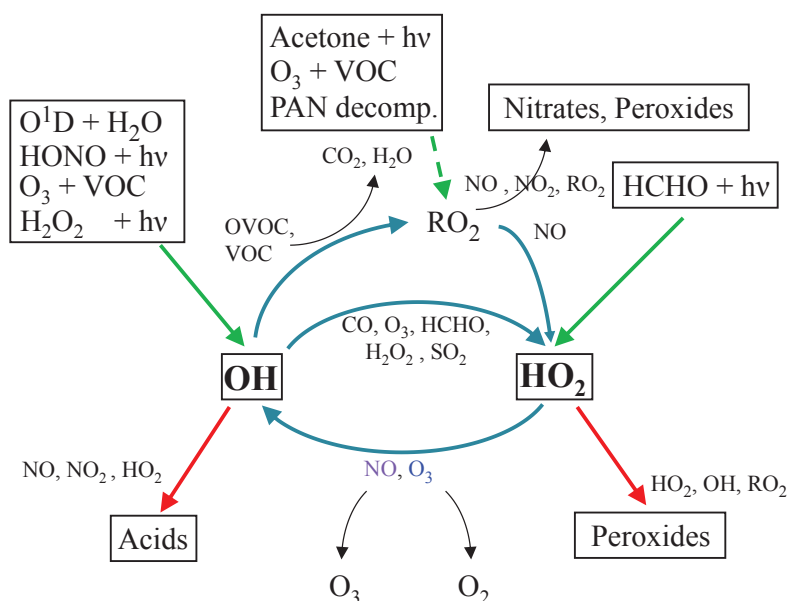
Abbildung 2.1.: Schematic overview of the HO$_x$ radical photochemistry in the troposphere. Radical production (green), recycling (blue), and loss (red) pathways are indicated by bold arrows. Some reactions are simplified. Refer to text for details.

predominantly by collision with molecular nitrogen and oxygen and returns to the ground state, O(^{3}P). Oxygen and O(^{3}P) recombine, forming back ozone. A minor portion of the excited oxygen atoms react with water vapour forming two OH radicals (Reaction R2.5).

$$O_3 + h\nu \rightarrow O_2 + O(^1D), \qquad\qquad \lambda < 320\,\text{nm}, \qquad\qquad\text{(R2.2)}$$
$$O(^1D) + M \rightarrow O(^3P) + M, \qquad\qquad M=N_2, O_2, \qquad\qquad\text{(R2.3)}$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M. \qquad\qquad\qquad\qquad\qquad\text{(R2.4)}$$

$$O(^1D) + H_2O \rightarrow 2\,OH. \qquad\qquad\qquad\qquad\qquad\text{(R2.5)}$$

The resulting primary production rate of OH radicals is given by

$$\frac{\mathrm{d}\,[\mathrm{OH}]}{\mathrm{d}t} = 2b_{\mathrm{O}(^1\mathrm{D})\to\mathrm{OH}}\mathrm{J}_{\mathrm{O}(^1\mathrm{D})}\,[\mathrm{O}_3],$$ (2.1)

where $\mathrm{J}_{\mathrm{O}(^1\mathrm{D})}$ is the associated photolysis frequency and $b_{\mathrm{O}(^1\mathrm{D})\to\mathrm{OH}}$ denotes the branching ratio

$$b_{\mathrm{O}(^1\mathrm{D})\to\mathrm{OH}} = \frac{k_{\mathrm{O}(^1\mathrm{D})+\mathrm{H}_2\mathrm{O}}\,[\mathrm{H}_2\mathrm{O}]}{k_{\mathrm{O}(^1\mathrm{D})+\mathrm{H}_2\mathrm{O}}\,[\mathrm{H}_2\mathrm{O}] + k_{\mathrm{O}(^1\mathrm{D})+\mathrm{O}_2}\,[\mathrm{O}_2] + k_{\mathrm{O}(^1\mathrm{D})+\mathrm{N}_2}\,[\mathrm{N}_2]}.$$ (2.2)

At 298 K and 1 % water vapour content about 14 % of the excited O(^{1}D) atoms lead to the formation of OH radicals (Atkinson et al., 2006).

The ozonolysis of alkenes, and particularly terpenes, represents a non-photolytic primary OH source. A primary ozonide and subsequently a Criegee Intermediate is formed within this reaction, which can release OH radicals during its decomposition (Criegee, 1975).

$$\mathrm{Alkene} + \mathrm{O}_3 \to \alpha\mathrm{OH} + \text{ products.}$$ (R2.6)
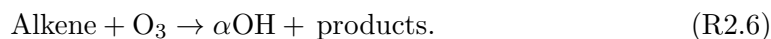
The photolysis of nitrous acid (HONO) at wavelenghts below 380 nm yields OH and nitric oxide (Reaction R2.7). HONO itself is formed on surfaces by reaction of nitrogen dioxide (NO$_2$) and water. It typically accumulates during nighttime and starts to decompose in the morning hours, when solar radiation increases (Aumont et al., 2003; Kleffmann et al., 2002, 2005).

$$\mathrm{HONO} + h\nu \to \mathrm{OH} + \mathrm{NO}, \qquad \lambda < 380\,\mathrm{nm}.$$ (R2.7)

HO$_2$ is produced within the radical channel of the photolysis reaction of formaldehyde (HCHO):

$$\mathrm{HCHO} + h\nu \xrightarrow{+2\mathrm{O}_2} 2\mathrm{HO}_2 + \text{ products.}$$ (R2.8)

From ozonolysis of hydrocarbons HO$_2$ radicals can form as well.

Beside those primary HO$_\text{x}$ sources, the photolysis of hydrogen peroxide as well as organic peroxides, which are products in the oxidation process of VOCs contribute as secondary OH sources.

$$\mathrm{H}_2\mathrm{O}_2 + h\nu \to 2\mathrm{OH}, \qquad \lambda < 557\,\mathrm{nm},$$ (R2.9)

$$\mathrm{ROOH} + h\nu \to \mathrm{OH} + \mathrm{RO}, \qquad \lambda < 360\,\mathrm{nm}.$$ (R2.10)
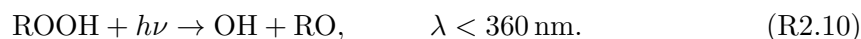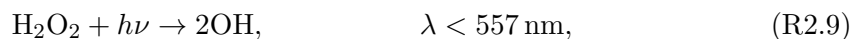
Especially in the upper troposphere, where the water vapour content in air is reduced and therefore, Reaction R2.5 is inhibited, hydrogen peroxide photolysis becomes more important.

2.2. HO_x **sinks**

HO_x radicals are primarily lost within radical-radical reactions forming peroxides and other products.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \tag{R2.11}$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2, \tag{R2.12}$$

$$OH + HO_2 \rightarrow H_2O + O_2. \tag{R2.13}$$
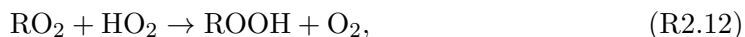
The photolysis of peroxides (see Reaction R2.9-R2.10) leads to the production of OH. However, peroxides are mainly lost by wet and dry deposition processes, thus, being removed from the HO_x cycle.

The formation of acids is another sink for OH and HO_2 radicals.

$$NO + OH \xrightarrow{M} HONO, \tag{R2.14}$$

$$NO_2 + OH \xrightarrow{M} HNO_3, \tag{R2.15}$$

$$NO_2 + HO_2 \xrightarrow{M} HNO_4. \tag{R2.16}$$

Heterogeneous chemistry and radical deposition can also contribute to the HO_x radical loss.

2.3. **Oxidation of volatile organic compounds and** HO_x **recycling**

The OH-initiated oxidation of carbon monoxide (CO) is on global average one of the most important loss reactions of the OH radical. Furthermore, HO_2 is produced when CO is converted into CO_2 by oxidation reaction.

$$CO + OH \rightarrow H + CO_2, \tag{R2.17}$$

$$H + O_2 + M \rightarrow HO_2 + M. \tag{R2.18}$$

Beside CO, ozone (O_3), formaldehyde (HCHO), hydrogen peroxide (H_2O_2), and SO_2 also react with OH radicals forming HO_2.

$$OH + O_3 \longrightarrow O_2 + HO_2 \tag{R2.19}$$

$$OH + HCHO \xrightarrow{+O_2} H_2O + CO + HO_2 \tag{R2.20}$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \tag{R2.21}$$

$$OH + SO_2 \xrightarrow{+O_2,H_2O} H_2SO_4 + HO_2 \tag{R2.22}$$
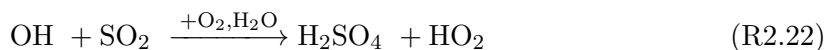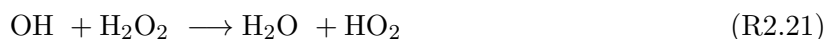
At NO levels of about $100\,\text{ppt}_V$ and higher the HO_2 radicals reacting with NO can recycle the hydroxyl radical, providing it for another oxidation process. Similarly the reaction of

HO$_2$ with ozone forms back OH (Reactions R2.23 - R2.24).

$$HO_2 + NO \rightarrow OH + NO_2, \tag{R2.23}$$

$$HO_2 + O_3 \rightarrow OH + 2O_2. \tag{R2.24}$$

The OH-initiated oxidation of volatile organic compounds represents another HO$_x$ recycling pathway. The most abundant atmospheric VOC is the greenhouse gas methane (CH$_4$). Due to its long chemical lifetime of about 8 years it is homogeneously distributed spatially within the troposphere. Methane is mainly oxidized by reaction with the OH radical, leading to the formation of methylperoxy radicals (CH$_3$O$_2$). CH$_3$O$_2$ reacting with NO yields methoxy radicals (CH$_3$O), which react rapidly with oxygen forming HO$_2$ and formaldehyde.

$$CH_4 + OH \rightarrow CH_3 + H_2O, \tag{R2.25}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M, \tag{R2.26}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2, \tag{R2.27}$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2. \tag{R2.28}$$
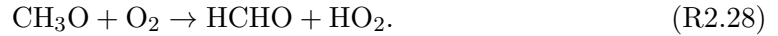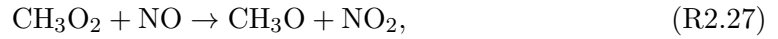
The HO$_x$-cycle is completed forming back OH radicals by Reactions R2.23 & R2.24. The oxidation of other VOCs follows a similar reaction chain:

$$RH + OH \rightarrow R + H_2O, \tag{R2.29}$$

$$R + O_2 + M \rightarrow RO_2 + M, \tag{R2.30}$$

$$RO_2 + NO \rightarrow RO + NO_2, \tag{R2.31}$$

$$RO + O_2 \rightarrow R'CHO + HO_2, \tag{R2.32}$$
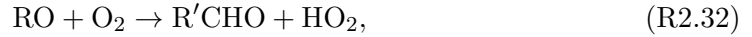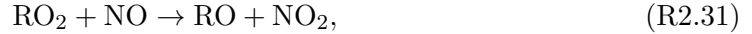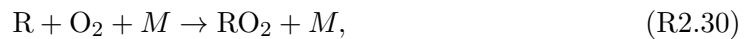
where R denotes an organic group.

Organic peroxy radicals (RO$_2$) are formed in the reaction of the hydrocarbon with OH. The subsequent reaction of RO$_2$ with NO leads to the formation of alkoxy radicals (RO), which rapidly react with oxygen, producing HO$_2$ radicals and organic aldehydes.

In close analogy to the HO$_x$ sinks described above, RO$_2$ radicals can be lost from the radical cycle by reactions with other RO$_2$ radicals, HO$_2$ (Reaction R2.12), and NO$_x$ forming peroxides and peroxynitrates.

$$RO_2 + R'O_2 \rightarrow products, \tag{R2.33}$$

$$RO_2 + NO \xrightarrow{M} RONO_2, \tag{R2.34}$$

$$RO_2 + NO_2 \xrightarrow{M} RO_2NO_2. \tag{R2.35}$$

Peroxynitrates thermally decompose, forming back peroxy radicals and NO$_2$, thus acting as a reservoir species for the peroxy radicals and NO$_x$.

$$RO_2NO_2 \rightarrow RO_2 + NO_2. \tag{R2.36}$$

The reaction of specific alkylperoxy radicals with HO$_2$, which was previously only considered as a radical termination process, represent an additional OH recycling pathway. Laboratory studies investigating the OH production from the reactions of ethyl peroxy, acetyl peroxy, and acetonyl peroxy radicals with HO$_2$ revealed OH yields up to 70 % (Thornton et al., 2002; Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008). A direct recycling mechanism, forming back OH from RO$_2$ in the absence of NO, by a 1,5-H-shift, was proposed by Peeters et al. (2009) for the OH-initiated degradation of isoprene. The occurence of a 1,6-H-shift leads to the recycling of an HO$_2$ radical (Figure 2.2).
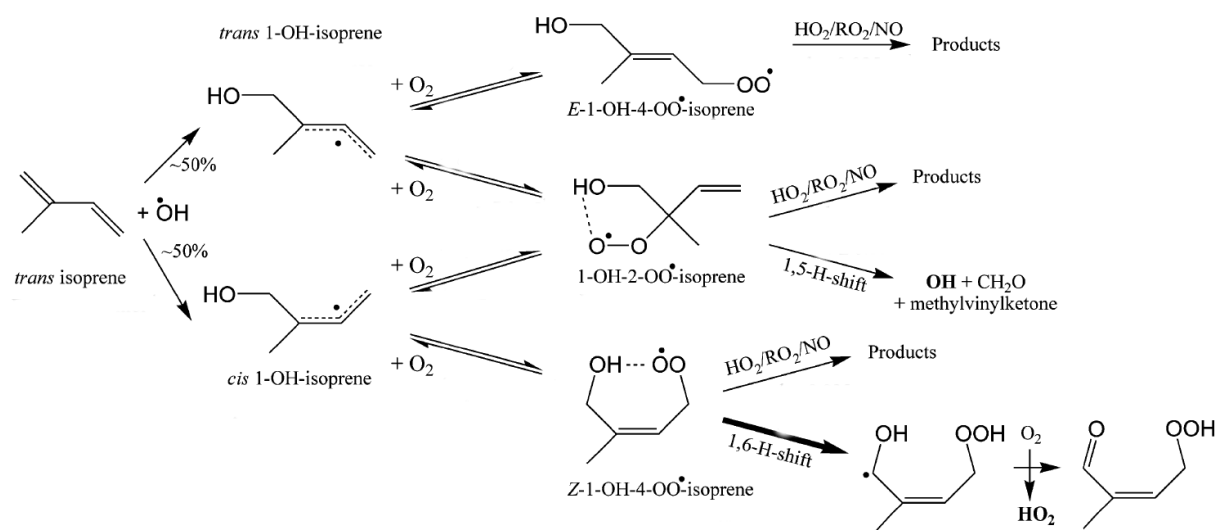
Abbildung 2.2.: Reaction scheme for OH and HO$_2$ radical formation following 1-OH addition to isoprene by a 1,5- and a 1,6-H-shift, respectively (Taken from Peeters et al., 2009, and modified).

2.4. The relationship between HO$_x$ and J$_{O(^1D)}$

When primary production is the predominant source of OH, the hydroxyl radical concentration follows the course of J$_{O(^1D)}$ (Rohrer and Berresheim, 2006). During daytime the main primary source of OH is the photolysis of O$_3$ and the reaction of O(^{1}D) with water vapour (Reaction R2.5). Under conditions of low NO, O$_3$, and non-methane hydrocarbon concentrations (clean background atmosphere) the secondary OH production, i.e. the recycling reactions forming back OH from HO$_2$ (Reactions R2.23 - R2.24), is inhibited. Stationary-

state can be assumed for OH due to its short lifetime:

$$\frac{d\,[OH]}{dt} = P_{OH}^{total} - L_{OH}^{total} = 0. \tag{2.3}$$

The production of OH under clean background atmosphere conditions is mainly determined by Reactions R2.5 and R2.24:

$$P_{OH}^{total} = 2b_{O(^1D)\rightarrow OH}J_{O(^1D)}\,[O_3] + k_{HO_2+O_3}\,[O_3]. \tag{2.4}$$

The most relevant OH loss processes are Reactions R2.17 and R2.25:

$$L_{OH}^{total} = k_{CH_4+OH}\,[CH_4]\,[OH] + k_{CO+OH}\,[CO]\,[OH]. \tag{2.5}$$

When $k_{O(^1D)+H_2O}\,[H_2O] \ll k_{O(^1D)+O_2}\,[O_2] + k_{O(^1D)+N_2}\,[N_2]$ and $k_{HO_2+O_3} \ll 2b_{O(^1D)\rightarrow OH}J_{O(^1D)}$ the hydroxyl radical concentration is approximately

$$[OH] = \frac{2J_{O(^1D)}\,[O_3]\,[H_2O]k_{O(^1D)+H_2O}}{k_{O(^1D)+M}\,[M] + k_{CH_4+OH}\,[CH_4]k_{CO+OH}\,[CO]}, \tag{2.6}$$

where $M = O_2$, N_2. The variability of the photolysis frequency $J_{O(^1D)}$ is typically large compared to the variability of CH_4, O_3, CO, and H_2O concentrations resulting in a quasi-linear relationship between OH and $J_{O(^1D)}$ (Holland et al., 2003; Rohrer and Berresheim, 2006).

As shown by the following equations, the HO_2 concentration is proportional to $\sqrt{J_{O(^1D)}}$ under clean background atmosphere conditions. The production of HO_2 is dominated by Reaction R2.17. HO_2 is mainly lost by reaction with O_3 and in radical-radical reactions (Reactions R2.11-R2.12, R2.24):

$$P_{HO_2}^{total} = k_{CO+OH}\,[CO]\,[OH], \tag{2.7}$$

$$L_{HO_2}^{total} = k_{HO_2+O_3}\,[HO_2]\,[O_3] + 2k_{HO_2+HO_2}\,[HO_2]^2 + ...$$
$$k_{HO_2+CH_3O_2}\,[HO_2]\,[CH_3O_2]. \tag{2.8}$$

Methylperoxy radicals are formed in the OH-initiated oxidation of CH_4 (Reactions R2.25 - R2.26) and mainly lost by reaction with other radicals:

$$P_{CH_3O_2}^{total} = k_{CH_4+OH}\,[CH_4]\,[OH], \tag{2.9}$$

$$L_{CH_3O_2}^{total} = k_{HO_2+CH_3O_2}\,[HO_2]\,[CH_3O_2]. \tag{2.10}$$

For the sum of CH_3O_2, HO_2, and OH radicals the steady-state is

$$\frac{d(\,[OH] + [HO_2] + [CH_3O_2]\,)}{dt} = 2b_{O(^1D)\rightarrow OH}J_{O(^1D)}\,[O_3] - 2k_{HO_2+HO_2}\,[HO_2]^2 + ...$$
$$- 2k_{HO_2+CH_3O_2}\,[HO_2]\,[CH_3O_2] = 0. \tag{2.11}$$

The resulting HO$_2$ concentration is proportional to the square root of the photolysis frequency J$_{O(^1D)}$(Penkett et al., 1997):

$$[\mathrm{HO_2}] = \left(\frac{\mathrm{b_{O(^1D) \to OH}} \mathrm{J_{O(^1D)}}\, [\mathrm{O_3}]}{\mathrm{k_{HO_2+HO_2}} + \alpha \mathrm{k_{HO_2+CH_3O_2}}} \right)^{\frac{1}{2}},$$ (2.12)

where α denotes the ratio $\frac{[\mathrm{CH_3O_2}]}{[\mathrm{HO_2}]}$.

Observed relationships between HO$_x$ and the photolysis frequency J$_{O(^1D)}$ may differ significantly from the basic relations (Equations 2.6 & 2.12), when the assumptions are not applicable. Nonetheless, often linear correlation between OH and J$_{O(^1D)}$ is found, at which the proportionality factor is different for different chemical regimes (Holland et al., 2003).

3. HO_x measurements using the HORUS instrument

3.1. Techniques for HO_x radical measurements

Because of their high reactivity towards trace gases and surfaces, the lifetime of hydroxyl radicals in the troposphere is typically less than one second. Average OH concentrations are in the order of $10^5 \, to \, 10^7 \mathrm{molec.\, cm^{-3}}$ during daytime. The strongly coupled HO_2 radical is about a factor of 100 times more abundant with a typical tropospheric lifetime in the range of seconds to minutes. Therefore, highly sensitive detection systems are required for measurements of these radicals. In the last decades several direct and indirect methods have been developed. The most relevant atmospheric HO_x radical measurement techniques are discussed in the following paragraphs.

3.1.1. Techniques for the detection of atmospheric OH

^{14}CO method
Based on the assumption of carbon monoxide being mainly oxidized by hydroxyl radicals, the OH concentration in sample air can be derived by addition of isotopically labeled ^{14}CO and subsequent freeze desalination of the CO_2 produced (Felton et al., 1988). The observed concentrations of ^{14}CO and $^{14}CO_2$ in combination with the known reaction rate constant of the reaction of CO with OH provide access to the OH concentration in sample air. The lower limit of detection of the radiochemical ^{14}CO method is about $2 \times 10^5 \mathrm{molec.\, cm^{-3}}$ at an integration time of 2 minutes. Integration times of several minutes and the elaborate sample handling are the disadvantages of this method.

Spin trapping - electron paramagnetic resonance
Electron paramagnetic resonance (EPR, also known as: electron spin resonance, ESR) spectroscopy is a method to detect substances with unpaired electrons, based on the resonant absorption of electromagnetic radiation (microwaves) by the sample substance in a magnetic field. Since the chemical lifetime of OH is short, highly resolved EPR spectroscopy is too slow for detection of hydroxyl radicals. In combination with spin trapping methods the measurement of atmospheric OH becomes feasible. Janzen et al. (1978) used this method

for measurement of OH in aqueous solution. Watanabe et al. (1982) accomplished measurements of atmospheric OH using α-4-pyridyl-N-tert-butylnitrone α-1-oxide (4-POBN) for spin trapping. The hydroxy-adduct of 4-POBN can subsequently be measured by EPR, to quantify the OH radicals. The lower limit of detection of this method is on the order of 5×10^5 molec. cm^{-3} at an integration time of 20 minutes.

Differential optical absorption spectroscopy – DOAS

The differential optical absorption spectroscopy (DOAS) is based on the wavelenght-dependent absorption of light by the molecules present in the atmosphere, following Beer-Lambert's law:

$$I(\lambda) = I_0(\lambda) \exp\left(\int_0^l -\sigma_{OH}(\lambda)\,[OH]\,dl\right). \tag{3.1}$$

I_0 and I are the intensities of light before and after transmission through the sampled air along the path l, with the absorption cross section of the OH radical at the wavelength λ, $\sigma_{OH}(\lambda)$. Light from artificial (e.g. laser) or natural (e.g. the sun) light sources passes the atmosphere and the absorption spectrum is recorded using spectrographs with a high spectral resolution. Subsequently the OH absorption spectrum is extracted. DOAS is an absolute technique, thus, calibration of the instrument is not necessary. The biggest uncertainty in OH measurement by DOAS is due to the uncertainty in the absorption cross section, which is about 7 % (Dorn et al., 1995). The lower limit of detection of this method depends on the length of the lightpath, scattering by aerosols, and absorption due to other trace gases. Typically values of about 1.5×10^6 molec. cm^{-3} at an integration time of 15 minutes (2σ) can be reached.

Chemical ionization mass spectroscopy – CIMS

Chemical ionization mass spectroscopy (CIMS) is an indirect method to determine the OH mixing ratio. The OH is titrated with isotopically labeled $^{34}SO_2$ and the emerging sulfuric acid ($H_2^{34}SO_4$) is measured subsequently.

$$OH + {}^{34}SO_2 + M \rightarrow H^{34}SO_3, \tag{R3.1}$$

$$H^{34}SO_3 + O_2 \rightarrow {}^{34}SO_3 + HO_2, \tag{R3.2}$$

$${}^{34}SO_3 + H_2O + M \rightarrow H_2^{34}SO_4 + M. \tag{R3.3}$$
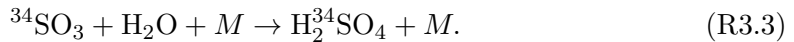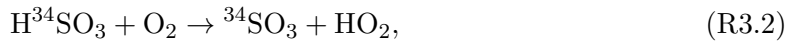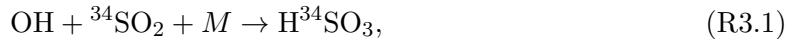
$^{34}SO_2$ is injected into the sample air in excess for efficient conversion of the OH radicals into sulfuric acid within a few miliseconds (Eisele and Tanner, 1991; Tanner and Eisele, 1995; Tanner et al., 1997; Berresheim et al., 2002; Petäjä et al., 2009). Ions of nitrate (NO_3^-) are used for ionization of the sulfuric acid by a charge transfer reaction. The nitrate ions exist mainly in a chemical complex with HNO$_3$ or H$_2$O.

$$H_2^{34}SO_4 + NO_3^- \bullet HNO_3 \rightarrow H^{34}SO_4^- \bullet HNO_3 + HNO_3. \tag{R3.4}$$
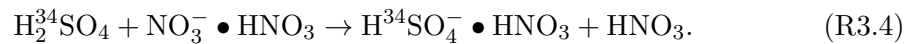
The resulting chemical complex H^{34}SO$_4^-$ ● HNO$_3$ becomes fragmented in a collision chamber and the fragments are detected by mass spectroscopy. Since the stable isotope ^{34}S makes only about 4 % of the naturally occurring sulfur, it can be distinguished between atmospheric H$_2$SO$_4$ and H$_2^{34}$SO$_4$ generated by OH titration. The measured concentration of H^{34}SO$_4^-$ is proportional to the OH concentration in sample air. The biggest uncertainty of this method is due to the uncertainty of reaction rate constants. In order to improve the uncertainty of the CIMS technique, calibrations are conducted. The lower limit of detection is on the order of 1×10^5 molec. cm^{-3} at an integration time of 5 minutes.

Laser-induced fluorescence - fluorescence assay by gas expansion – LIF-FAGE
Wang and Davis (1974) reported the first measurement of hydroxyl (OH) in air by detecting the resonance fluorescence excited by a tunable laser source in the ultraviolet. OH radicals were selectively exited at a wavelength $\lambda = 282.58$ nm on resonance with the P$_1$(2) line in the A$^2\Sigma^+ -$X$^2\Pi$, v$'$=1 $\leftarrow$ v$''$=0 transitions of OH. The transition back to the ground state occurs via various rotationally and vibrationally excited states with a high fluorescence intensity in the wavelength range between $307 - 315$ nm. However, at atmospheric pressure, most of the electronically excited OH molecules lose their energy by collisional quenching due to other molecules present in air at a typical collision lifetime of about 1 ns (Heard and Pilling, 2003). The lifetime of the excited state of OH is approximately 700 ns, and hence very few of the initially excited OH molecules will fluoresce. Large background signals due to laser scatter at aerosols, other molecules in sample air and walls inside the detection system and the low yield from OH fluorescence led to a lower limit of detection of 5×10^6 molec. cm^{-3} (Wang and Davis, 1974). Furthermore, the measurement of atmospheric OH by LIF technique as described by Wang and Davis (1974) is subject to severe limitations. The laser radiation at $\lambda \approx 282$ nm which is used to excite the OH molecules, leads also to photodissociation of atmospheric ozone, yielding O(^{1}D) atoms. The subsequent reaction of the laser-generated O(^{1}D) atoms with atmospheric water vapour leads analog Reaction R2.1 to the formation of hydroxyl radicals, so the laser radiation itself is a source of OH (Ortgies et al., 1980). The development of the FAGE (fluorescence assay by gas expansion) method was a major step in order to overcome the disadvantages of atmospheric OH measurements by LIF due to low fluorescence yields and the interference caused by laser radiation, ozone and water vapour. Hard et al. (1979) for the first time detected atmospheric OH at reduced pressure ($\sim 1-5$ hPa). OH detection at low pressure reduces the number density of water vapour and ozone, thus, limiting the production of laser-generated OH. The reduction of pressure leads to a smaller number of OH radicals available for detection and increased wall losses, due to the larger mean free path for the OH molecules inside the detection cell. Nonetheless, there is an increase in the OH fluorescence quantum yield, as the rate of collisional quenching of the excited OH radicals is reduced. The lifetime of the excited state extends to several hundred nanoseconds inside the FAGE detection system. An overview of the combined effects is presented in Figure 3.1.

15
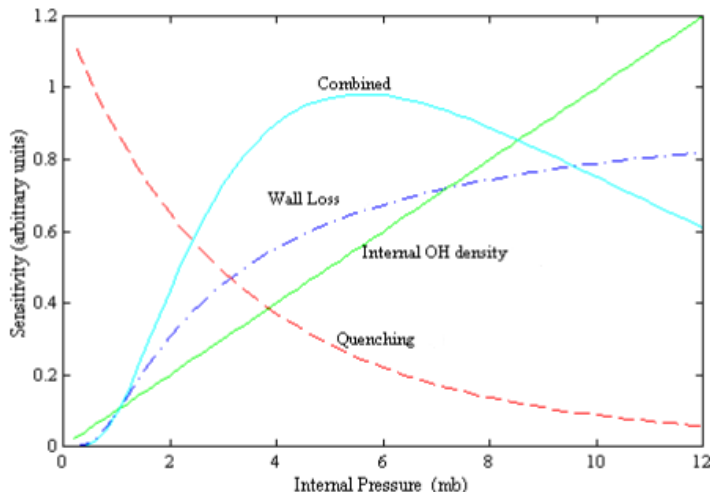
Abbildung 3.1.: Three pressure dependent components of the LIF sensitivity: the internal density (green solid line), OH transmission (blue dash-dotted line), and quenching (red dashed line). The product of these three functions (turqoise solid line) is the expected form of the pressure dependent sensitivity (Taken from Faloona et al., 2004, and modified).

Furthermore, background signals are suppressed efficiently. Background from sunlight is reduced by the sampling nozzle, used to suck ambient air into the low pressure detection cell. Baffles and black anodized walls inside the detection system are used to further suppress background photons by multiple reflections on these black surfaces. The laser-scattered background signal due to Rayleigh scattering and Mie scattering (fluorescence from aerosols) and fluorescence from the walls of the detection system can be discriminated against the OH fluorescence using a pulsed laser for excitation and a gated photon counting detection scheme (Figure 3.2). The detectors are switched off during the laser pulse by electronic gating, enabling discrimination against the much more intense background signals that exhibit the same temporal characteristics as the laser pulse (Heard and Pilling, 2003).

Present-day LIF-FAGE instruments widely use the electronic transition A$^2\Sigma^+$−X$^2\Pi$, v'=0 ← v''=0 at around 308 nm for excitation of the OH radicals, and the fluorescence is subsequently detected at similar wavelengths. This became feasible with the introduction of gated photon counting. The interference due to laser-generated OH is about a factor of 25
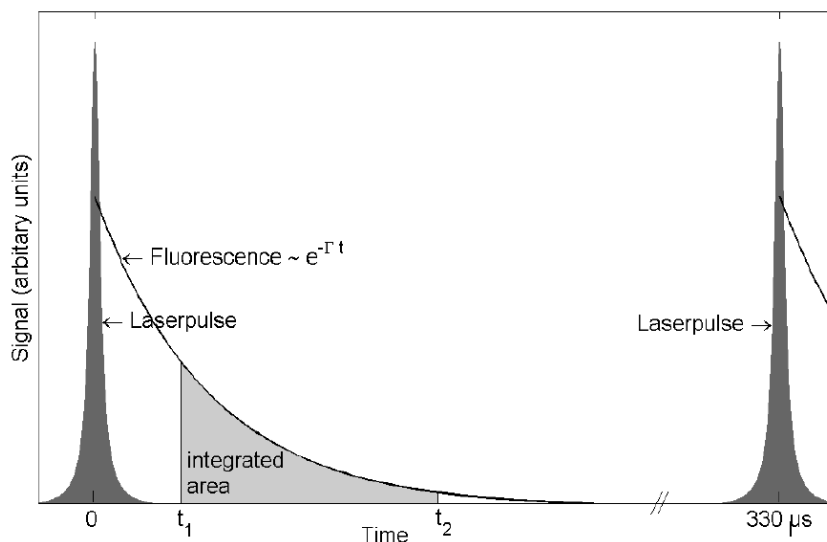
Abbildung 3.2.: Schematic representation of the timing of photon counting process that is used to quantify OH concentrations by LIF-FAGE technique. The detectors are switched off during the laser pulse by electronic gating, to discriminate against the much more intense background signals that exhibit the same temporal characteristics as the laser pulse. The integrated fluorescence signal is proportional to the number concentration of hydroxyl radicals in sample air (Taken from Faloona et al., 2004, and modified).

times smaller compared to the excitation at around 282 nm, because of the lower absorption cross section of O$_3$ and the reduced O(^{1}D) quantum yield at $\lambda = 308$ nm. The absorption cross section of OH at 308 nm is about four times larger compared to $\lambda = 282$ nm, leading to a larger OH fluorescence signal (Chan et al., 1990). The lower limit of detection of this method is typically on the order of 1×10^5 molec. cm^{-3} at an integration time of 30 seconds. Recently further development of the LIF-FAGE method in order to avoid interferences in hydroxyl radical measurements due to other atmospheric compounds is under progress and will be discussed in more detail in Section 3.2.5.

3.1.2. Techniques for the detection of atmospheric HO$_2$

Matrix isolation ESR

Measurement of atmospheric HO$_2$ radicals with Matrix isolation and electron spin resonance spectroscopy (MIESR) was developed by Mihelcic et al. (1978) and is currently the only selective method to detect HO$_2$ directly. The air is sampled by expansion through a nozzle into a chamber with reduced pressure ($\sim 10\,\mathrm{hPa}$) and the radicals are subsequently frozen out in a matrix formed by D$_2$O molecules on a sampling finger which is cooled with liquid nitrogen in order to avoid further chemical interactions between reactive molecules. Subsequently, the measurement is accomplished by electron spin resonance (ESR) spectroscopy in the laboratory. Furthermore, MIESR spectroscopy has the capability to measure the concentrations of HO$_2$, RO$_2$, CH$_3$C(O)O$_2$, NO$_3$, and NO$_2$ simultaneously in one sample. Typical sampling times of about 30 minutes are required to collect sufficient number of HO$_2$ radicals. The lower limit of detection of this method is about $1 \times 10^7\,\mathrm{molec.\,cm^{-3}}$ for HO$_2$. The sample handling, i.e. taking the samples and the necessity to store them cryogenically, results in a relatively low time resolution. The subsequent ESR analysis of the samples in laboratory is also time-consuming. However, the MIESR method does not require calibrations, thus, it is appointed as a reference method for intercomparison to other instruments.

Chemical ionization mass spectroscopy – CIMS

Chemical ionization mass spectroscopy can be used to detect HO$_2$ and RO$_2$ radicals indirectly by chemical conversion to OH (Reiner et al., 1997; Cantrell et al., 2003). The conversion is accomplished by addition of NO and O$_2$:

$$\mathrm{RO_2 + NO \rightarrow RO + NO_2,} \tag{R3.5}$$

$$\mathrm{RO + O_2 \rightarrow R'CHO + HO_2,} \tag{R3.6}$$

$$\mathrm{HO_2 + NO \rightarrow OH + NO_2.} \tag{R3.7}$$
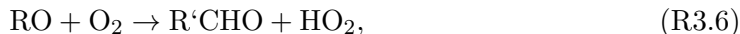
The resulting OH radicals can be subsequently detected by addition of SO$_2$, which leads to the formation of sulfuric acid (Reactions R3.1 - R3.3). Chemical ionization mass spectroscopy is used for quantification, as already described above. In contrast to measurements of atmospheric OH it is not necessary to use isotopically labeled SO$_2$, since the HO$_2$ + RO$_2$ radical concentration is about 100 times larger compared to OH, thus, the atmospheric H$_2$SO$_4$ background on the signal is small. The conversion efficiency from RO$_2$ to OH strongly depends on the amount of NO, O$_2$, and SO$_2$ injected into sample air. To detect HO$_2$ selectively, nitrogen instead of oxygen is injected, suppressing Reaction R3.6. Only ambient O$_2$ remains for conversion of RO to HO$_2$. Under these conditions 70 % to 75 % of the H$_2$SO$_4$ stem from atmospheric HO$_2$ (Heard and Pilling, 2003). The lower limit of detection of this method is about $7 \times 10^5\,\mathrm{molec.\,cm^{-3}}$ for HO$_2$ at an intergration time of 1 minute.

Laser induced fluorescence - fluorescence assay by gas expansion – LIF-FAGE
Another indirect method for the detection of HO_2 radicals is also based on the chemical conversion of HO_2 to OH by adding NO in excess to the sample air (Reaction R2.23). Following the conversion, the OH radicals are detected by LIF-FAGE technique (Heard and Pilling, 2003; Faloona et al., 2004). In order to achieve a high conversion efficiency within the short period (typically a few milliseconds) between injection of NO into the sample air and excitation of the resulting hydroxyl radicals by laser light and the subsequent detection of the fluorescence signal, high mixing ratios of NO ($\sim 500 - 1500\,\mathrm{ppm_V}$) are used. Nonetheless, the conversion efficiency is limited by the efficiency of mixing the injected NO with the sample air, and wall losses. At very high NO mixing ratios the Reaction R2.14

$$\mathrm{OH + NO} + M \rightarrow \mathrm{HONO} + M$$
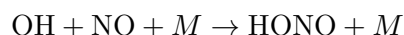
becomes a relevant loss process. Conversion efficiencies up to 95 % were established in LIF-FAGE instruments (Heard and Pilling, 2003). According to Reaction R2.31, organic peroxy radicals quickly react with NO forming RO. These RO radicals can form additional HO_2 by reaction with atmospheric oxygen (Reaction R2.32). Due to the low pressure inside the LIF-FAGE detection system this reaction is slow compared to ambient conditions and contributes less than 10 % to the total signal (Holland et al., 2003). However, it is meanwhile known, that RO_2 radicals from OH plus alkene- and aromatic precursors including isoprene (mainly OH-addition) can form specific RO by reaction with NO. These RO radicals can decompose under low pressure conditions forming HO_2 rapidly (Fuchs et al., 2011; Dillon, 2011). Interferences from these RO_2 species can be significantly reduced by reducing the reaction time and/or the NO concentration in the detection cell at the expense of a reduced HO_2 detection sensitivity. A lower detection limit of less than $1 \times 10^6\,\mathrm{molec.\,cm^{-3}}$ at an integration time of 30 seconds is typically achieved by HO_2-LIF-FAGE instruments.

3.2. HORUS

Observations of OH and HO_2 concentrations within the scope of this thesis, in particular during the HUMPPA-COPEC2010 field campaign, were conducted using the Max Planck Institute for Chemistry (Mainz, Germany) HO_x instrument based on laser-induced fluorescence, HORUS (*H*ydr*O*xyl *R*adical Measurement *U*nit based on fluorescence *S*pectroscopy). The HORUS instrument is originally based on the design of GTHOS (Ground-based Tropospheric Hydrogen Oxides Sensor), the Penn State HO_x instrument described by Faloona et al. (2004). HORUS is described in detail by Martinez et al. (2010). HORUS has been deployed for a variety of campaigns on ground-based, shipborne, and airborne platforms (Schlosser et al., 2009; Hosaynali Beygi et al., 2011; Kubistin et al., 2010; Martinez et al., 2010; Regelin et al., 2012).

3.2.1. Measurement principle

The LIF-FAGE method used by HORUS is based on the resonant absorption of laser light by the OH molecules and the subsequent detection of the fluorescence signal. The intensity of the fluorescence signal is proportional to the OH radical concentration. The excitation of OH radicals used in HORUS can be explained by transitions between the ground state X$^2\Pi$ and the first excited state A$^2\Sigma^+$ (Figure 3.3). The electron configuration of the ground state is $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(\pi^+)^2\,(\pi^-)^1$ with an unpaired electron in the π-orbital (Freeman, 1958). The electron configuration of the first electronically excited state A$^2\Sigma^+$ is $(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^1\,(\pi^+)^2\,(\pi^-)^2$. The rotational states of the ground state separate because of the spin-orbit coupling (fine structure) into two electronic substates X$^2\Pi_{1/2}$ and X$^2\Pi_{3/2}$. There is no spin-orbit coupling in the excited electronic state A$^2\Sigma^+$ due to the lack of any angular momentum.

Quantum numbers in Figure 3.3 refer to:

- K: angular momentum (rotation+orbit)

- J: total angular momentum (including spin)

The energy levels of the substates within the $^2\Pi$ state are labeled with $f_i(K)$ and $f_i'(K)$, where $i = 1$ denotes $(K + \Sigma)$ and $i = 2$ refers to $(K - \Sigma)$, in which Σ is the projection of the spin to the molecule axis (z-axis). The energetically higher level (caused by lambda doubling interaction) is labeled $f_i'(K)$. In analogy to this, the substates within the $^2\Sigma^+$ state (γ-splitting) are labeled with $F_i(K)$ and $F_i'(K)$. Absorption lines are labeled by X$_i$(K) whereby X denotes the rotational branch $P(\Delta K = -1)$, $Q(\Delta K = 0)$, or $R(\Delta K = 1)$ and K is the quantum number of the angular momentum in the ground state. Subscripts i represent again the fine structure of the ground state. For transitions with changing spin projection $(K \pm \frac{1}{2})$, so-called satellite branches that occure at similar energies but show lower intensities compared to main branches, the index i' for the excited state is added in front of the ground state index (e.g. Q$_{21}$(2)). A more detailed description of the OH absorption spectrum can be found in Freeman (1958); Dieke and Crosswhite (1962); Langhoff et al. (1982) and references therein.
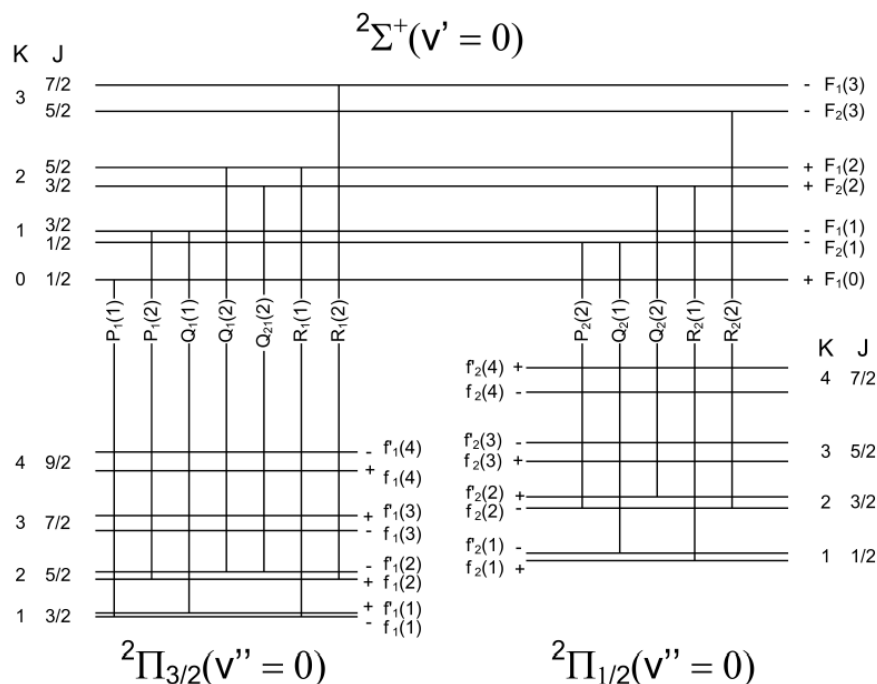
Abbildung 3.3.: Schematic of the branches in the rotational structure of OH showing the transitions used for laser excitation ($A^2\Sigma^+ - X^2\Pi$, $v'=0 \leftarrow v''=0$). K is the quantum number of the angular momentum (rotation + orbit) and J is the quantum number of the total angular momentum (including spin). For notation of transition lines refer to text.

In HORUS OH molecules are selectively excited at low pressure by pulsed UV light at around 308 nm on resonance with the $Q_1(2)$ transition line. Subsequently, the fluorescense signal from the excited hydroxyl radical molecules is detected at low pressure ($\sim 3 - 5$ hPa). Since the fluorescence is detected at around 308 nm, similar to the excitation wavelength, a gated photon counting technique as presented in Figure 3.2 using micro channel plate detectors (MCP) is applied. The integrated fluorescence signal is proportional to the con-

centration of hydroxyl radicals in sample air:

$$S \sim \int_{t_1}^{t_2} I(t)\, dt \sim \ [OH^*] \int_{t_1}^{t_2} e^{-\Gamma t}\, dt \tag{3.2}$$

The concentration of excited OH radicals $[OH^*]$ is proportional to the total OH concentration, the Boltzmann correction factor f_b and the laser power P. With the fluorescence efficiency factor

$$Q = \int_{t_1}^{t_2} e^{-\Gamma t}\, dt \tag{3.3}$$

and the constant of proportionality C' we obtain

$$S = C' \cdot Q\, f_b\, P\ [OH]. \tag{3.4}$$

The product of fluorescence efficiency factor, Boltzmann correction factor and C' is the normalized sensitivity of the LIF instrument:

$$\zeta = C' \cdot Q \cdot f_b. \tag{3.5}$$

The total instrument sensitivity is given by

$$\mathscr{C}_{\mathrm{LIF}} = \zeta \cdot P \tag{3.6}$$

and can be determined by calibration of the HORUS instrument (see Section 3.2.3).

The decay rate of the excited OH radicals, Γ, is defined by the natural lifetime of the excited state, γ_{nat}^{-1} and the deactivation by collisional quenching due to other molecules X:

$$\Gamma = \gamma_{nat} + \sum k_X(T)\ [X], \tag{3.7}$$

where $X = N_2, O_2$, and H_2O are the most relevant collision partners in ambient air. The temperature dependency of the associated rate constants can be approximated within a temperature range of $-70\,^\circ$ C to $50\,^\circ$ C (Faloona et al., 2004):

$$k_X(T) = aT^{\frac{1}{2}} - bT^{\frac{3}{2}} + c. \tag{3.8}$$

The coefficients a, b, c are experimentally determined (Bailey et al., 1997, 1999) and listed in Table 3.1. Particularly H_2O is an efficient quenching gas for the excited OH molecules, leading to a decrease of the fluorescence efficiency factor Q and therefore a decrease in instrument sensitivity with increasing water concentration.

Tabelle 3.1.: Parameters of temperature dependency for collisional quenching rate coefficients.

Collision gas	a (in $cm^3\,(molec.\,s\,K^{\frac{1}{2}})^{-1}$)	b (in $cm^3\,(molec.\,s\,K^{\frac{3}{2}})^{-1}$)	c (in $cm^3\,molec.^{-1}\,s^{-1}$)
N_2	-1.668×10^{-11}	-1.731×10^{-14}	2.313×10^{-10}
O_2	1.008×10^{-11}	1.655×10^{-14}	5.129×10^{-11}
H_2O	-4.017×10^{-10}	-4.4686×10^{-14}	5.3137×10^{-9}

3.2.2. Instrument setup

HORUS consists of four main components: the laser system, the low pressure detection system, the vacuum system, and the instrument control and data acquisition unit. A comprehensive description of the HORUS instrument setup is given in Kubistin et al. (2010). The most relevant characteristics for HUMPPA–COPEC–2010 and recent instrument developments are presented in the following paragraphs.

Laser system
The UV light for excitation of the hydroxyl radicals is provided by a Nd:Yag pumped, pulsed, tunable dye laser system (Martinez et al., 2010; Wennberg et al., 1994) operated at a pulse repetition frequency of 3 kHz. A diode-pumped, quality-switched Nd:Yag laser (Type Navigator I, Spectra Physics) is applied for optical pumping of the custom-made dye laser system at 532 nm (frequency doubled). In order to focus the beam of the pumplaser precisely on the dye cell the beam (with an approximate initial diameter of 0.65 mm) is expanded, using a tenfold beam expander (Linos - Qioptic) and a collecting lens ($f = 100$ mm, Thorlabs). Furthermore, the incoupling of the green laser beam is actively controlled by two piezo-actuated mirrors to compensate changes due to thermal and mechanical influences on the laser base plate.

The dye laser setup is shown in Figure 3.4. The incoming beam of the pump laser ($\lambda = 532$ nm) hits the dye cell under the brewster angle. The laser dye, Pyrromethene-597 (Exciton, USA) dissolved in high purity grade isopropanol ($> 99.9\,\%$), has an absorption maximum in the green and fluoresces in the green to red wavelength range. To avoid saturation of the excited states of the laser dye, the dye solution is continuously circulated through a reservoir at a high flow rate of 1.7 liters per minute in order to exchange the dye inside the dye cell between two consecutive laser pulses. The fluorescence light is collected and amplified within the cavity. The cavity is defined on one end by the end mirror and on the other by the outcoupling mirror (see Figure 3.4). Primary wavelength selection in the
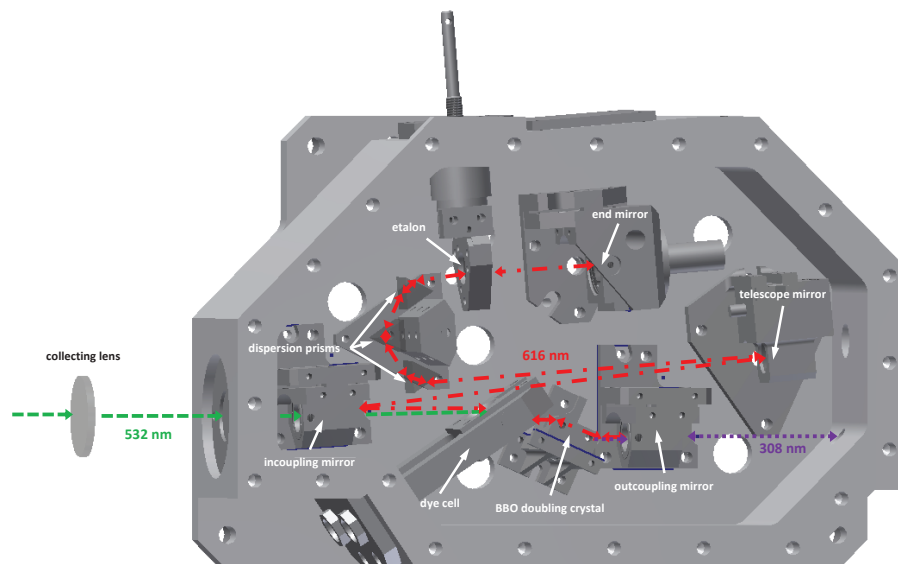
Abbildung 3.4.: Dye laser setup. The incoming beam of the pump laser ($\lambda = 532\,\mathrm{nm}$) is focussed on the dye cell. The fluorescence from laser dye (Pyrromethene-597) at $\lambda = 616\,\mathrm{nm}$ is amplified inside the optical resonator. UV light at $\lambda = 308\,\mathrm{nm}$ is produced using a nonlinear doubling crystal (BBO) for intracavity frequency doubling.

cavity is achieved by means of a dispersion prism array, then further narrowed by a rotatable intracavity etalon, which is actively controlled by a stepper motor. When the intracavity power builds up sufficiently to permit frequency doubling in the doubling crystal (BBO - β-barium borate) the UV light then exits via the outcoupling mirror.

Since the instrument sensitivity $\mathscr{C}_\mathrm{LIF}$ is directly proportional to the laser power P (see Equation 3.6) it is desired to achieve high and stable laser power at the excitation wavelength of OH. Furthermore, the lower limit of detection improves at higher UV power. This is important, when long optical fibers causing high losses have to be used to transport the UV light to the detection system. To improve the UV power output of the laser system the design of the cavity was analyzed and slightly modified. The biggest positive impact on the UV power was gained by the exchange of the dispersion prisms material. The transmission of

the p-polarized light is strongly dependend on the incidence angle. Previously three isosceles brewster prisms ($\alpha = 60°$) made in LaFN8 were used in the HORUS dye laser system. For the mechanical setup - three prisms with theoretical brewster angle of 60° and total deflection angle between input and output plane of 60° (for each prism) - a different material (e.g. SF10) fits the requirements better. The transmission for such a prism (for p-polarized, s-polarized and mixed-polarized light) is shown in Figure 3.5 for different glass types. During
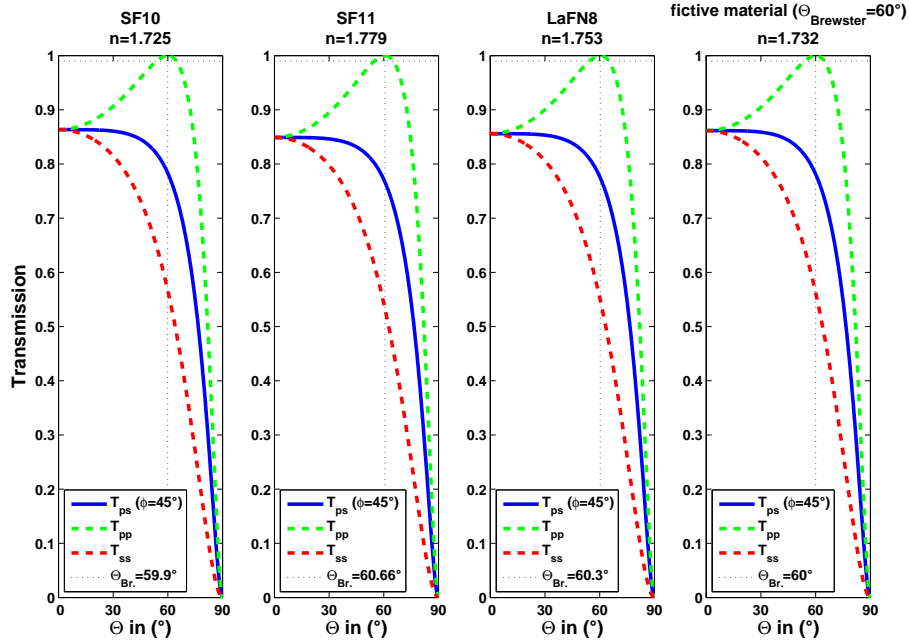
Abbildung 3.5.: Transmission curves for isosceles brewster prisms (for p-polarized, s-polarized and mixed-polarized light) of different glass types. The material SF10 fits the requirements of the HORUS dye laser system best.

the HUMPPA–COPEC–2010 campaign, optical fibers about 4 meters in length were used to transfer the 308 nm light to the detection system. Optical fibers allow complicated pathways and provide robust and stable coupling of the UV light into the detection system. However, along with the transmission losses also backreflections of the laser pulses are a disadvantage of using optical fibers. Depending on the length of the optical fiber (l) and the refractive index of the fiber material (n_{fiber}), the delay between laser pulse and its first backreflection can be calculated:

$$t = \frac{2l \cdot n_{fiber}}{c} \tag{3.9}$$

where c is the speed of light in vacuum.

In case of the fibers used during HUMPPA–COPEC–2010 the first backreflection would occure approximately 40 ns after the laser pulse and a second backreflection with another 40 ns delay. Thus, backreflections of the laser pulse can (especially for long fibers, e.g. of ~ 10 meters in length) overlap parts of the fluorescence signal and reduce the instrument sensitivity. To overcome this issue, angled polished fibers were used the first time during HUMPPA–COPEC–2010. The angled polished incoupling and outcoupling surfaces helped to suppress backreflections significantly (see Figure 3.6).
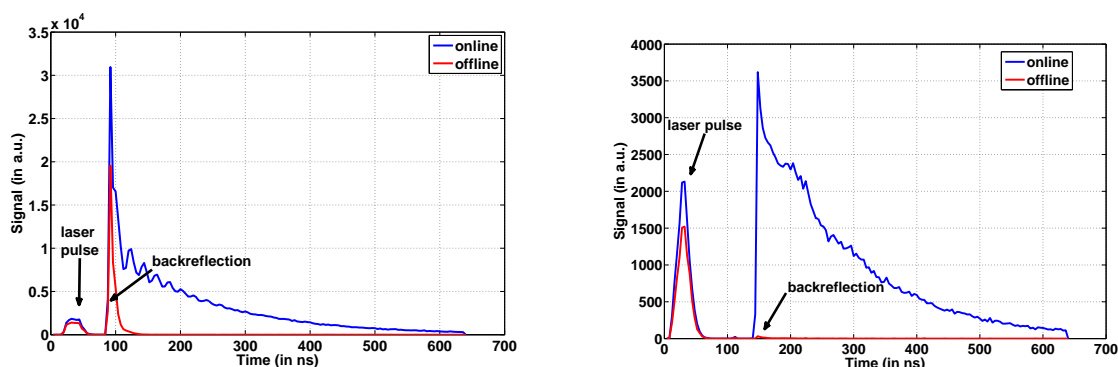
Abbildung 3.6.: Suppression of laser pulse backreflections and OH fluorescence signal. A flat polished fiber produces backreflections that can overlap the fluorescence signal (left panel). Using an angled polished fiber helps to suppress the backreflection of the laser pulse significantly (right panel).

Low pressure detection system

A schematic overview of the detection system setup of HORUS is shown in Figure 3.7. The sample air is drawn through a critical orifice (pinhole size of about 1.2 mm) into the low pressure detection cells, achieving a constant volume flow of about 10 slm (p = 1013 hPa, T = 273.15 K). The resulting exchange rate of sample air is necessary to avoid excitation of the sample air by two consecutive laser pulses, producing laser-generated OH. In order to maximize the fluorescence signal at a certain radical level (i.e. maximizing the instrument sensitivity) a White Cell setup crossing the detection volume with 32 light paths is used (see Figure 3.8), (White, 1942).

The detection of HO$_2$ is achieved via chemical conversion to OH by adding NO in excess to the total flow of sample air downstream of the OH detection. The sum of remaining ambient OH plus OH originating from HO$_2$ conversion is measured in a second detection axis (see Figure 3.7).
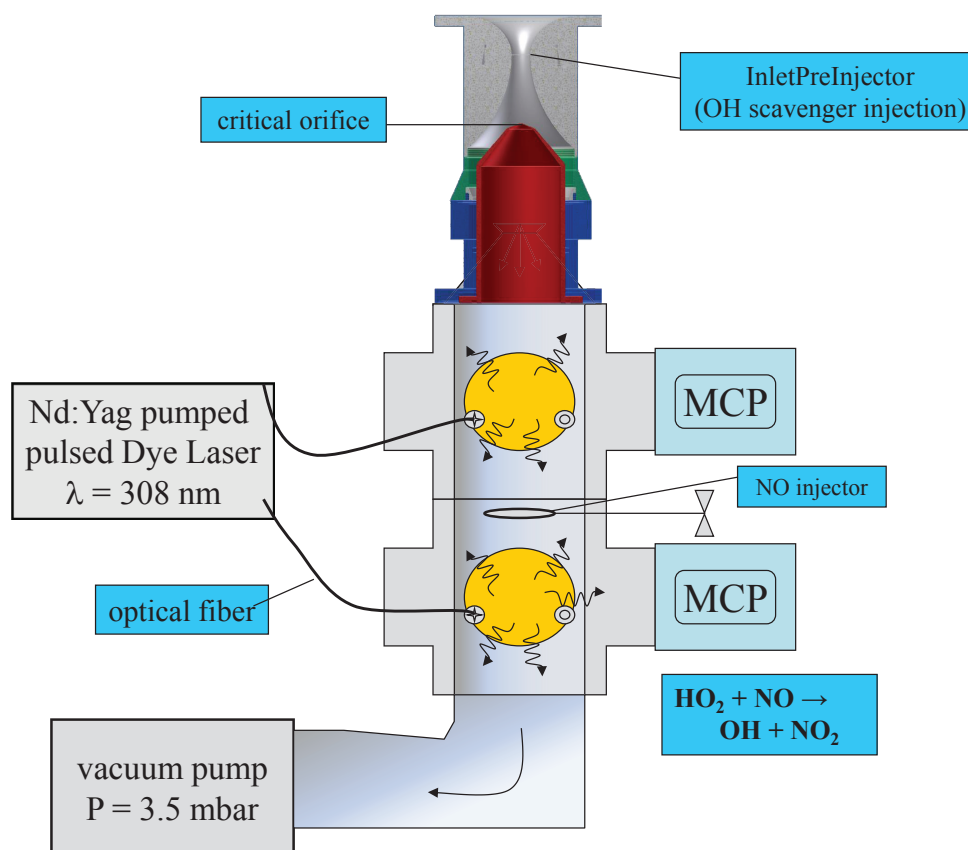
Abbildung 3.7.: Setup of the HORUS detection system. The sample air is drawn through a critical orifice into the low pressure detection cell. OH radicals are excited by laser light at around 308 nm and the fluorescence of these molecules is detected using a multi channel plate detector (MCP). In a second detection axis, placed in line with the OH detection cell, HO_2 is detected after conversion to OH by reaction with NO, which is injected between the first and the second detection cell. An InletPreInjector is mounted on top of the standard LIF inlet for chemical background detection. For details refer to text.
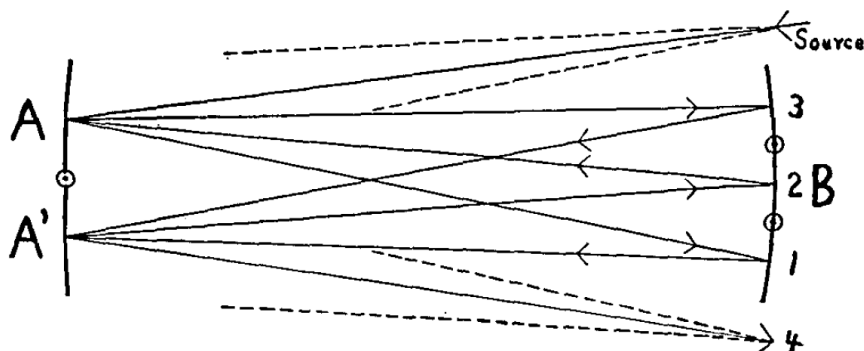
Abbildung 3.8.: Schematic representation of the optical path inside a White Cell. The incoming laser beam is multiple reflected using three mirrors before exiting the cell (Taken from White, 1942).

Taking the information from the so-called first axis OH measurement into account, the HO$_2$ concentration is calculated. The proportionality between fluorescence signal and hydroxyl radical concentration is given by the instrument sensitivity $\mathscr{C}_\mathrm{LIF}$, which is normalized by laser power. Nevertheless, the sensitivity still depends on many other parameters, including the density inside the fluorescence cell, the water vapour concentration in sample air (quenching effects), the transition probability, the overlap of the laser and fluorescence transition lines, the transmissivity of the White Cell setup, as well as the sensitivity of the detector. Some of those parameters are difficult to be determined separately and might even change in time (e.g. contamination of optical surfaces or changing detector efficiency due to ageing). Therefore, calibrations of the HORUS instrument were performed on a regular basis (see Section 3.2.3).

The usual LIF method to determine the background signal is changing the excitation wavelength, to get off-resonant for the OH molecule and measure the background signal periodically. In HORUS 5 seconds of "online" measurement are followed by 5 seconds "offline", which is 1000 etalon steps ($\sim 37\,\mathrm{GHz}$) alternating left and right of the Q$_1$(2) transition line. Furthermore, the ambient OH can be removed from sample air by periodic addition of a chemical OH reactant (e.g. propane, propene, C$_3$F$_6$) to determine the background signal (Figure 3.9). Since both methods do not exclude each other the addition of a chemical reactant was done on top of the wavelength modulation method for the HORUS instrument during HUMPPA–COPEC–2010.
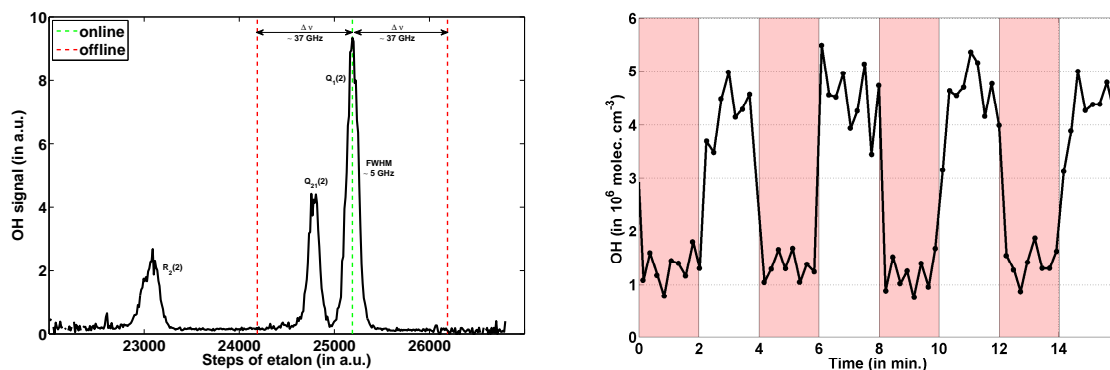
Abbildung 3.9.: Two ways to determine OH background signal: (left panel) by wavelength change and (right panel) by periodic addition of an OH reactant (periods with colored background) using an InletPreInjector (Brune et al., 2010; Novelli et al., 2012; Mao et al., 2012).

Vacuum system

The HORUS instrument requires a vacuum system to create a low pressure, forcing the sample air through a critical orifice into the detection cells. Therefore, a compressor (roots blower, Type M90, Eaton) and a vacuum pump (scroll pump, Type XDS-35, Edwards) are connected in series. With this setup the sample air is compressed and the pressure in front of the vacuum pump is enhanced, leading to an improved pumping efficiency, which is mandatory to achieve the low pressure of a few hPa inside the detection cells. The characteristics of the vacuum system are shown in Figure 3.10. It is proved to be stable within longterm measurements running continuously for several weeks.

Instrument control and data acquisition unit

The HORUS instrument is controlled using an embedded PC running a Debian LINUX operating system. Analogue and digital sensors as well as actuators, such as valves or stepper motors, are connected to the data acquisition using a modular system of electronic cards, which was developed at the Max-Planck-Institute, Mainz. The connection to the embedded PC is established via the ISA bus. The software design of HORUS is based on the client-server model, programmed in "C". The server controls the communication with the hardware and periodically stores records from the sensors on a harddrive. UDP sockets are used to query data from clients and/or send actuator commands (e.g. move stepper motor). The graphical user interface (GUI, programmed in MatLab, Mathworks, Inc.) is also realized as a client. Thus, the data acquisition is running as an independent process and will not be
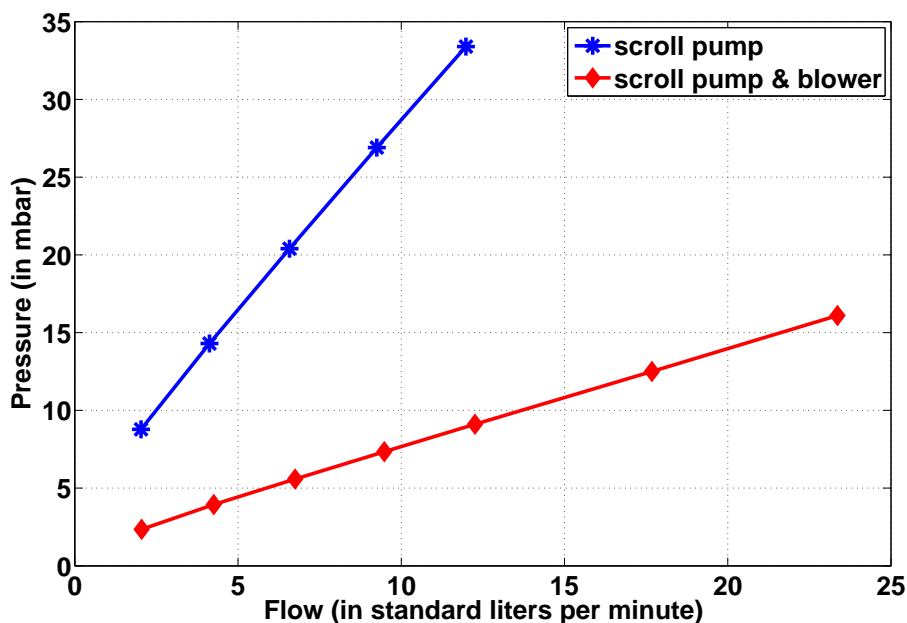
Abbildung 3.10.: Characteristics of the vacuum system. To improve the pumping efficiency of the scroll pump (Type XDS-35, Edwards) a roots blower (Type M90, Eaton) is used for precompaction.

affected by malfunctions of the GUI. Furthermore, it is possible to run the graphical user interface on a different computer (within the same network) than the data acquisition.

3.2.3. Calibration

The instrument sensitivity $\mathscr{C}_{\text{LIF}}$ is determined by regular calibrations of the LIF system. For calibration of the HORUS instrument, different mixtures of dry and humid air was flown turbulently through a 16 mm square aluminium tube at a rate of 50 liters per minute. The resulting water vapour concentration is measured with an infrared absorption instrument (LI-7000, Licor), which is calibrated against a dew point generator (LI-610, Licor) within a typical range of 0-25 mmol mol^{-1} of H$_2$O in calibration air. The dew point generator itself is calibrated against a certified primary standard (NIST). A mercury lamp (Penray line source, LOT-QuantumDesign, Europe) is attached to the tube to produce equal concentrations of OH and HO$_2$ radicals by photolysis of water vapour. From the flow speed, which is derived from the measured mass flow (DryCal sensor, NIST traceable certified

Calibration Unit
Principle of operation
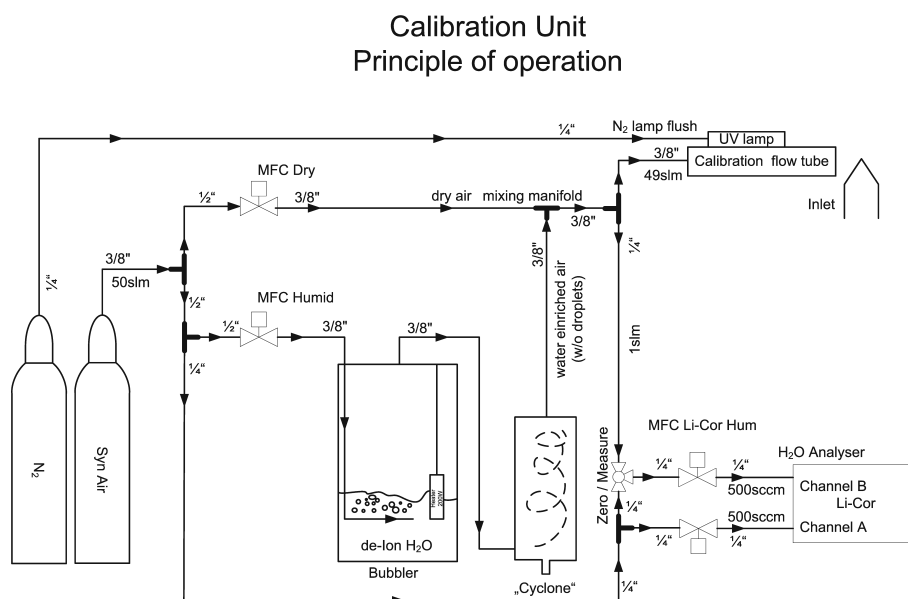
Abbildung 3.11.: Schematic of the setup used for calibration of the HORUS instrument. Different mixtures of dry and humid air are established using a bubbler device and subsequently the water vapour mixing ratio is measured by a H_2O analyser. The humidified air is flown through the calibration flow tube, where OH and HO_2 radicals are produced in equal amounts by photolysis of the water vapour at $184.9\,nm$ (Taken from Kubistin et al., 2010).

by Westphal, Germany), and the resulting residence time, t, of calibration air within the illuminated volume, the absorption cross section of water at $185\,nm$, σ_{H_2O}, and the actinic flux density of the lamp, Φ_0, the radical concentration can be calculated (Faloona et al., 2004). The absorption by oxygen and the resulting reduction of the actinic flux density across the tube height, h, is taken into account by application of a correction factor, f_{O_2}, following Beer-Lambert's law.

$$[OH]=[HO_2]=\Phi_0\sigma_{H_2O}[H_2O]tf_{O_2},\tag{3.10}$$

with the correction factor for absorption by oxygen

$$f_{O_2} = \frac{\int\limits_0^h e^{-\sigma_{O_2}[O_2]x}\,dx}{h}. \tag{3.11}$$

A schematic of the setup used for calibration of the HORUS instrument is shown in Figure 3.11.

Exact knowledge of the actinic flux density is crucial for this calibration method. The mercury lamp used for calibration of the HORUS instrument during HUMPPA–COPEC–2010 was calibrated using the actinometry method by N$_2$O photolysis, as described by Martinez et al. (2010), immediately before and after the campaign. N$_2$O photolysis produces O(^{1}D) molecules which partly react with N$_2$O producing NO. The actinic flux density of the lamp is determined by measuring NO from the photolysis of known concentrations of N$_2$O in nitrogen with a NO$_x$ chemiluminescence analyzer (C42, Thermo Environmental Instruments). The analyzer itself is calibrated using a NIST standard. It is to be considered that the sensitivity of the analyzer varys with different quenching efficiency of the carrier gas, as shown in Figure 3.12.
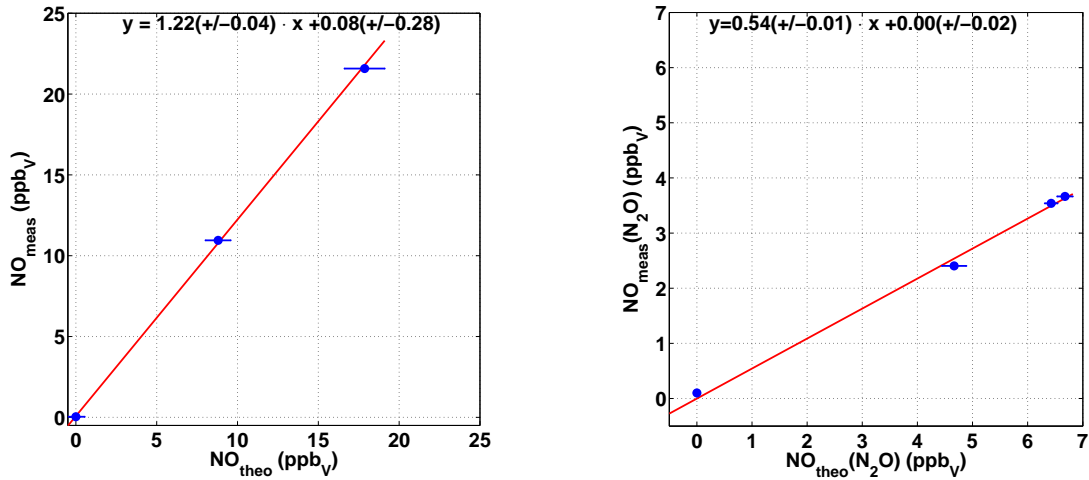
Abbildung 3.12.: Calibration of the NO analyzer (C42, Thermo Environmental Instruments) for NO in N$_2$ and N$_2$O. The sensitivity of the analyzer varys with different quenching efficiency of the carrier gas.

At mixing ratios of about 15% N_2O, NO concentrations reach up to $5\,ppb_V$, well above the detection limit of the NO_x analyzer ($< 50\,ppt_V$ @ $120\,sec$ averaging time). The absorption of the $185\,nm$ light across the calibrator tube increases with increasing N_2O concentration. This effect was taken into account for the calculation of the lamp actinic flux (Kubistin, 2009). The resulting actinic flux density at different N_2O mixing ratios is shown in Figure 3.13.
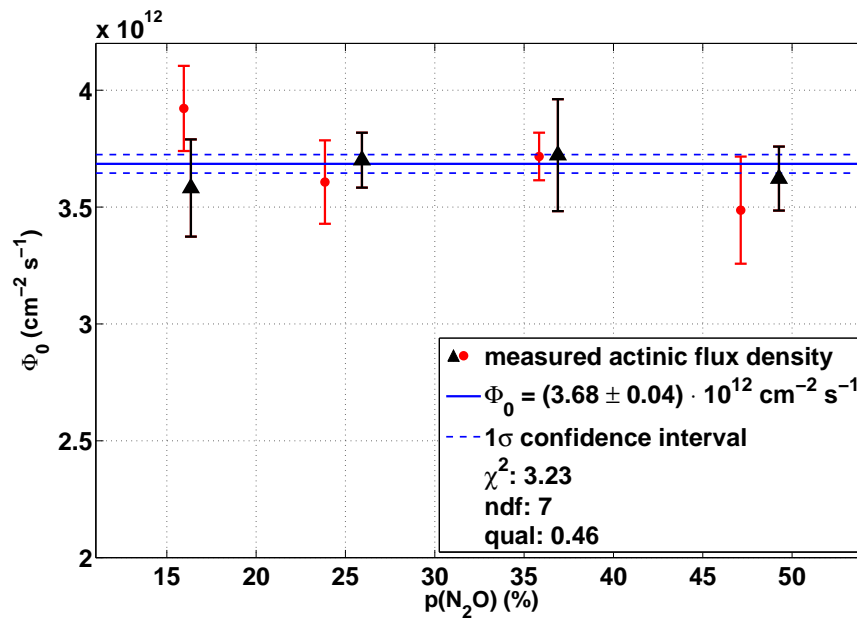
Abbildung 3.13.: Actinic flux density of the mercury lamp used for calibration of the HORUS instrument. The actinic flux density Φ_0 is derived from the photolysis of N_2O at different mixing ratios and the subsequent detection of the NO yields. The data shown here is the combined dataset from two actinometric measurements, one of them conducted before (red dots) and a second one after (black triangles) the field campaign, indicating a good long-term stability of the lamp actinic flux density. Errorbars indicate the propagated statistical variability of the calculated flux density.

Both measurements of the actinic flux density, Φ_0, before and after the field campaign, agree within uncertainties and indicate the long-term stability of the actinic flux density. From the overall fit we obtained $\Phi_0 = (3.68 \pm 0.04) \times 10^{12}\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ with a reasonable quality of fit. The systematic error of the actinic flux density measurement is calculated to be about $17\,\%$, similar to the value by Martinez et al. (2010) taking the contribution of all components summarized in Table 3.2 into account.

Tabelle 3.2.: Systematic uncertainties during actinometric measurement.

Instrument/Quantity	systematic uncertainty
NO Monitor (TEI)	$6\,\%$
NO Standard (NIST)	$1\,\%$
Mass flow controler (MKS)	$2\,\%$
Absorption cross section $\sigma_{\mathrm{H_2O}}$	$2\,\%$
Quantum yield	$1\,\%$
Kinetic rate coefficients	$12\,\%$
Dimensions of reaction chamber	$3\,\%$
Pressure sensor (MKS)	$2\,\%$
Long-term stability of act. meas.	$10\,\%$
Overall system. error estimate	$17\,\%$

3.2.4. Other dependencies of the instrument sensitivity

Furthermore, the instrument sensitivity is limited by quenching of the fluorescence, which happens mainly due to water vapour. To minimize this effect, the HORUS system is operated at low pressure ($\sim 3 - 5\,\mathrm{hPa}$), but still high enough to keep wall losses small and provide enough molecules for excitation. The quenching effect by H_2O is considered in our calculations. An additional dependency on water vapour of about $12\,\%$ and $17\,\%$ decrease in sensitivity per $1\,\%$ increase in water vapour mixing ratio was observed for the first and second fluorescence cell, respectively. This additional water effect indicates further losses at higher water mixing ratios possibly due to formation of OH-water clusters during the cold-adiabatic expansion of the sample air while entering the low pressure detection system. Changing instrument sensitivity with respect to water vapour mixing ratio, which is not

caused by quenching, was reported by others (Hofzumahaus et al., 1996; Holland et al., 1998) hypothesizing that condensation processes during the cold-adiabatic expansion are causing this effect. The above mentioned quantification of the additional water dependency during instrument calibration was used to correct for this dependency.

Unfortunately, the MCP detectors changed in sensitivity during the HUMPPA–COPEC–2010 field campaign, decreasing over time. Calibrations of the instrument were conducted about every second day to keep track of changes in sensitivity. Within some limitations, the behaviour of the laser scattering inside the system is an indicator of the sensitivity changes in the system. For the laser scatter signal, factors such as laser power fluctuations and background reflections have to be taken into account. Differing amounts and composition of aerosols in the sample air therefore might cause variable scatter. However, comparison of the laser scatter signal in ambient air with the quasi-simultaneous measured sensitivity during calibration shows a linear dependency. This functional dependency was applied to correct for the changing sensitivity (see Figure 3.14).

3.2.5. Interferences

Knowledge about possible interferences and avoiding those when indicated is required in order to measure OH and HO_2 reliably. Interferences can be caused by processes in the instrument itself and/or atmospheric substances which fluoresce at wavelengths similar to the hydroxyl radical. Laboratory studies testing the effect of sulfur dioxide, formaldehyde, nitrous acid, nitric acid, acetone, hydrogen peroxide, and various hydrocarbons on the OH signal did not show any significant interference for measurements in the atmosphere (Kubistin, 2009; Faloona et al., 2000; Ren et al., 2004). A negative interference on the OH signal by naphtalene was observed in polluted urban environments and can be used for the specific measurement of this compound (Martinez et al., 2004). It was recently reported that LIF measurements can be affected from internally generated OH (Mao et al., 2012; Novelli et al., 2012). Therefore, a chemical modulation method to determine the background signal for the measurement of atmospheric OH (as proposed by Brune et al., 2010) was applied to the HORUS-LIF for the first time during HUMPPA–COPEC–2010. A new injection unit IPI (*InletPreInjector*) was developed and optimized to scavenge more than 95 % of atmospheric OH by periodic injection of a chemical reactant in front of the standard inlet. In order to minimize wall losses, a bypass flow, large compared to the sample flow into the detection system, was established. Optimization of this injection system included tests using different reactants, e.g. propylene and hexafluoropropene, and varying injection and bypass flow conditions to determine the best parameters for continuous operation. A different publication on the characterisation of the OH scavenger injection device *IPI* is in preparation by Novelli et al. (2013).
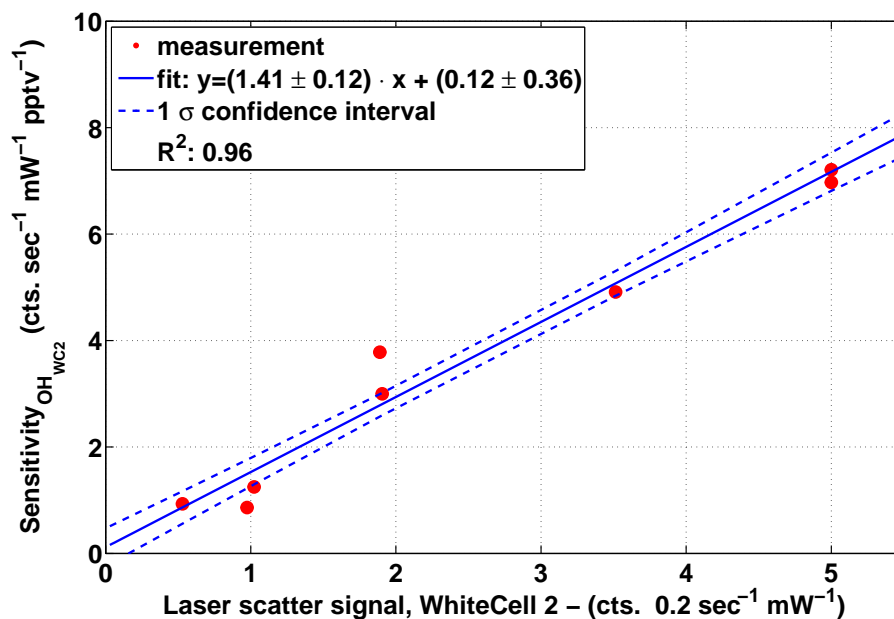
Abbildung 3.14.: Sensitivity change inside the second detection axis of HORUS as a function of the associated laser scatter signal. A linear correlation (R^2=0.96) with a non-significant offset was observed during instrument calibrations. The functional dependency obtained from linear regression was applied to the measurements to correct for changes in instrument sensitivity by continuously monitoring the laser scatter signal. A similar correction function for the change in sensitivity of the first detection cell has also been determined empirically and applied.

Measurements of HO$_2$ concentrations are conducted using chemical conversion into OH via the reaction with NO and the subsequent detection of the hydroxyl radicals by the LIF technique (Reaction R3.8):

$$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \tag{R3.8}$$
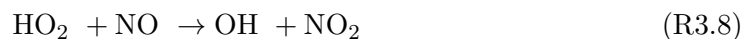
In the atmosphere, RO$_2$ is also converted into HO$_2$ in the presence of NO (Reactions R3.9 - R3.10). These reactions were expected to be negligible in low pressure FAGE detection systems due to the reduced oxygen concentration and the short reaction time between

injection of NO and detection of OH within the system (Heard and Pilling, 2003).

$$RO_2 + NO \rightarrow RO + NO_2 \tag{R3.9}$$

$$RO + O_2 \rightarrow R'CHO + HO_2 \tag{R3.10}$$
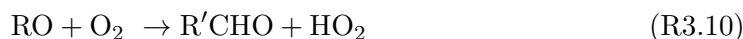
We observed a small interference ($< 10\%$) originating from methyl peroxy radicals in the laboratory for the HORUS instrument, comparable to the results reported by Holland et al. (2003), who detected an interference smaller than 5% for their LIF-FAGE instrument. Significant interferences in HO_2 measurements by the LIF-FAGE technique from RO_2 species resulting from the OH-initiated oxidation of alkenes and aromatics have been observed by Fuchs et al. (2011) and others (Dillon, 2011). In contrast to alkane-based peroxy radicals, which are formed in the reaction of VOC + OH via H-atom abstraction, alkene-based peroxy radicals (mainly produced via OH-addition on the C-C double bond) form specific RO by reaction with NO, that can decompose under the low pressure conditions forming HO_2 rapidly. The conversion efficiency is limited by Reaction R3.9. The ratio of HO_2 to RO_2 converted by reaction with NO under excess conditions (see Reactions R3.8 & R3.9) is given by the pseudo-first-order approximation

$$\frac{[HO_2](t)}{[RO_2](t)} = \frac{[HO_2]_0}{[RO_2]_0} \cdot \frac{e^{-k_{R3.8}\,[NO]\,t}}{e^{-k_{R3.9}\,[NO]\,t}} = \frac{[HO_2]_0}{[RO_2]_0} \cdot e^{-(k_{R3.8}-k_{R3.9})\,[NO]\,t}, \tag{3.12}$$

while $k_{R3.8} > k_{R3.9}$.

The ratio in Equation 3.12 becomes small, i.e. HO_2 is converted more efficiently compared to RO_2 when the product $[NO] \cdot t$ is small. Thus, any potential interference from alkenes on HO_2 can be reduced by reducing reaction time and/or NO concentration. During HUMPPA–COPEC–2010 NO mixing ratios of about $400\,\mathrm{ppm_V}$ occurred inside the detection system of HORUS by injection of pure NO into sample air, yielding a conversion efficiency from HO_2 to OH of more than 95% at the operating conditions of the instrument. This could also have caused a high conversion efficiency for interfering RO_2 species as described above. Nevertheless, this interference depends strongly on the available VOCs for the production of RO_2 in the investigated environment as well as on the instrumental setup which defines the conversion efficiency of those peroxy radicals inside the instrument. The observed HO_2 can be interpreted as the sum of atmospheric HO_2 and a contribution from the effective interference by specific RO_2:

$$[HO_2]^{\mathrm{obs.}} = [HO_2]^{\mathrm{atm.}} + \sum_i (\alpha_{RO_2}^i \times [RO_2]_i) \tag{3.13}$$

The relative detection sensitivities $\alpha_{RO_2}^i$ for the specific RO_2 compared to HO_2 are strongly dependend on the instrumental setup and can reach values up to about 0.9 (Fuchs et al., 2011; Lu et al., 2012; Whalley et al., 2013). However, the speciation of RO_2 in the observed environment strongly influences the effective interference. Based on model simulations the

magnitude of the RO$_2$ interference on HO$_2$ measurements by some LIF instruments in different environments was estimated between 10 % up to about 30 % (Lu et al., 2012; Fuchs et al., 2011; Mao et al., 2012; Whalley et al., 2013; Griffith et al., 2013).

NO titration experiments during calibration and ambient air measurements in two forest environments in Germany have been conducted after HUMPPA–COPEC–2010, quantifying the maximum interference by RO$_2$ in the HORUS instrument in these environments to be less than 20 % (Tatum Ernest et al., 2012). For the purpose of these titrations the NO injection of HORUS was varied to accomplish internal NO mixing ratios of approximately 1 to 1600 ppm$_V$. The resulting NO dependency of the signal caused by a constant HO$_2$ concentration during a calibration is presented in Figure 3.15.
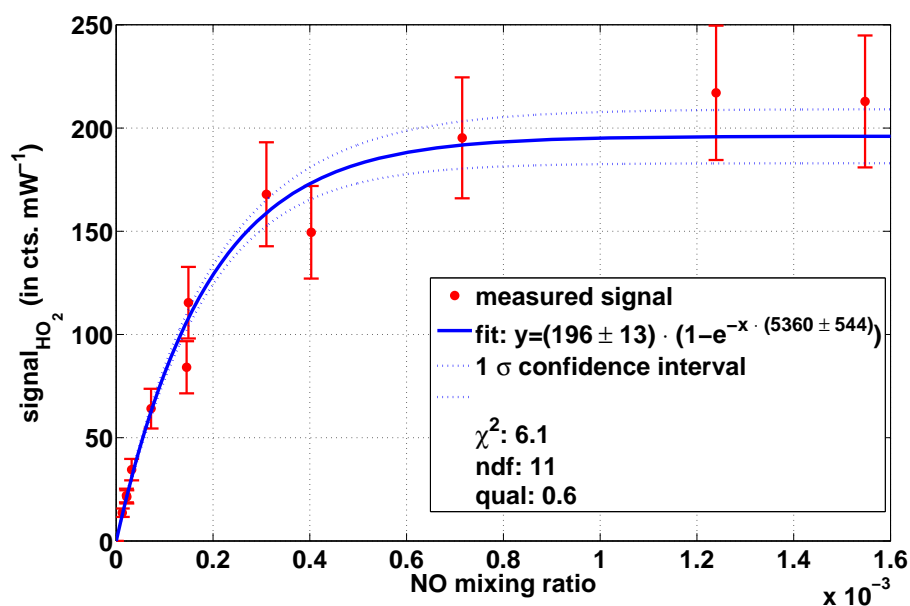
Abbildung 3.15.: NO dependency of the HO$_2$ signal during a calibration. A constant HO$_2$ concentration is provided to the LIF instrument by the calibrator unit. The NO mixing ratio for conversion from HO$_2$ to OH inside HORUS is varied from approximately 1 to 1600 ppm$_V$. Above $\sim$ 800 ppm$_V$ a rather constant conversion efficiency is found.

From this dependency a conversion efficiency from HO_2 to OH as a function of the NO mixing ratio is derived. The observed signal can be expressed by

$$S_{HO_2}(NO) = \mathscr{C}_{LIF}^{NO_{Cal}} \cdot \epsilon'(NO) \cdot [HO_2]^{Cal}, \tag{3.14}$$

where $\mathscr{C}_{LIF}^{NO_{Cal}}$ is the instrument sensitivity at the NO level during HORUS calibration and $\epsilon'(NO)$ represents the NO-dependent conversion efficiency, fullfilling the constraint

$$\epsilon'(NO_{Cal}) = 1. \tag{3.15}$$

The signal during a titration experiment using ambient air shows a similar NO dependency, representing the conversion efficiency for the sum of HO_2 and interfering RO_2 species, assuming constant conditions, i.e. only minor changes in HO_2 and RO_2 concentrations during the titration. It can be written as

$$S_{HO_2+RO_2}(NO) = S_{HO_2}(NO) + S_{RO_2}(NO)$$
$$= \mathscr{C}_{LIF}^{NO_{Cal}} \cdot \epsilon'(NO) \cdot [HO_2] + S_{RO_2}(NO). \tag{3.16}$$

At a very low reference NO level, NO_{ref}, the contribution from RO_2 to the total signal is assumed to be less than 10%, which is the upper limit for the RO_2 interference by methyl peroxy radicals determined in laboratory experiments. Under these conditions Equation 3.16 simplifies to

$$0.9 \cdot S_{HO_2+RO_2}(NO_{ref}) = S_{HO_2}(NO_{ref})$$
$$= \mathscr{C}_{LIF}^{NO_{Cal}} \cdot \epsilon'(NO_{ref}) \cdot [HO_2]. \tag{3.17}$$

Therefore, it is possible to quantify the HO_2 concentration as well as the contribution from RO_2 interference to the total signal at a certain NO level. The result of a titration in ambient air and the expected HO_2 signal are shown in Figure 3.16. The difference between the two curves provides the magnitude of the interference. In the presented titration (Figure 3.16) this difference makes $\sim 12\%$ of the total signal at the maximum NO level. However, even the expected HO_2 curve is systematically lower compared to the total observed signal, the observed deviation is not significant.

Furthermore, titration experiments were conducted at different water vapour mixing ratios within the calibration air, to rule out a potential dependency of the conversion efficiency on the water vapour mixing ratio. Between 20% and 90% of the calibration air were flushed through the bubbler of the calibration unit, yielding H_2O mixing ratios of $3.7 - 12.5$ mmole mole^{-1}. The normalized instrument sensitivities are plotted in Figure 3.17.

There is no clear water dependency observed on the HO_2 conversion efficiency. Nonetheless, the titration curves show at the highest NO level a variability of $\sim 20\%$, which provides an estimate on the precision of these titration experiments.
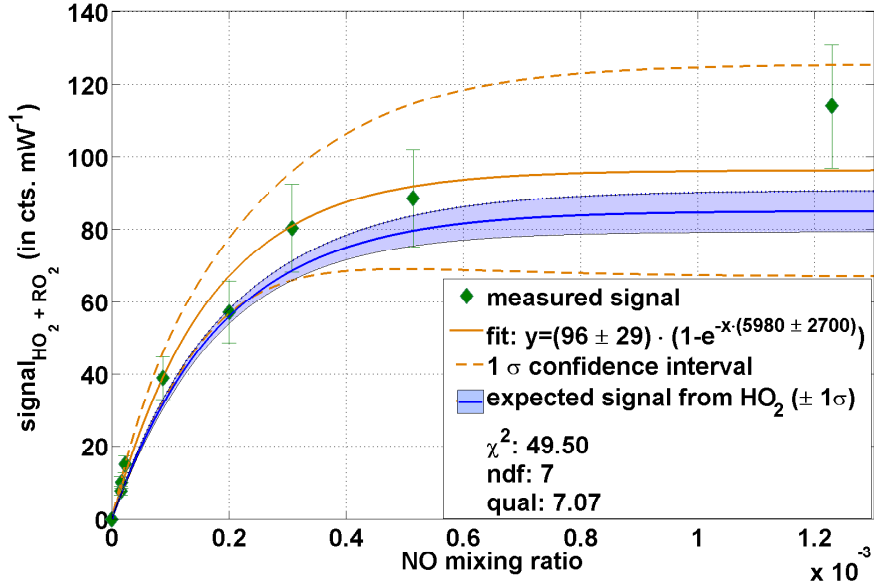
Abbildung 3.16.: NO dependency of the total (HO$_2$+ RO$_2$) signal during ambient air mea-
surement and expected HO$_2$ signal (blue line) applying the conversion effi-
ciency derived from titration experiment during calibration. At maximum
NO mixing ratio the signals differ by $\sim 12\,\%$. However, even the expected
HO$_2$ curve is systematically lower compared to the total observed signal,
the observed deviation is not significant.

To further investigate the effect of RO$_2$ interference on the measurement of HO$_2$ con-
centrations during HUMPPA–COPEC–2010, we calculated the H$_2$O$_2$ budget taking the
production by the self-reaction of HO$_2$ and the loss via photolysis and deposition into ac-
count and compared the calculated hydrogen peroxide with the measurements (Figure 3.18).
The production of H$_2$O$_2$ by HO$_2$ shows a quadratic dependency and is therefore highly sen-
sitive to the HO$_2$ concentration. The decay of hydrogen peroxide in the afternoon is mainly
determined by the deposition process. A reasonable deposition rate of $4 \times 10^{-5}\,\mathrm{s}^{-1}$, corre-
sponding to a deposition velocity of $4\,\mathrm{cm\,s}^{-1}$ in a 1 km high boundary layer, was used for the
calculation. This is comparable to values reported by Hall and Claiborn (1997) for a boreal
forest, ranging from 1 to $5\,\mathrm{cm\,s}^{-1}$. Removal of hydrogen peroxide by photolysis makes up to
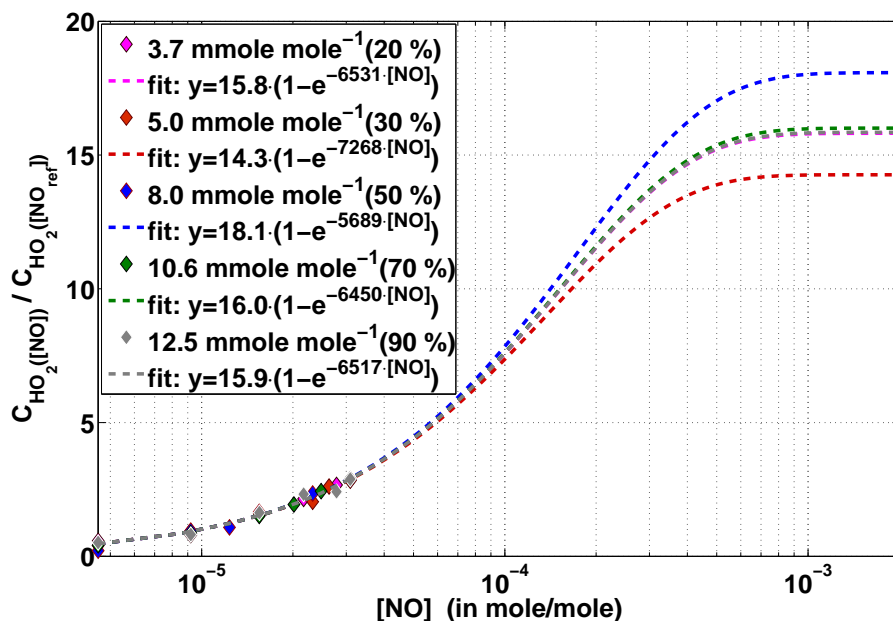
Abbildung 3.17.: Titration experiments at different water vapour mixing ratios within the calibration air, to rule out a potential water dependency on the HO_2 conversion efficiency. The titration curves show at the highest NO level a variability of $\sim 20\%$, which provides an estimate on the precision of these titration experiments. Percentages in parentheses denote the portion of humidified air to the total flow of calibration air.

10% of the total H_2O_2 loss. Hydrogen peroxide concentrations derived using the measured HO_2 is in reasonable agreement with the measured H_2O_2. In some cases measured HO_2 is still not sufficient to explain the measured H_2O_2 concentrations. Even though under some conditions hydrogen peroxide measurements might be affected by mixing with different air masses, e.g. from the residual layer, which have not been considered in our calculation, the comparison gives confidence that the measurements of HO_2 are not subject to a major interference. Although the magnitude of the RO_2 interference during HUMPPA–COPEC–2010 cannot be conclusively derived there is no evidence for an extraordinary large interference in the HORUS instrument compared to other LIF systems. Therefore, a contribution of 30% to the observed HO_2 signal (presently the maximum value observed in LIF instruments) is considered as an upper limit estimate of the RO_2-interference for further analysis.
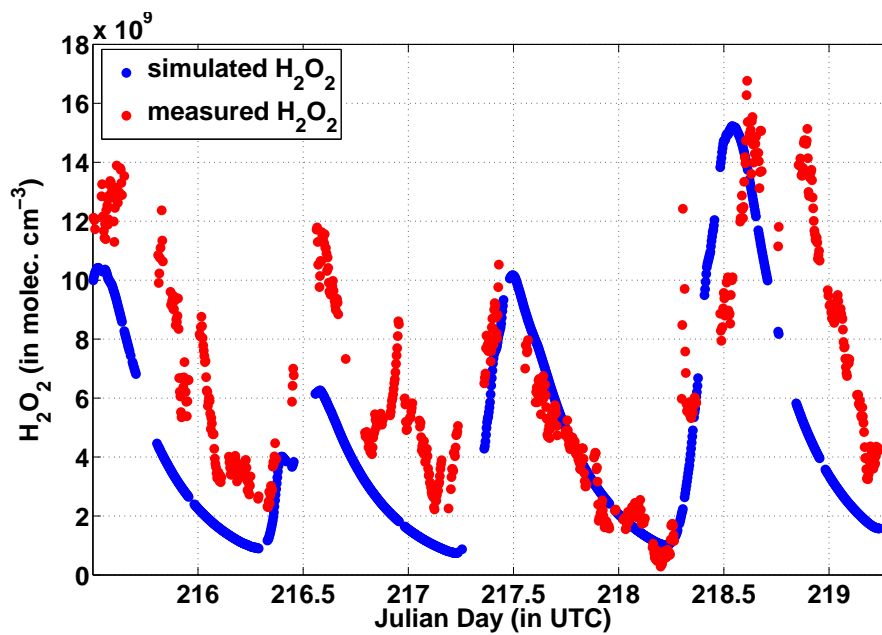
Abbildung 3.18.: Comparison of the measured H$_2$O$_2$ with simulation based on HO$_2$ measurements by LIF. The measured HO$_2$ is needed to explain the observed hydrogen peroxide.

4. HUMPPA–COPEC–2010

The boreal forest ecosystem represents the world largest interconnected woodland. It extends over an area of about $15 \times 10^6 \, km^2$ between 50 and 65 ° N and makes up 27 % of the world's forest (FAO, 2010). Hence, the boreal forest is expected to influence significantly the chemistry and physics of the atmosphere. The vegetation of the boreal forest comprises mainly coniferous trees, such as pine and spruce, that are known to emit significant quantities of reactive biogenic volatile organic compounds (e.g. monoterpenes) to the atmosphere as a function of temperature and to a lesser extent light (Williams et al., 2011, and references therein).

During HUMPPA-COPEC (*H*yytiälä *U*nited *M*easurements of *P*hotochemistry and *Pa*rticles in *A*ir – *C*omprehensive *O*rganic *P*recursor *E*mission and *C*oncentration study) a comprehensive dataset including measurements of the main oxidants OH, O_3, and NO_3; important trace gases such as CO, NO_x, H_2O_2, HCHO, HONO; anthropogenic and biogenic VOCs, and their oxidation products, inorganic chemical constituents, aerosol properties, aerosol size distributions, as well as photolysis frequencies and other meteorological parameters was collected at the boreal forest field station SMEAR II (*S*tation for *M*easuring Forest *E*cosystem-*A*tmosphere *R*elations). An overview can be found in Williams et al. (2011).

The general objective of the HUMPPA–COPEC–2010 campaign was to comprehensively characterize the atmospheric physics and chemistry over a boreal forest site in summer. This includes the characterization and speciation of volatile organic compounds, investigation of the formation and growth mechanisms of secondary organic aerosol, and the observation and analysis of radical chemistry as well as the extent of OH recycling processes.

In order to measure OH and HO_2 radicals the HORUS instrument was deployed during the intensive HUMPPA-COPEC field experiment in summer 2010.

4.1. Measurement site and instrumentation

The field site is located in a boreal forest in Hyytiälä, Southern Finland (61° 51' N, 24° 17' E, 181 m a.s.l.) (Vesala et al., 1998). The largest city near the station is Tampere (about 200 000 inhabitants), located about 60 km S-SW of the measurement site (Figure 4.1), (Hari and Kulmala, 2005). The SMEAR II station is equipped with several masts and towers surrounded by a more than 40-year-old pine dominated forest (*Pinus Sylvestris L.*). The canopy height during the measurement period was about 20 meters (For more detailed

information about the continuous measurements and the infrastructure see Vesala et al., 1998; Kulmala et al., 2001; Hari and Kulmala, 2005).
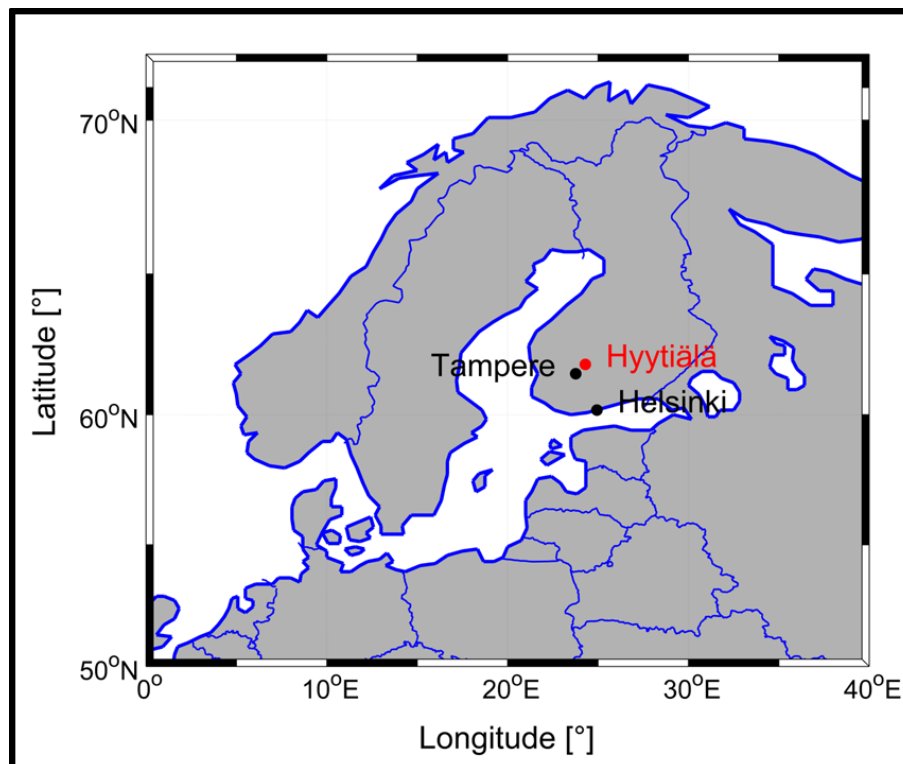
Abbildung 4.1.: SMEAR II field station, Hyytiälä, Southern Finland (61° 51' N, 24° 17' E, 181 m a.s.l.)

During the intensive measurement period of the HUMPPA–COPEC–2010 campaign an additional scaffolding tower was set up at the field site within a clearing (the HUMPPA tower, ~ 24 m high), reaching about 2-3 m above the canopy top. The sensors and inlet lines of instruments measuring reactive species like OH, HO_2, O_3, NO_x, NO_3, HONO, H_2O_2, organic peroxides, HCHO, monoterpenes, as well as the associated photolysis frequencies (J_{NO_2}, $J_{O(^1D)}$), and the total OH reactivity were collocated on the top platform of the HUMPPA tower to investigate the photochemistry at the ecosystem-atmosphere interface (see Figure 4.2).

Since the campaign instrumentation and meteorological conditions are described elsewhere (Williams et al., 2011), only a brief description of the instruments used in this study is given here; time resolution and lower limits of detection are summarized in Table 4.1.

Abbildung 4.2.: Setup of the HORUS instrument on the HUMPPA tower. Simultaneous side-by-side measurements of hydroxyl radicals were conducted at the start of the campaign with two instruments using chemical ionization mass spectrometry (CIMS) and laser induced fluorescence within the forest. The two instrument inlets (shown on the pictures in the lower right corner) were co-located at the side of the container, about 1m a.g.l. .

Ozone was measured using a UV instrument, sharing an inlet line with the chemiluminescence detection system (CLD) for measuring NO and NO_2. NO_2 was measured indirectly by conversion to NO using a blue light converter. The instrument setup was similar to the well-established one described by Hosaynali Beygi et al. (2011) for a different field campaign. NO_3 and N_2O_5 were measured by cavity-ring-down spectroscopy (Schuster et al., 2009; Crowley et al., 2010). Two long path absorption photometer systems (LOPAP) were set up within the forest and on the HUMPPA tower, measuring HONO (Kleffmann et al., 2002). Hydrogen peroxide and the sum of organic peroxides were observed with a wet chemical system based on derivatisation and fluorescence enzyme (DEF) described by Klippel et al.

(2011). Measurements of carbon monoxide were conducted using a commercial vacuum-UV resonance fluorescence CO instrument (AeroLaser GmbH, Garmisch-Partenkirchen, Germany). Detection of HCHO was based on the Hantzsch reaction and subsequent quantification of the reaction product via fluorescence detection. BVOCs were measured by several mass spectrometers. Gas chromatograph mass spectrometry (GC-MS) was used to investigate alkanes, alkenes, and particularly isoprene and monoterpenes (Yassaa et al., 2012). Proton transfer reaction mass spectrometry (PTR-MS) was applied for the observation of methanol, acetone, acetonitrile, isoprene, total monoterpenes, benzene and toluene. In the case of isoprene measurements, GC-MS data is used for further analysis, due to higher uncertainty in PTR-MS measurements, probably caused by a cold-trap connected to the PTR-MS instrument. Furthermore, the PTR-MS isoprene data might be affected by an interference due to 2-methyl-3-buten-2-ol (MBO) which is detected at the same mass to charge ratio as isoprene using conventional H_3O^+ ionization (Goldan et al., 1997; Williams et al., 2001; Karl et al., 2012).

Photolysis frequencies (J_{NO_2}, $J_{O(^1D)}$) were measured within the clearing at the forest ground, as well as on top of the HUMPPA tower with a set of filter radiometers at each position (Junkermann et al., 1989; Bohn et al., 2008; B.Bohn, personal communication, 2012). Water vapour, temperature, and pressure were recorded at several different levels on a 75 m meteorological mast located about 100 m away. The total reactivity towards OH was determined by a comparative reactivity method (Sinha et al., 2008; Nölscher et al., 2012). This method is based on the competitive scavenging of OH by a reference gas (pyrrole) and atmospheric trace gases. A chemical ionization mass spectrometry (CIMS) instrument was deployed to measure OH on ground (Petäjä et al., 2009).

4.2. HO_x observations

During the HUMPPA–COPEC–2010 field experiment gradients of the hydroxyl radical were measured using the CIMS instrument from University of Helsinki on ground (Petäjä et al., 2009) and the HORUS-LIF instrument above the canopy. To assure the comparability of both instruments and techniques they had to be compared side-by-side under ambient conditions. The HORUS-LIF instrument already participated in the international HO_xComp 2005 project, a ground-based intercomparison of six OH instruments (4 LIF, 1 CIMS, 1 DOAS) performing measurements in the atmosphere simulation chamber SAPHIR as well as in ambient air. The HORUS-LIF showed good agreement with CIMS measurements ($R^2 = 0.96$) during daytime. However, we were expecting from that study to see a nighttime signal in ambient air whereas the CIMS method usually does not detect nighttime OH (Schlosser et al., 2009).

During HUMPPA–COPEC–2010 the two OH instruments were intercompared at the beginning of the field experiment (27th−30th of July) before starting the gradient measurement of OH concentrations. The inlet system of the LIF was placed next to the CIMS inlet on

Tabelle 4.1.: Instrumentation applied for above canopy observations during HUMPPA-COPEC2010

Species/Quantity	Time resolution	Accuracy (1σ)	Precision (1σ)	Lower limit of detection	Technique[†]
OH	~4 min	30 % (2σ)	~5×10^5 molec. cm^{-3}	~9×10^5 molec. cm^{-3}	IPI-LIF-FAGE
HO$_2$	~15 s	30 % (2σ)	< 0.8 pptv	0.4 pptv	LIF-FAGE
OH	30 s	32 %	—	~5×10^4 molec. cm^{-3}	CIMS
O$_3$	3 s	1 %	—	~1 ppbv	UV
NO, NO$_2$	1 s	~5 %	~14 pptv	5 pptv	CLD (+Bluelight converter)
NO$_3$	5 s	—	—	2-4 pptv	CRD
N$_2$O$_5$	5 s	—	—	5-10 pptv	CRD
HONO	30 s	10 %	~1-2 %	< 5 pptv	LOPAP
H$_2$O$_2$ and ROOH	5 min	25-30 %	8 pptv (3σ)	15 pptv	Dual enzyme
CO	1 s	<10 %	<10 %	~1 ppbv	UV
HCHO	5 min	19 %	~700 pptv (3σ)	9 pptv	Hantsch
Alkanes, alkenes, isoprene, monoterpenes	60 min	—	—	1 pptv	GC-MS
Methanol, acetone, acetonitrile, total terpenes, benzol, toluene isoprene*	6 min	—	—	~50 pptv	PTR-MS
Total OH reactivity	1 min	16 %	3-4 s^{-1}	3 s^{-1}	CRM
J$_{O(^1D)}$, J$_{NO_2}$	1 s	~15 %	1 %	—	Filterradiometer

* Isoprene measurements might be affected by 2-methyl-3-buten-2-ol (MBO) detected at the same mass to charge ratio.

[†] IPI-LIF-FAGE = InletPreInjector - Laser Induced Fluorescence - FAst Gas Expansion; CIMS = Chemical Ionization Mass Spectrometry; UV = UltraViolet absorption/fluorescence; CLD=ChemiLuminensence Detector; CRD= Cavity Ring Down; LOPAP = Long Path Absorption Photometer; GC-MS = Gas Chromatography - Mass Spectrometry; PTR-MS = Proton Transfer-Reaction Mass Spectrometer; CRM = Comparative Reactivity Method.

ground. The meteorological conditions at the field site within the four days of instrument intercomparison were dominated by above average temperatures, exceeding $25\,^\circ$ C during noon, and mainly south-easterly winds, without rainy periods. Timeseries of meteorological parameters and trace gas concentrations can be found in Appendix A.
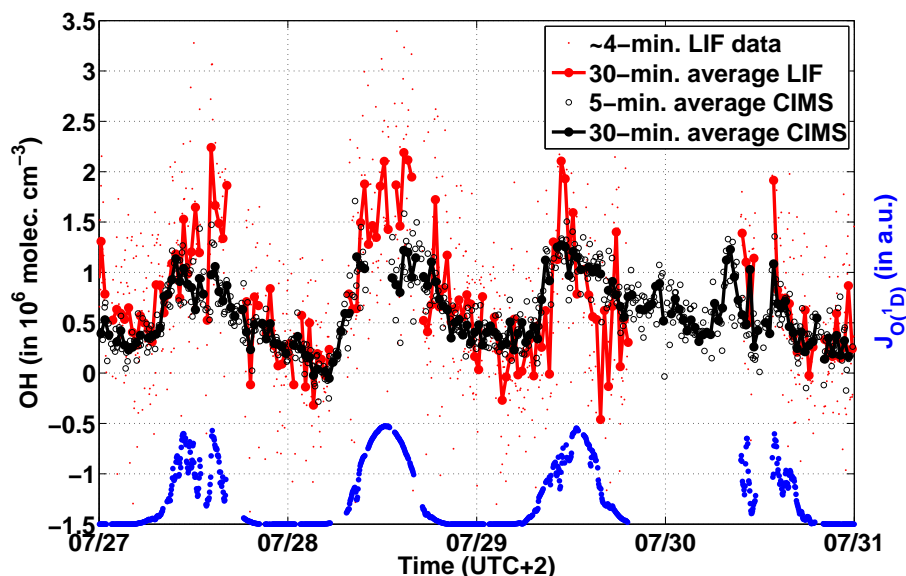
Abbildung 4.3.: Comparison of OH measurements by IPI-LIF-FAGE technique and by CIMS on ground (University of Helsinki, Petäjä et al., 2009). Nighttime OH was observed by both techniques.

The result of these four days of instrument intercomparison is shown in Figure 4.3. OH radical concentrations observed by both techniques are generally in agreement. The LIF data shows stronger fluctuations compared to the measurements by CIMS on the same averaging interval timescale of 30 minutes. Daytime maximum OH concentrations reached about $(1.5 - 2) \times 10^6$ molec. cm^{-3}. During nighttime, both instruments observed OH concentrations below 5×10^5 molec. cm^{-3}, but still well above the lower limit of detection of the CIMS, which was 5×10^4 molec. cm^{-3} at a time resolution of 30 s. For the LIF the detection limit was 4.8×10^5 molec. cm^{-3} at a time resolution of 60 minutes. The larger limit of detection as well as the increased fluctuations in the LIF observation compared to CIMS is mainly caused by application of the chemical modulation method. To determine atmospheric OH the interference signal is subtracted from the total observed signal. The detection limit is therefore not only given by instrument properties, like laser power, optical properties, and detector efficiency. It is also prone to the atmospheric variability both of

OH and of the species causing the interference inside the detection unit. Nevertheless, the good agreement during the intercomparison (Figure 4.4) provides confidence in the chemical modulation method and that the LIF measurements are not affected by additional unknown OH interferences resulting from the laser fluorescence technique (Novelli et al., 2012).
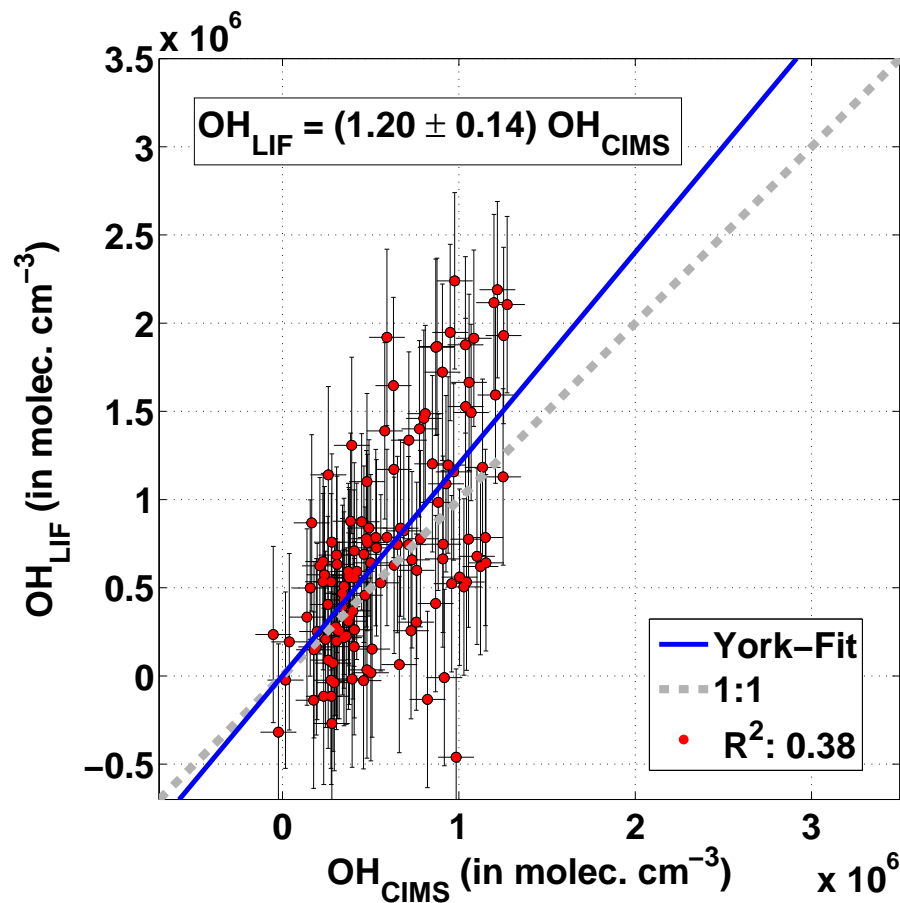
Abbildung 4.4.: Comparison of OH measurements by IPI-LIF-FAGE technique and by CIMS (University of Helsinki, Petäjä et al., 2009) based on 30-minute average data. Errorbars indicate the precision of the associated measurements. Linear regression following the method by York et al. (2004) yields a slope of 1.20 ± 0.14 and an insignificant offset (Offset: $(2 \pm 93) \times 10^3$ molec. cm^{-3}).

Finally, the LIF instrument was moved to the top of the HUMPPA tower to investigate the radical chemistry at the interface between atmosphere and ecosystem while the CIMS stayed on the ground. The resulting hydroxyl radical measurements are presented in Figure 4.5.
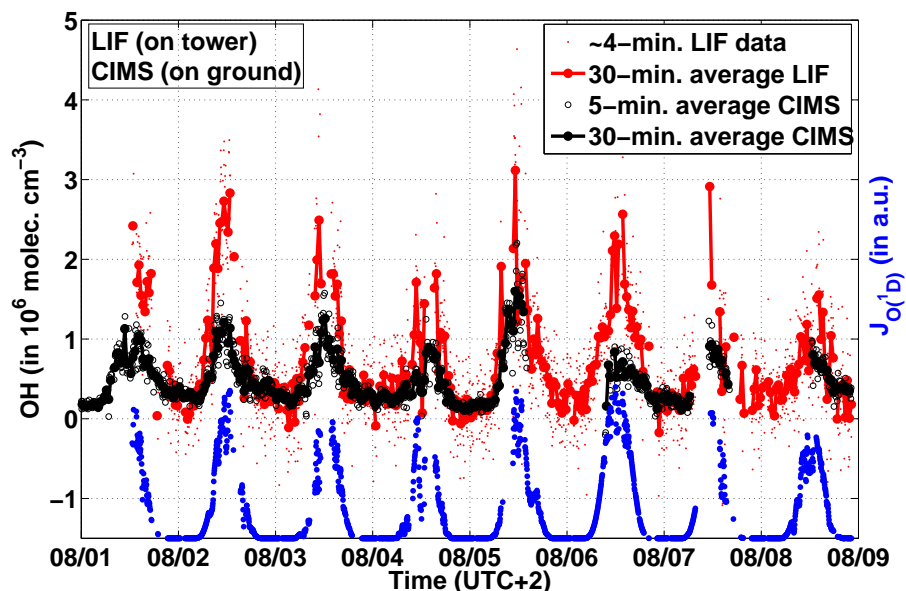
Abbildung 4.5.: Simultaneous OH measurements on the ground and above the canopy. Concentration maxima observed on the tower are up to a factor of 3 times higher than on the ground. Both instruments measured similar values during night.

Simultaneous OH measurements on ground and above canopy revealed a factor of 2-3 difference in observed concentration maxima, reaching values up to about $3 \times 10^6 \, \text{molec. cm}^{-3}$ on the tower. During nighttime, the hydroxyl radical observations above canopy and on ground showed similar values. Linear correlation of OH and photolysis frequency $J_{O(^1D)}$ was previously found during ground-based campaigns (Rohrer and Berresheim, 2006). However, the slope varies with location, depending on the abundance of VOCs and NO_x (see Section 2.4). The comparison of the correlation on ground and above canopy shows that higher OH values on the tower are driven by higher radiation but does not suggest differences in the chemical regime (Figure 4.6).

The nighttime OH, which was occassionally well above the detection limit of both instruments, can not be explained by the supporting observations, with known sources accounting for about 20% of the total OH production necessary to explain the measured concentrations. NO_3 was always below the lower limit of detection of about 1 ppt_V (at 5 min. time
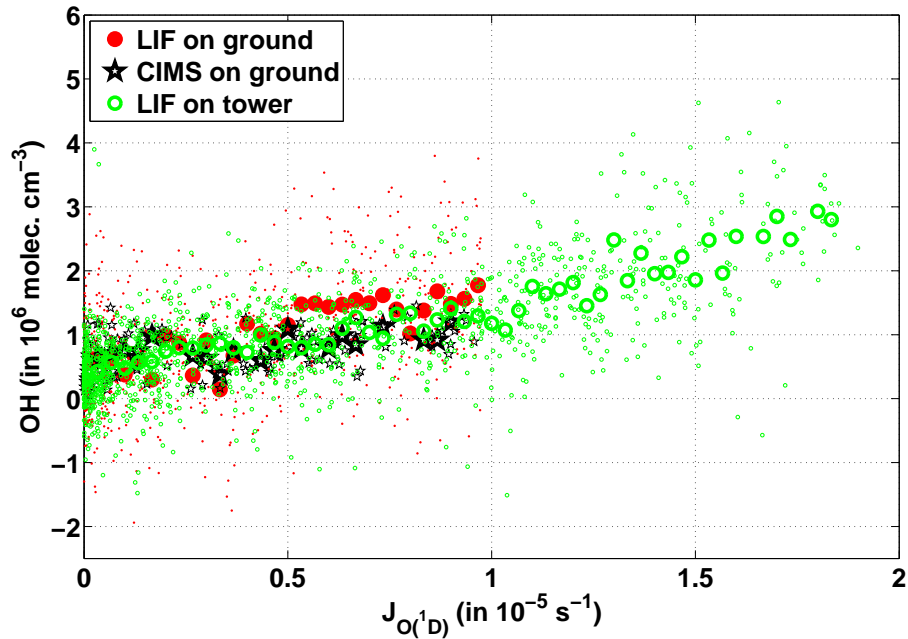
Abbildung 4.6.: Linear correlation of OH and J$_{O(^1D)}$ is found during HUMPPA–COPEC–2010. The comparison of the correlation on ground and above canopy shows that higher OH values on the tower are driven by enhanced radiation. Similar slopes, mainly depending on the abundance of VOCs and NO$_x$, do not suggest differences in the chemical regime. Small symbols show 5-minute dataset, large symbols are means of data binned in steps of $3 \times 10^{-7}\,\mathrm{s}^{-1}$.

resolution) for the CRD instrument (Rinne et al., 2012). However, the production rate for NO$_3$ from the reaction of NO$_2$ and O$_3$ is of the order of $1 \times 10^6\,\mathrm{molec.\,cm}^{-3}\,\mathrm{s}^{-1}$. Assuming this would directly cause an equally high OH production in the oxidation process of VOCs, which is an unlikely high upper estimate, this would still only explain an additional 10 to 15 % of the missing production during nighttime. The ozonolysis of unmeasured VOCs and their oxidation products, as well as enhanced HO$_x$ recycling are potential candidates to explain the missing OH production. A more detailed analysis of the most relevant OH production terms is given in Section 4.4.

4.3. Primary HO_x production

Subsequent to the ground-level comparison with the OH-CIMS ($1^{st} - 8^{th}$ of August), the HORUS instrument was moved to the top of the HUMPPA tower to investigate the photochemistry at the ecosystem-atmosphere interface. Making use of the comprehensive measurements of atmospherically relevant species, described in section 4.1, the known primary production rates of HO_x can be calculated considering the Reactions R4.1 - R4.5.

$$O(^1D) + H_2O \rightarrow 2\,OH, \tag{R4.1}$$

$$HONO + h\nu \rightarrow OH + NO, \tag{R4.2}$$

$$BVOCs + O_3 \rightarrow HO_x \ + products, \tag{R4.3}$$

$$HCHO + h\nu \xrightarrow{+O_2} HO_2 + products, \tag{R4.4}$$

$$H_2O_2 + h\nu \rightarrow 2OH. \tag{R4.5}$$
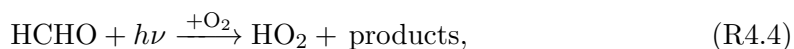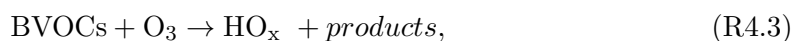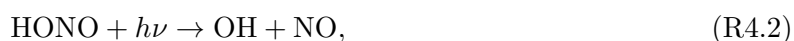
The contributions to the primary HO_x production during HUMPPA–COPEC–2010 are presented in Figure 4.7.
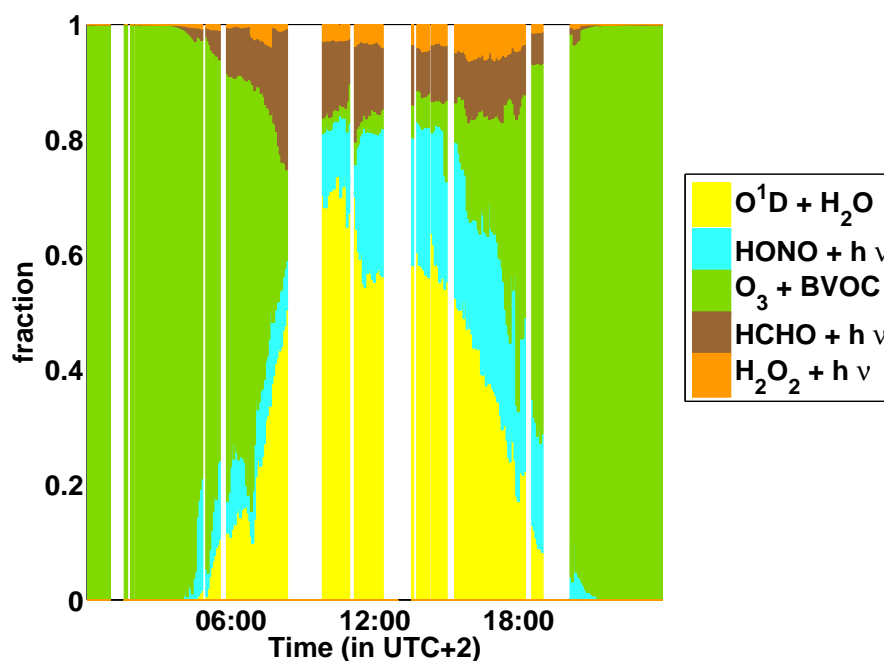
Abbildung 4.7.: Contributions to the primary HO_x production.

During daytime the photolytic production from $O(^1D) + H_2O$ emerges as the most important HO_x source with a contribution of more than $50\,\%$ around noon. The photolysis of hydrogen peroxide contributes less than $10\,\%$ at maximum in the late afternoon hours. Slightly more relevant for the primary HO_x production is the direct formation of HO_2 from formaldehyde photolysis. The contribution to the HO_x production by photolysis of HONO is remarkable. The steady-state concentration of HONO due to reaction of NO with OH and photolysis backreaction (Reaction R4.2) was calculated and subtracted from the measured HONO concentration, to separate the primary OH production by HONO. This starts earlier in the morning and lasts longer in the evening hours compared to the production via $O(^1D) + H_2O$. Furthermore, it is comparable in magnitude in the early morning and late afternoon hours. During nighttime, when the photolytic sources vanish, the ozonolysis of BVOCs remains. During daytime the contribution due to $O_3 + BVOC$ is negligible.

The primary HO_x production seems to be dominated by the primary OH production. Nonetheless, other direct HO_2 sources, such as RO_2 radicals produced from acetone photolysis reacting with NO or the photolysis of glyoxal, forming hydroperoxyl radicals, were not considered. Acetone photolysis provides only a RO_2 production rate on the order of $1 \times 10^4 \, \mathrm{molec.\,cm^{-3}\,s^{-1}}$. This rate, considered as an upper limit of the additional HO_2 production does not contribute significantly to the total HO_x production. Glyoxal was not measured during HUMPPA–COPEC–2010. However, glyoxal is detected at the same mass like acetone in the PTR-MS instrument. Therefore, the acetone mixing ratio (Median: $\sim 3\,\mathrm{ppb_V}$) can be assumed as an upper limit estimate for the glyoxal mixing ratio. A HO_2 production rate on the order of $1 \times 10^6 \, \mathrm{molec.\,cm^{-3}\,s^{-1}}$ by photolysis of glyoxal is feasible, which is equivalent to a contribution of about 10 to $30\,\%$ to the total HO_x production. Similarly peroxyacyl nitrates (PAN) that can be transported, i.e. it is not necessarily locally produced, decompose forming peroxyacyl radicals. These peroxy radical species can react with HO_2 forming OH (see Section 2.3). Thus, PAN does not directly contribute to the HO_x production, but it can represent a radical source, driving additional OH recycling processes.

4.4. OH **budget – calculated based on observations**

Similarly to the primary HO_x production, the budget of hydroxyl radicals is derived using the comprehensive measurements of atmospheric species. Besides the photolytic sources (Reaction R4.6 - R4.7), ozonolysis of different biogenic VOCs (Reaction R4.8) contributes to the primary production of OH. Secondary sources, e.g. the recycling of HO_2 by NO and O_3 (Reaction R4.11 - R4.12) and peroxide photolysis (Reaction R4.9 - R4.10), additionally play an important role in OH radical production. Based on available observations we define:

Primary production

$$O(^1D) + H_2O \rightarrow 2\,OH, \tag{R4.6}$$

$$HONO + h\nu \rightarrow OH + NO, \tag{R4.7}$$

$$BVOCs + O_3 \rightarrow OH + products. \tag{R4.8}$$

Secondary production/Recycling

$$H_2O_2 + h\nu \rightarrow 2\,OH, \tag{R4.9}$$

$$ROOH + h\nu \rightarrow OH + RO, \tag{R4.10}$$

$$HO_2 + NO \rightarrow OH + NO_2, \tag{R4.11}$$

$$HO_2 + O_3 \rightarrow OH + 2\,O_2. \tag{R4.12}$$

Under steady-state conditions, which can be assumed for short-lived compounds like OH, the sum of these production rates should equal the total loss of hydroxyl radicals, which can be derived from the product of the measured OH concentration and the measurements of the total OH reactivity (k'_{OH}).

$$P_{OH}^{total} = \sum_i P_{OH,i} \tag{4.1}$$

$$L_{OH}^{total} = \sum_i L_{OH,i} = k'_{OH}\,[OH] = \tau^{-1}\,[OH] \tag{4.2}$$

$$P_{OH}^{total} \stackrel{!}{=} L_{OH}^{total} \tag{4.3}$$

The calculated hydroxyl radical production reaches a maximum of about 1×10^7 molec. $cm^{-3}\,s^{-1}$ on ground and 1.4×10^7 molec. $cm^{-3}\,s^{-1}$ above canopy around local solar noon as shown in Figure 4.8. Since NO and NO_2 were not measured at ground level, they were derived from the above canopy measurements assuming constant NO_x with height, using the filter radiometer measurements of the photolysis frequency J_{NO_2} on ground and above the canopy to calculate partitioning between NO_2 and NO. The enhanced radical production above canopy is caused by higher $J_{O(^1D)}$ observed on the tower and the enhanced recycling (Figure 4.8). The dominant primary source of OH (21%) is the reaction of $O(^1D)$ with water. HONO photolysis, with a contribution during noon time of about 7%,

is also significant. However, the conversion of HO_2 to OH via the reactions with NO and O_3 dominates the total production of hydroxyl radicals (60-80 %). The ozonolysis of measured biogenic VOCs plays a minor role as a source of OH during daytime but becomes more important during nighttime.

The budget of steady-state OH was calculated as described above, using the available measurements of the chemical species contributing to the production rates and the total OH reactivity observed above canopy as constraints. Mean OH reactivity measured during this period was $11.5\,s^{-1}$ varying typically between the lower limit of detection $(3-4\,s^{-1})$ and about $30\,s^{-1}$, with some peaks reaching above $70\,s^{-1}$ (Nölscher et al., 2012). The known
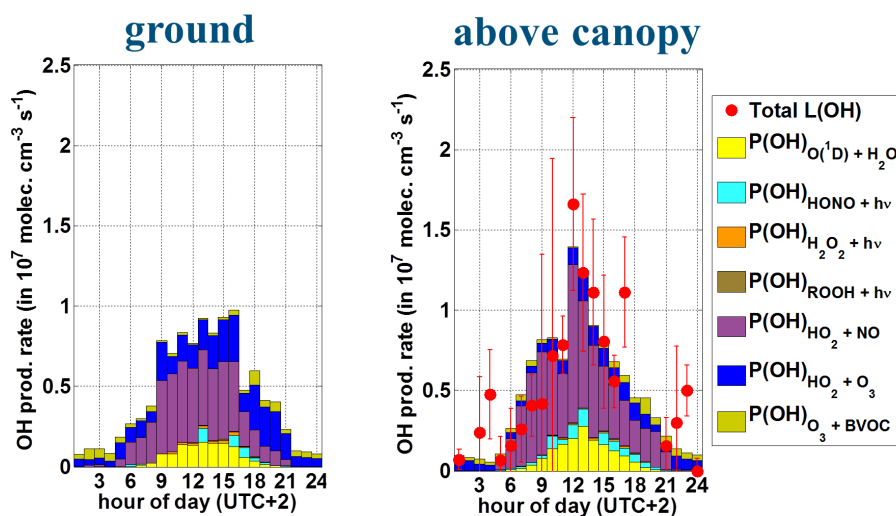
Abbildung 4.8.: Average diurnal OH production below (left panel) and budget above (right panel) the canopy. The whiskers indicate the variability of the total loss rate, calculated from total OH reactivity and hydroxyl radical measurement using LIF data.

OH sources are almost sufficient to close the budget above the canopy. Isoprene contributes less than 10% at maximum to the total OH reactivity measured during HUMPPA–COPEC–2010 due to its low mixing ratio (typically below $200\,ppt_V$). Measured terpenes, being similar or slightly less reactive than isoprene, e.g. $\alpha-$pinene (up to 5 %), $\beta-$pinene (up to 4 %), $\beta-$myrcene (up to 6 %), and Δ^3-carene (up to 9 %) were more abundant, thus providing in sum a higher reactivity towards OH.

The reactions of OH with $CO, O_3, HCHO, H_2O_2$, and SO_2 are important sources of HO_2 radicals:

$$OH + CO \xrightarrow{+O_2} CO_2 + HO_2 \tag{R4.13}$$

$$OH + O_3 \longrightarrow O_2 + HO_2 \tag{R4.14}$$

$$OH + HCHO \xrightarrow{+O_2} H_2O + CO + HO_2 \tag{R4.15}$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \tag{R4.16}$$

$$OH + SO_2 \xrightarrow{+O_2,H_2O} H_2SO_4 + HO_2 \tag{R4.17}$$
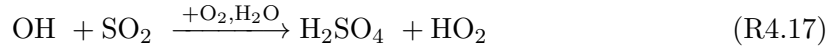
In addition, HCHO photolysis is a direct radical source, also contributing to HO_2 production during daytime. The cycling reactions of RO_2 species with NO can become the largest contributor to hydroperoxyl radical production, depending on the abundance of organic peroxy radicals and NO.

$$HCHO + h\nu \xrightarrow{+2O_2} CO + 2\,HO_2 \tag{R4.18}$$

$$RO_2 + NO \longrightarrow HO_2 + products \tag{R4.19}$$
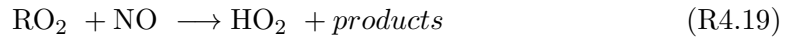
The loss of HO_2 is dominated by reactions with NO and O_3, which are at the same time the predominant source of OH. Radical-radical termination reactions (Reactions R4.22-R4.24) yielding peroxides and water act as a sink for HO_x radicals.

$$HO_2 + NO \rightarrow OH + NO_2 \tag{R4.20}$$

$$HO_2 + O_3 \rightarrow OH + 2\,O_2 \tag{R4.21}$$

$$HO_2 + OH \rightarrow H_2O + O_2 \tag{R4.22}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{R4.23}$$

$$HO_2 + RO_2 \rightarrow ROOH + O_2 \tag{R4.24}$$
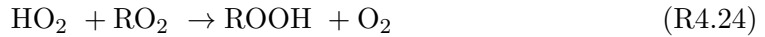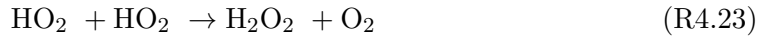
Unfortunately, RO_2 was not measured during HUMPPA–COPEC–2010 prohibiting the calculation of a HO_2 budget from observations in a similar manner as the OH budget. Nevertheless, assuming steady-state conditions for HO_2 and taking the hydroperoxyl radical measurements into account, the RO_2 concentration can be estimated.

$$
\begin{aligned}
\frac{d\,[HO_2]}{dt} &= 0 \\
&= P_{HO_2}^{total} - L_{HO_2}^{total} \\
&= P_{HO_2}^{known} + bk_{R4.19}\,[NO]\,[RO_2] - L_{HO_2}^{known} - k_{R4.24}\,[HO_2]\,[RO_2] \\
&= P_{HO_2}^{known} - L_{HO_2}^{known} + (bk_{R4.19}\,[NO] - k_{R4.24}\,[HO_2])\,[RO_2]
\end{aligned}
\tag{4.4}
$$

where b is a branching ratio and k_i denotes the reaction rate constant associated with Reaction i. From this it follows

$$[\mathrm{RO_2}] = \frac{L_{\mathrm{HO_2}}^{known} - P_{\mathrm{HO_2}}^{known}}{bk_{R4.19}\,[\mathrm{NO}] - k_{R4.24}\,[\mathrm{HO_2}]}. \tag{4.5}$$

Typically there was about twice as much $\mathrm{RO_2}$ as $\mathrm{HO_2}$ ($\mathrm{RO_2}/\,\mathrm{HO_2}$: median 1.8; min. 0.5; max. 4.5). This result was confirmed by calculation of the modified Leighton ratio ($\mathrm{RO_2}/\mathrm{HO_2}$: median 1.8; min. 0.1; max. 6.3) (Leighton, 1961).

$$\Phi := \frac{\mathrm{J_{NO_2}}\,[\mathrm{NO_2}]}{[\mathrm{NO}](\mathrm{k_{NO\,+O_3}}\,[\mathrm{O_3}] + \mathrm{k_{R4.19}}(\,[\mathrm{RO_2}] + \,[\mathrm{HO_2}]))}, \tag{4.6}$$

$$[\mathrm{RO_2}]_{\Phi\overset{!}{=}1} = \frac{\mathrm{J_{NO_2}}\,[\mathrm{NO_2}]}{k_{R4.19}\,[\mathrm{NO}]} - \frac{k_{\mathrm{NO\,+O_3}}}{k_{R4.19}}\,[\mathrm{O_3}] - \,[\mathrm{HO_2}]. \tag{4.7}$$

Thus, organic peroxy radicals seem to play a major role in the radical photochemistry in the observed boreal forest environment, providing a strong link between OH and $\mathrm{HO_2}$.

The importance of radical cycling via $\mathrm{HO_2}$ shown in the budget demands careful examination of the reliability of $\mathrm{HO_2}$ measurements. The measurement of $\mathrm{HO_2}$ by conversion to OH using NO can be severely affected by $\mathrm{RO_2}$ reacting with NO also producing hydroxyl radicals (Fuchs et al., 2011). However, this interference depends on the instrumental setup (Whalley et al., 2013). It is to be quantified specifically for each instrument and depends on the composition of $\mathrm{RO_2}$ in ambient air. The $\mathrm{HO_2}$ observed during HUMPPA–COPEC–2010 therefore gives an upper limit for the atmospheric $\mathrm{HO_2}$ including an unknown contribution from $\mathrm{RO_2}$. To put limits on the atmospheric $\mathrm{HO_2}$, the budget of $\mathrm{H_2O_2}$ was analyzed. The $\mathrm{H_2O_2}$ intercomparison (Figure 3.18) does not suggest that the $\mathrm{HO_2}$ measurements by HORUS during HUMPPA–COPEC–2010 were affected by a major $\mathrm{RO_2}$ interference (see Section 3.2.5). Nevertheless, assuming an interference by $\mathrm{RO_2}$ species on the $\mathrm{HO_2}$ measurements during HUMPPA–COPEC–2010 of 30 % would increase the gap between total OH production and total loss of OH. Recycling via $\mathrm{HO_2}$ would still be the predominant source of OH. Not yet considered in the budget is the reaction of specific alkylperoxy radicals with $\mathrm{HO_2}$ forming back OH (see Section 2.3). Assuming, as an upper limit, all $\mathrm{RO_2}$ reacts with $\mathrm{HO_2}$ like the peroxy acetyl radical does, this causes an additional OH production rate of up to 1×10^7 molec. cm^{-3} s^{-1}. The speciation of $\mathrm{RO_2}$ for HUMPPA–COPEC–2010 is unknown, thus the contribution of $\mathrm{RO_2}$ species forming OH in the reaction with $\mathrm{HO_2}$ cannot be estimated. Nonetheless, as shown above such recycling mechanisms have the potential to close the hydroxyl radical budget.

4.5. OH / HO_2 **ratio**

The chemistry of OH and HO_2 in the atmosphere is closely linked by various hydroxyl recycling mechanisms. The ratio OH / HO_2 can be used to describe the state of equilibrium between both radicals. The equilibrium shifts depending on the concentrations of NO, O_3, CO, VOCs, and radiation. Typically during daytime a minimum of about 100 to 200 times more HO_2 was abundant compared to OH. During the dark ($J_{O(^1D)} < 10^{-6}\,s^{-1}$) the HO_2 concentrations were up to three orders of magnitude higher than the hydroxyl radical concentrations observed. The observed radical ratio (Figure 4.9) shows a good correlation ($R^2 = 0.80$) with the NO / CO ratio for average and high photolysis frequencies ($J_{O(^1D)} > 10^{-6}\,s^{-1}$). Increasing NO concentrations and decreasing CO shift the equilibrium towards the hydroxyl radical, as it is expected for an environment dominated by classical HO_x recycling pathways. The variability of CO is typically small compared to the variability of NO which therefore dominates the variability of the NO / CO ratio. At lower photolysis frequencies, when classical recycling via HO_2 + NO is no longer the predominant hydroxyl radical source (see Figure 4.8) the OH / HO_2 ratio shows no clear dependency on the ratio of NO and CO.

4.6. OH **reycling probability and cycling-lifetime**

The hydroxyl radical concentration significantly defines the oxidation capacity of the atmosphere. Beside primary production of the oxidant, recycling mechanisms are of major importance in hydroxyl radical production. The stability of tropospheric HO_x chemistry strongly depends on the occurence of such processes. Self-amplifying radical production (auto-catalytic conditions) would cause the chemical system to be unstable. Similarly, total absence of recycling processes might lead to an accumulation of reduced gases in the atmosphere (catastrophic conditions) (Lelieveld et al., 2002). Thus, the probability for an OH radical to be recycled can be interpreted as a measure for the stability of tropospheric hydroxyl radical chemistry. Furthermore, a lifetime for the hydroxyl radical in units of cycles completed - the "cycling-lifetime" - can be derived from this quantity.

During HUMPPA–COPEC–2010 primary production (P) of hydroxyl radicals by photolysis of ozone and HONO together with ozonolysis of biogenic VOCs only contributes up to one third of the total OH production (Figure 4.8). Regeneration of OH from recycling reactions (Reaction R4.11 - R4.12) and photodissociation of peroxides (Reaction R4.9 - R4.10), which are products in the OH oxidation chain, can play an important role in the total OH formation. The ratio of these secondary OH sources (S) to the total hydroxyl radical production was defined by Lelieveld et al. (2002) as the OH reycling probability r:

$$r = \frac{S}{P + S} \tag{4.8}$$
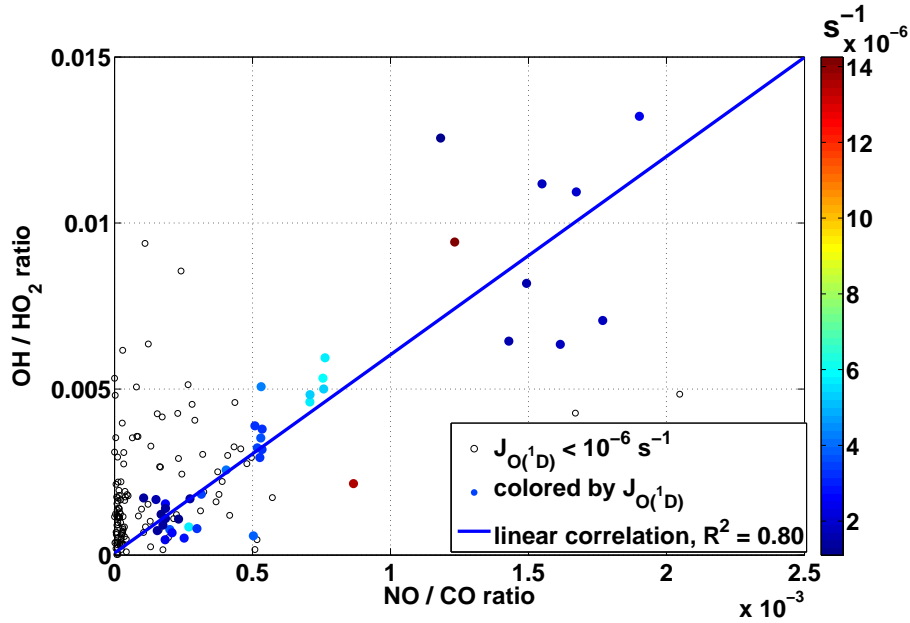
Abbildung 4.9.: Observed OH / HO_2 ratio vs. NO / CO ratio. For $J_{O(^1D)} > 10^{-6}\,\mathrm{s}^{-1}$ a linear correlation was found ($R^2 = 0.80$). At lower photolysis frequencies the radical ratio does not show a clear dependency on the ratio of NO and CO.

The recycling probability as a function of the NO concentration can be approximated considering only the predominant contributions to P and S:

$$
\begin{aligned}
r(\,[NO]) &= \frac{S(\,[NO])}{P + S(\,[NO])} \\
&\approx \frac{k_{R4.11}\,[NO]\,[HO_2] + k_{R4.12}\,[O_3]\,[HO_2]}{2b_{O(^1D)\to OH}J_{O(^1D)}\,[O_3] + k_{R4.11}\,[NO]\,[HO_2] + k_{R4.12}\,[O_3]\,[HO_2]}.
\end{aligned}
\tag{4.9}
$$

The expected NO dependency of the recycling probability r (Equation 4.9) is shown in Figure 4.10. In case of high NO levels the secondary production terms exceed the magnitude of the primary production due to ozone photolysis, yielding high recycling probability values close to unity. The course of the NO dependency of r in Equation 4.9 is influenced by three parameters; the HO_2 concentration, the O_3 concentration and the photolysis frequency $J_{O(^1D)}$. The latter one only acts on the production term P. Increasing photolysis causes an increased primary production and thus, a diminished r-value. O_3 shows the same influence
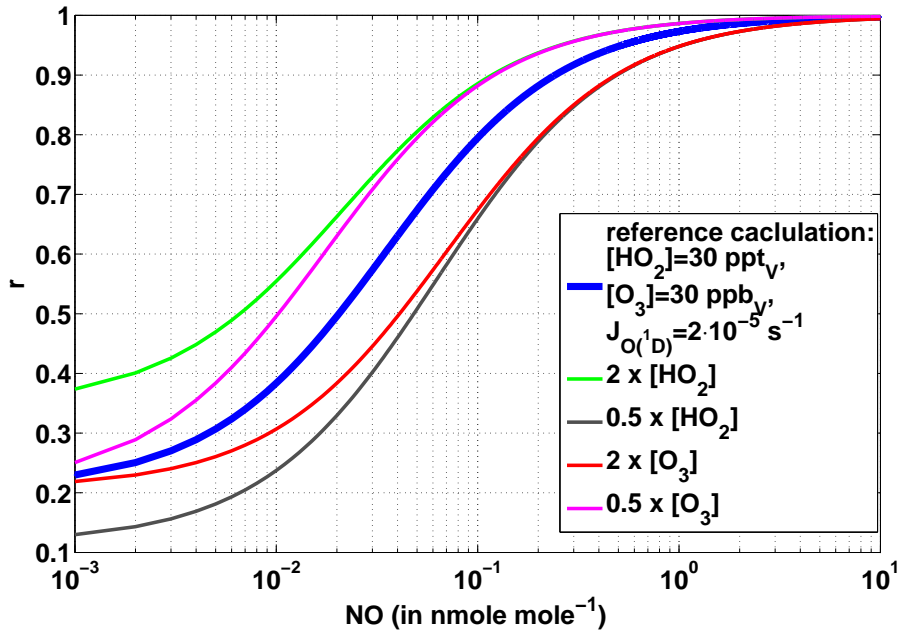
Abbildung 4.10.: Expected NO dependency of the recycling probability r at constant levels of HO_2, O_3 and photolysis frequency $J_{O(^1D)}$ (blue line). Sensitivity to these parameters is presented in different colors (see legend). Doubling the photolysis frequency (not shown in Figure) leads to a similar dependency like reducing the HO_2 concentration by 50 %.

on the primary production. Furthermore, the secondary OH production includes the term $k_{R4.12}\,[O_3]\,[HO_2]$, which is important, when $k_{R4.12}\,[O_3]$ is similar or large in magnitude compared to $k_{R4.11}\,[NO]$. Therefore, the overall sensitivity on O_3 is strongly depending on the NO level (see Figure 4.10). At very low NO mixing ratios $k_{R4.11}\,[NO]$ can be small compared to $k_{R4.12}\,[O_3]$. When NO converges to zero, Equation 4.9 yields:

$$
\begin{aligned}
r(\,[NO]) &\approx \frac{k_{R4.12}\,[O_3]\,[HO_2]}{2b_{O(^1D)\to OH}J_{O(^1D)}\,[O_3] + k_{R4.12}\,[O_3]\,[HO_2]} \\
&\approx \frac{k_{R4.12}\,[HO_2]}{2b_{O(^1D)\to OH}J_{O(^1D)} + k_{R4.12}\,[HO_2]} \\
&\approx \frac{k_{R4.12}}{2b_{O(^1D)\to OH}\frac{J_{O(^1D)}}{[HO_2]} + k_{R4.12}}
\end{aligned}
\tag{4.10}
$$

The recycling probability is no longer dependent on the concentration of O_3 and the limit of r is defined by the ratio of $J_{O(^1D)}$ and the concentration of HO_2 (see Equation 4.10).

OH recycling probabilities calculated from observations as a function of the ambient NO mixing ratio for different environments are shown in Figure 4.11.
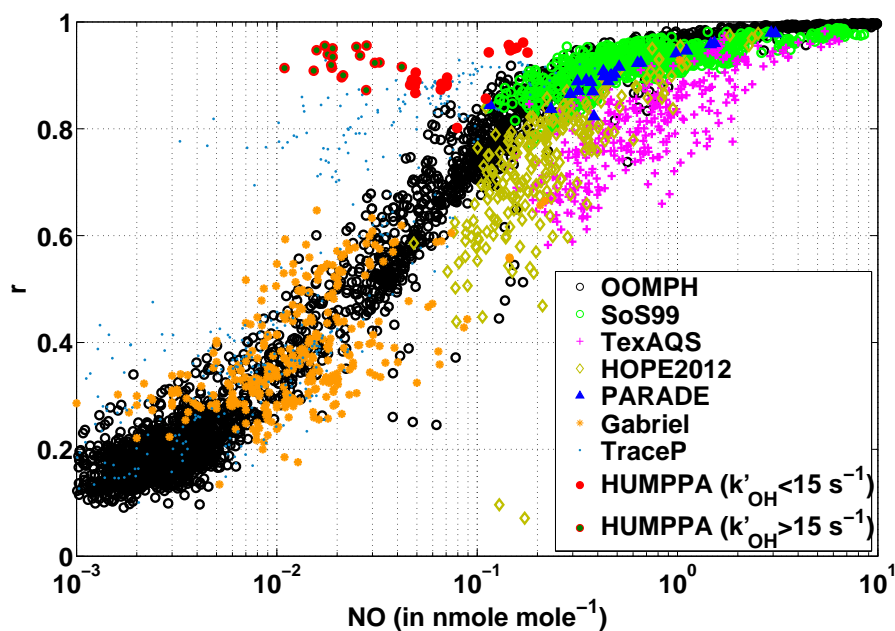
Abbildung 4.11.: OH reycling probability (r) as a function of the ambient NO mixing ratio in different environments. OOMPH – marine boundary layer, ship stack plume; SOS99 – metropolitan, biogenic VOCs; HOPE12 and PARADE – biogenic and anthropogenic VOCs; TexAQS – metropolitan, anthropogenic VOCs; Gabriel – tropical rainforest; Trace-P – east asia and western pacific; HUMPPA–COPEC–2010 – boreal forest.

Nighttime data ($J_{O(^1D)} < 1 \times 10^{-5}\,s^{-1}$) is omitted for this calculation. Data from aircraft campaigns is filtered for observations below 2 km altitude. Measurements in the marine boundary layer (OOMPH[3]) are typically characterized by low NO mixing ratios and low concentrations of biogenic and/or anthropogenic VOCs. However, during the OOMPH ship cruise depending on the wind direction sometimes the chemistry in the stack plume of the

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[3] *Organics over the Ocean Modifying Particles in both Hemispheres.*

ship was observed, rather than uninfluenced air from the marine boundary layer. Therefore, the OOMPH dataset includes also conditions of high NO_x levels. When the emissions from the ship stack plume perturb the chemical system of the marine boundary layer, a strong sensitivity of the recycling probability to the NO_x concentration is observed. The enhanced NO leads to a stronger conversion from HO_2 to OH, finally reaching values of r close to unity for high NO_x levels. Measurements in an environment with enhanced NO levels (NO > $100\,ppt_V$), dominated by biogenic VOC emissions (SOS99[4]) the recycling probability is slightly reduced compared to the observations during OOMPH. Another field campaign at similar NO mixing ratios in an anthropogenically polluted environment (TexAQS[5]) show even lower calculated recycling probabilities, i.e. at the same primary production (P), the secondary production of OH (S) is reduced under the influence of additional VOCs. The reduced S at one NO level is equivalent to a reduced HO_2 concentration due to weaker production and/or enhanced destruction of the hydroperoxyl radicals, caused by the biogenic as well as anthropogenic influences. Measurements in two german forests during HOPE12[6] and PARADE[7] are influenced by biogenic as well as anthropogenic VOC emissions. The resulting recycling probabilities lie in between the observations from SOS99 and TexAQS. At low NO mixing ratios (ppt_V-range) observed above the tropical rainforest during Gabriel[8] the calculated recycling probabilities are similar to the values calculated for the marine boundary layer. However, the recycling probability considering the reactions of HO_2 with NO and O_3 as secondary OH production pathways is not representative for this environment. Direct OH recycling mechanisms, not via HO_2, as proposed for Gabriel (Kubistin et al., 2010; Lelieveld et al., 2008) are not taken into account. Efficient OH recycling in isoprene chemistry of the order of 40 to $80\,\%$ was reported by Lelieveld et al. (2008). Observations from an aircraft campaign over the pacific (Trace-P[9]) are in large part consistent with the results from OOMPH. Nonetheless, for a part of the measurements during Trace-P enhanced recycling probabilities were calculated compared to OOMPH at similar NO levels. This might be caused by two different effects. Higher values of r occure, when the primary production P is not well represented by the reaction of $O(^1D)$ with water vapour, since other primary sources that are not considered are dominant. An additional direct HO_2 source, i.e. not from OH + VOC, would lead to an increase of S and thus, yield elevated r values that do not necessarily represent a pure recycling probability of OH. The enhanced recycling probabilities during Trace-P were observed above the east china sea and the sea of japan, southwest of Korea and Japan, respectively, where enhanced alcyl nitrate concentrations were measured. As already mentioned in Section 4.3 PAN decomposes forming RO_2 radi-

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[4] *Southern Oxidants Study.*

[5] Texas *Air Quality Study*

[6] *HOhenpeissenberg Photochemistry Experiment 2012*

[7] *PArticles and RAdicals: Diel observations of the impact of urban and biogenic Emissions*

[8] *Guyanas Atmosphere-Biosphere Exchange and Radicals Intensive Experiment with the Learjet*

[9] *TRAnsport and Chemical Evolution over the Pacific*

cals. By reaction of these RO_2 species with NO, this radical source can act as a source of HO_2, which is not due to OH. Furthermre, the reaction of alcylperoxy radicals with HO_2 represent an additional OH source. In case of HUMPPA–COPEC–2010 the dataset, separates for moderate and high observed total OH reactivity into two regimes. When moderate conditions prevail ($k'_{OH} \leq 15$), the recycling probabilities are in line with the observations from SOS99, dominated by biogenic VOC emissions that reduce the recycling probability only slightly compared to the results from OOMPH. Under conditions of high observed total OH reactivity ($k'_{OH} > 15$) and lower NO levels enhanced recycling probabilities were calculated compared to OOMPH. This points to a missing primary OH production rate in the calculation, which is important compared to the photolytic production from O_3 and H_2O. Including HONO photolysis and the photolysis of H_2O_2 decreases r. It is also possible that an additional direct HO_2 source, e.g. ozonolysis of terpenes producing RO_2 that are converted by reaction with NO to HO_2, leads to the enhanced recycling probabilities under these conditions.

Recycling probabilities calculated from the observations during HUMPPA–COPEC–2010 considering all known primary and secondary production pathways are in the range $0.7 < r < 0.95$. These high values of r are consistent with the importance of radical recycling in the OH budget.

The recycling probability r can be used to calculate the cycling-lifetime, which is the number of cycles n the OH radicals completed until only $1/e$ of the initial radical concentration remains:

$$n = -\frac{1}{\ln(r)} \tag{4.11}$$

The observed median OH recycling probability of $r = (0.86 \pm 0.05)$ results in typical cycling-lifetimes of about $n = (6.6 + 4.0 / -1.9)$ cycles. Due to their relevance in the observed boreal forest environment, recycling pathways are further investigated by rate calculations based on observations.

4.7. HO$_x$ reycling pathways

Production, loss, and recycling pathways of HO$_x$ above the canopy under various conditions are shown in Table 4.2. Average rates calculated from observations highlight once more the importance of OH recycling via HO_2. Ozonolysis of BVOCs is an important primary radical source at low radiation levels. Photolytic OH production from O_3 as well as HONO photolysis are more relevant primary radical sources during daytime. The contribution of acetone photolysis to HO_2 formation is small at the surface, typically less than $1\,\%$ of the total direct radical sources. The main sink terms are radical self-reactions, particularly $HO_2 + RO_2$. Since RO_2 was not measured during HUMPPA–COPEC–2010, it is estimated from HO_2 steady-state (see Section 4.4). The total OH production, P_{OH}^{total},

is calculated from total OH reactivity data and the hydroxyl radical measurements assuming steady-state (Equations 4.2 & 4.3). The loss rate of OH via reaction with VOCs and oxygenated VOCs (OVOCs) is derived by subtracting the known OH loss rates caused by $CO, O_3, HCHO, H_2O_2, NO_2, NO, SO_2$, and HO_2 from the total loss observed (k'_{OH} [OH]).

The dataset can be grouped by conditions of low and high radiation, and moderate and high observed total OH reactivity. The resulting four cases (see Table 4.2) are described in more detail in the following paragraphs. Associated average tace gas concentrations and variabilities are summarized in Section A, Table A.1.

Assuming steady-state, the total OH production is equal to the product of the measured total OH reactivity and the OH concentration (Equation 4.2, 4.3). Under **daylight** conditions ($J_{O(^1D)} > 3 \times 10^{-6}\,s^{-1}$), at **moderate** observed total **OH reactivity** ($k'_{OH} \leq 15\,s^{-1}$) (Table 4.2, upper left) $L_{OH}^{total} \approx 3.3 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$ is calculated from observations. Primary production of OH radicals is on average $1.2 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$. The reactions of HO_2 with NO ($\chi(NO) \approx 46\,ppt_V$) and O_3 produce about $3.3 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$ OH, which is $73\,\%$ of the known summed OH production. The known OH sources are more than sufficient to close the OH budget. An OH loss rate of about $1.2 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$ is missing under these conditions, which is close to the combined uncertainty of $40\,\%$. OH is directly lost at a rate of $0.1 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$ by radical termination reactions with NO_2, NO, and HO_2. OH reacts with $CO, O_3, HCHO, SO_2$, and H_2O_2 yielding HO_2 radicals at a rate of $0.8 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$. The remaining observed total OH reactivity (equivalent to an average OH loss rate of $2.4 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$) constrains the maximum production of RO_2 from the reaction of OH with VOCs. However, this is only $75\,\%$ of the RO_2 loss rate via reaction with NO, which is the dominant source of HO_2. This indicates a missing RO_2 source. Besides the ozonolysis of unmeasured BVOCs, reservoir species such as PAN, which thermally decompose (showing a strong temperature dependency), could contribute to the missing RO_2 production rate of the order of $1.2 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$. The photolytic HO_2 production by HCHO $+ h\nu$ contributes with a rate of $0.2 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$. Radical-radical termination reactions govern the HO_2 loss (on average about $0.9 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$).

Under conditions of **low radiation** ($J_{O(^1D)} \leq 3 \times 10^{-6}\,s^{-1}$) and **moderate** observed total **OH reactivity** ($k'_{OH} \leq 15\,s^{-1}$) (Table 4.2, upper right) the known primary production of OH radicals is only $0.3 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$. Also, the classical recycling of HO_2 to OH by reaction with NO ($\chi(NO) \approx 3\,ppt_V$) and O_3 is inhibited ($0.9 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$), mainly due to the low NO concentration. Comparison with the derived total production rate (Equation 4.3) reveals a missing fraction of $40\,\%$ ($P_{OH}^{missing} \approx 1 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$). This is in the same order of magnitude of the observed NO_3 production rate of $1 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$. Since the NO_3 concentration always remained below the lower limit of detection its reactivity had to be fast, potentially to some extent producing OH. Also ozonolysis of unmeasured BVOCs could directly produce OH and possibly close the OH budget.

Under **daylight** conditions ($J_{O(^1D)} > 3 \times 10^{-6}\,s^{-1}$), with **high** observed total **OH reactivity** ($k'_{OH} > 15\,s^{-1}$) (Table 4.2, lower left) the primary production of OH radicals is

on average 1.5×10^6 molec. cm^{-3} s^{-1}. Less than 10% of these primary produced OH radicals are directly lost by radical termination reactions with NO$_2$, NO, or HO$_2$, forming acids and H$_2$O. The largest known source of OH is again HO$_2$ recycling by reaction with NO (χ(NO) $\approx$ 28ppt$_V$) and O$_3$ with an average OH production rate of 6.3×10^6 molec. cm^{-3} s^{-1}. However, only about 30% of the total OH production is known. The excess OH reactivity (equivalent to an average OH loss rate of 27×10^6 molec. cm^{-3} s^{-1}) is available for production of RO$_2$ radicals. RO$_2$ radicals react with NO forming HO$_2$ with a yield of about 90%, representing the main source of HO$_2$. In comparison to this, the direct production of HO$_2$ radicals from HCHO photolysis is negligible (0.2×10^6 molec. cm^{-3} s^{-1}). Through the relationship between the RO$_2$ loss (forming HO$_2$) and the potential production rate of RO$_2$ by unaccounted observed total OH reactivity it can be estimated that about 50% of the remaining OH reactivity, equivalent to a rate of 14×10^6 molec. cm^{-3} s^{-1}, is from other processes, e.g. direct OH recycling, not via the reaction of HO$_2$ + NO/O$_3$. Furthermore, an OH production rate of the order of 20×10^6 molec. cm^{-3} s^{-1} is missing, to close the OH budget under these conditions. The reaction of specific alkylperoxy radicals with HO$_2$ could represent an additional RO$_2$ sink and OH source. Laboratory studies investigating the OH production from the reactions of ethyl peroxy, acetyl peroxy, and acetonyl peroxy radicals with HO$_2$ revealed OH yields up to 70% (Thornton et al., 2002; Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008). Assuming that all RO$_2$ species, as an upper limit, would react with HO$_2$ forming OH, this would contribute an additional 10×10^6 molec. cm^{-3} s^{-1} to the OH production. However, this would still not be sufficient to close the OH budget under these conditions of high radiation and high OH reactivity. A direct recycling mechanism, returning OH from RO$_2$ in the absence of NO, by a 1,5-H-shift, was proposed by Peeters et al. (2009) for the OH-initiated degradation of isoprene. A recent chamber study suggests a reduced reaction rate constant by about a factor of two with respect to the value given by Peeters et al. (2009) for this 1,5-H-shift (Fuchs et al., 2013). Nevertheless, at low NO levels (χ(NO) $\approx$ 100 ppt$_V$) these isomerization reactions for isoprene-related RO$_2$ radicals forming OH directly become competitive with the traditional reactions of RO$_2$ with HO$_2$, RO$_2$, and NO. Similarly, other RO$_2$ radicals, specifically all conjugated alkadienes, e.g. myrcene, many mono-cyclic monoterpenes, and also sesquiterpenes, can undergo a fast H-shift isomerization (Peeters et al., 2001; Vereecken et al., 2007, 2012). Monoterpenes and sesquiterpenes have many more pathways to oxidise than isoprene, and the channels that allow for H-migration are therefore a smaller percentage than in isoprene. Still, an OH production rate of the order of 6×10^6 molec. cm^{-3} s^{-1} is missing. A direct OH source or additional RO$_2$ production, balanced by an equivalent loss of RO$_2$ forming OH via mechanisms like the ones mentioned above could close the OH budget.

Similarly, at **low radiation** ($J_{O(^1D)} \leq 3 \times 10^{-6}$ s^{-1}) and **high** observed total **OH reactivity** ($k'_{OH} > 15$ s^{-1}) (Table 4.2, lower right) the known production of OH radicals is on average only about 20% of the total OH production. HO$_2$ reacts with NO (χ(NO) $\approx$ 17ppt$_V$) and O$_3$ producing about 3.9×10^6 molec. cm^{-3} s^{-1} OH, the largest known contribution to P_{OH}^{total}. For the production of RO$_2$ radicals the remaining observed total OH reactivity sug-

gests a rate of 20.6×10^6 molec. $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$. About 7×10^6 molec. $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ of the RO_2 radicals react with NO forming HO_2. An RO_2 loss rate of about 12×10^6 molec. $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ remains, e.g. for direct recycling mechanisms, recycling OH as proposed above, i.e. alkylperoxy radicals reacting with HO_2 and/or H-shift isomerization or similar mechanisms are likely, potentially providing a large fraction of the missing OH production rate of 17×10^6 molec. $\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$.

Tabelle 4.2.: HO_x budget under different conditions of observed radiation (high, left; low, right panels) and total OH reactivity (moderate, upper; high, bottom panels). Radical production (green), recycling (blue), and loss (red) pathways are indicated by bold arrows. All rates are given in $10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$.

	$J_{O(^1D)} > 3 \times 10^{-6}\,\mathrm{s^{-1}}$	$J_{O(^1D)} \le 3 \times 10^{-6}\,\mathrm{s^{-1}}$
$k'_{OH} \le 15\,\mathrm{s^{-1}}$	(diagram)	(diagram)
	• $P_{OH}^{total} = (3.3 \pm 1.4) \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$ • OH budget is almost closed (Missing sink: $1.2 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • 73 % of P_{OH}^{known} by $HO_2 + NO/O_3$ ($P_{OH,HO_2+NO/O_3} \approx 3 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • additional RO_2 source is required e.g. by $VOC + O_3$ and/or decomposition of nitrates, (PAN)	• $P_{OH}^{total} = (2.1 \pm 0.8) \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$ • $HO_2 + NO/O_3$ is inhibited ($P_{OH,HO_2+NO/O_3} \approx 1 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • ~40 % of P_{OH}^{total} is unknown ($P_{OH}^{missing} \approx 1 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • Potential OH sources: - Ozonolysis of unmeasured VOCs - could be related to NO_3 ($P_{NO_3} \approx 1 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$)
$k'_{OH} > 15\,\mathrm{s^{-1}}$	(diagram)	(diagram)
	• $P_{OH}^{total} = (27.7 \pm 9.4) \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$ • ~70 % of P_{OH}^{total} is unknown ($P_{OH}^{missing} \approx 20 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • about 25 % of P_{OH}^{total} by $HO_2 + NO/O_3$ ($P_{OH,HO_2+NO/O_3} \approx 6 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • up to 50 % of the RO_2 production rate imply unknown loss processes that could lead to direct OH recycling	• $P_{OH}^{total} = (21.3 \pm 7.2) \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$ • ~80 % of P_{OH}^{total} is unknown ($P_{OH}^{missing} \approx 17 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • about 16 % of P_{OH}^{total} by $HO_2 + NO/O_3$ ($P_{OH,HO_2+NO/O_3} \approx 4 \times 10^6\,\mathrm{molec.\,cm^{-3}\,s^{-1}}$) • ~60 % of the RO_2 production rate imply unknown loss processes that could lead to direct OH recycling

• RO_2 sink is missing → potential OH source

$\implies$ alkylperoxy radicals $+ HO_2$ (Thornton et al., 2002; Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008) and H-shifts (Peeters et al., 2009) are likely

5. Box model simulations

Numerical models are applied to describe the complex nonlinear chemistry and physical processes in the atmosphere. For short-lived trace gas species, such as radicals, transport and mixing processes that typically occure on larger time-scales can be neglected. Zero-dimensional box models are used to simulate the chemistry disregarding the coupling to physical processes. Despite the chemical reactions, emission and deposition processes are usually represented in these models. In order to analyse the observations during HUMPPA–COPEC–2010, box model simulations using the CAABA/MECCA box model were conducted.

5.1. Box model CAABA/MECCA

To investigate the influence of unmeasured intermediate reaction products, the observations were compared to simulations with version 3.0 of the chemical box model CAABA/MECCA (*C*hemistry *A*s *A B*oxmodel *A*pplication / *M*odule *E*fficiently *C*alculating the *C*hemistry of the *A*tmosphere) by Sander et al. (2011a). The model was constrained with observed, complete 5-minute datasets. Each simulation was terminated when both OH and HO_2 reached steady-state, typically after about 48 hours.

MECCA contains a comprehensive atmospheric chemistry reaction scheme. However, since we focus on organics, we switched off halogen and sulfur chemistry, as well as heterogeneous and aqueous phase reactions. A list of the chemical reactions used in this study, including rate coefficients and references, is available in the appendix (Section B). In the base configuration, version 2 of the isoprene chemistry from the "Mainz Isoprene Mechanism" (MIM2) was used, considering 68 species and 195 reactions (Taraborrelli et al., 2009 based on Pöschl et al., 2000). For sensitivity studies, the recently developed isoprene mechanism MIM3 (Taraborrelli et al., 2012), which includes additions to the isoprene chemistry; such as the photo-oxidation of unsaturated hydroperoxy-aldehydes; and a preliminary version of the monoterpene mechanism MTM (Taraborrelli et al., in preparation) were also used. The latter is based on a MIM2-like version of MIM3 (MIM3*), i.e. hydroperoxy-aldehyde chemistry, H-shifts, and RO_2 + HO_2 reactions are considered the way of MIM2, while updated estimates of rate constants from MIM3 were retained. Furthermore, it has a representation for the oxidation of the major terpenes during HUMPPA–COPEC–2010 that being $\alpha-$pinene, $\beta-$pinene, $\beta-$myrcene, Δ^2-carene, Δ^3-carene, and $\alpha-$farnesene chemistry. The oxidation

of the first two monoterpenes is taken from the MCM[10], with updates based on recent literature. Carene is assumed to yield the same products as $\alpha-$pinene. Finally the oxidation of $\beta-$myrcene and $\alpha-$farnesene is simplified and partially follows an isoprene-like oxidation. Deposition was included for the species listed in Table 5.1, according to values given in literature or derived from measurements. For the numerical integration of the resulting set of ordinary differential equations (ODEs), the KPP software (Sandu and Sander, 2006) with a positive definite Rosenbrock solver and automatic time-step control was used. For the photolysis frequencies of NO_2 and $O(^1D)$, measured values (as described above) were used. Photolysis frequencies for other observed photolabile species are calculated based on measured $J_{O(^1D)}$ and J_{NO_2} and will be presented in a separate publication by B. Bohn et al. Therefore effects of cloud coverage and aerosols are considered implicitly. In case of missing methane (CH_4) data, box model simulations were conducted using the median value of CH_4 observed, $1.79\,\mu mol\,mol^{-1}$. The 1σ variability in CH_4 measurements during the entire campaign was $0.03\,\mu mol\,mol^{-1}$. Measured photolysis frequencies below the lower limit of detection were set to zero, which affects the derived photolysis frequencies from other species accordingly. The uncertainty of simulated HO_x caused by these assumptions is less than $10\,\%$. Datasets missing any other of the species used as model input were omitted from this study. An overview of the data availability and the resulting model input datasets are shown in Figure 5.1.
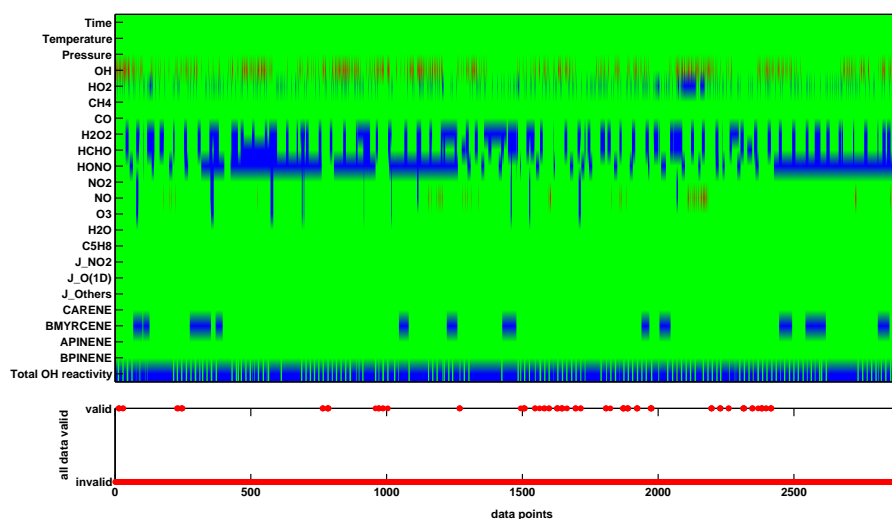
Abbildung 5.1.: Data availability for model simulations:
OK (green), missing (blue), negative (red).

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[10]Master Chemical Mechanism, MCM v3.2

Tabelle 5.1.: Deposition rates/velocities used in the model

Species	v_D (cm s^{-1})	Deposition rate (s^{-1})	Reference
O$_3$	0.56	-	mean value derived from measurements during HUMPPA–COPEC–2010
NO	0.44	-	Evans et al. (2000)
NO$_2$	0.44	-	Evans et al. (2000)
HCHO	0.50	-	Evans et al. (2000)
HNO$_3$, org. nitrates	3.50	-	Evans et al. (2000)
PAN	0.29	-	Evans et al. (2000)
H$_2$O$_2$, org. peroxides	-	4×10^{-5}	estimated by best fit of calculated to measured H$_2$O$_2$ mixing ratio

5.1.1. Significance and sensitivity

The significance of the discrepancies between observed and simulated HO$_x$ concentrations depends on the uncertainty of the HO$_x$ measurements as well as on the uncertainty of the model simulation. The latter comprises the uncertainties of all measured input variables such as trace gas concentrations and meteorological parameters as well as the uncertainties due to the chemical mechanism applied. Sensitivity analysis on measured species by varying constraint parameters within their uncertainty can be used to identify the impact on the model result. In the case of unmeasured species, e.g. oxidation products and intermediates, the uncertainties depend on the uncertainty of their production and destruction pathways as well as the uncertainty of the chemical mechanism. The uncertainties of the simulated OH and HO$_2$ concentrations related to the reaction rate coefficients were estimated by Monte-Carlo simulations as described by Sander et al. (2011a). Each Monte-Carlo simulation consists of 9999 model runs using a slightly different set of reaction rate coefficients for the individual runs. Different sets of rate coefficients are achieved by multiplying the original reaction rate coefficients from literature with a random uncertainty factor distributed around one and scaled on the uncertainty of the measured or estimated rate coefficient. This value

can usually be found in publications of laboratory studies or summaries like the JPL or Atkinson evaluation (Sander et al., 2011b; Atkinson et al., 2006). If no value from literature is available a relative uncertainty of 25 % is assumed, which corresponds to a scaling factor of 1.25 (Sander et al., 2011a). The result of one Monte-Carlo simulation in case of OH applying the isoprene mechanism (MIM2) is shown as an example in Figure 5.2. The histogram shows a binned frequency distribution of the model OH resulting from the individual Monte-Carlo runs, simulated with diverse sets of rate coefficients. This yields a 1σ-uncertainty of the simulated OH resulting from the uncertainty of rate coefficients of 15%.
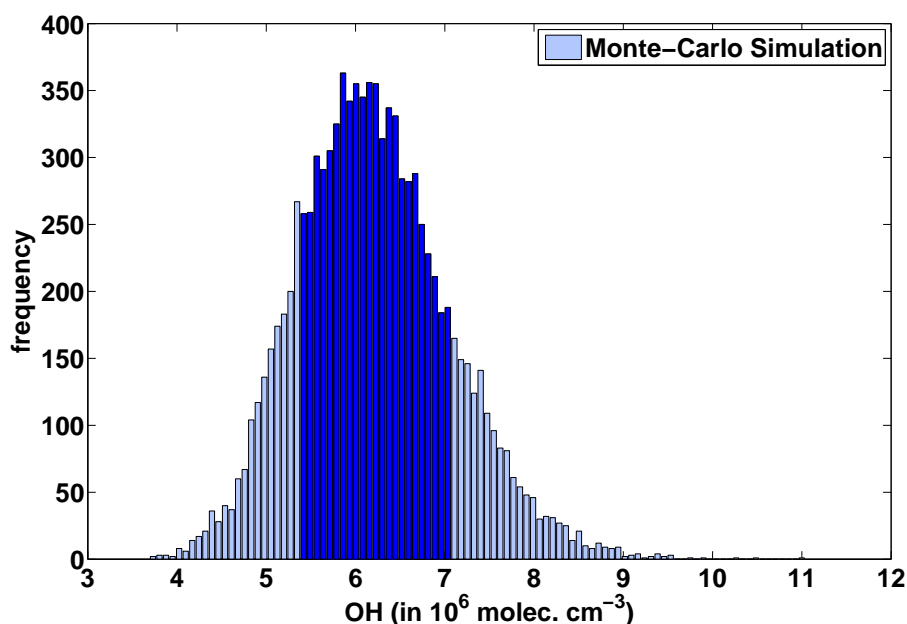
Abbildung 5.2.: Histogram of the Monte-Carlo simulation ($N = 9999$) for the reaction rate coefficients on a single dataset in the early afternoon above canopy. The resulting distribution shows a slight skewness with a median of $6.15 \times 10^6 \mathrm{molec.\, cm^{-3}}$ and a mean of $(6.21 \pm 0.86) \times 10^6 \mathrm{molec.\, cm^{-3}}$. The dark blue bars indicate the $\pm 1\sigma$ range.

5.2. HO$_\text{x}$ simulations using CAABA/MECCA

The discussion of the observations in Section 4 indicates, that under conditions of low reactivity and high radiation, recycling of OH in this environment occurs mainly by HO$_2$. In order to identify the influence of unmeasured oxidation products on the HO$_\text{x}$ budget and to examine the current understanding of the underlying processes box model simulations have been conducted.

The CAABA/MECCA box model was applied in steady-state mode with concentrations of NO, CO, O$_3$, H$_2$O$_2$, organic peroxides, isoprene (C$_5$H$_8$), terpenes, HONO, HCHO, and H$_2$O as well as photolysis frequencies constrained to measured values. Simulations were only done when data of all key constraints were available (see Section 5.1).

Applying the chemistry scheme from the "Mainz Isoprene Mechanism" (MIM2), OH concentrations are overestimated by the model by about 40% on average (Figure 5.3). HO$_2$ is underestimated in the simulation. The model-measurement discrepancy can be divided into two groups: The ratio of simulated to observed HO$_2$ concentrations is about 0.7 for a minor part of the dataset, while the simulation significantly underestimates the observed total OH reactivity for the rest of the dataset. The ratio between simulated and observed HO$_2$ concentrations in this case is only about 0.3. A recently published chemical reaction scheme (MIM3) including new additions to the isoprene chemistry, such as the photo-oxidation of unsaturated hydroperoxy-aldehydes (Taraborrelli et al., 2012), produces even more hydroxyl radicals leading to an overestimation by a factor of up to three in the simulation as compared to the observations. The ratio between simulated and observed hydroperoxyl radicals increases to HO$_2$$^{mod.}$/HO$_2$$^{obs.}$=0.6 on average, still separating into two regimes with a minor part of the dataset showing a ratio of HO$_2$$^{mod.}$/HO$_2$$^{obs.}$=1.5, while most of the data shows a ratio of HO$_2$$^{mod.}$/HO$_2$$^{obs.}$=0.6.

Since isoprene was not the predominant biogenic VOC during HUMPPA–COPEC–2010, contributing less than 10% to the total OH reactivity measured, the terpene mechnism MTM was added to the chemistry mechanism. Inclusion of terpene chemistry helped to reproduce the OH reasonably in the simulation (Figure 5.4). The ratio between simulated and observed HO$_2$ slightly increased compared to the isoprene chemistry reference run, but still separates into two regimes. At lower observed HO$_2$ levels, a ratio of up to HO$_2$$^{mod.}$/HO$_2$$^{obs.}$=0.8 is reached for a minor fraction of the dataset. Only about 30% of the observed HO$_2$ concentration can be reproduced by the model on average, when the simulated total OH reactivity does not match the observed reactivity.

The underprediction of HO$_2$, when OH reactivity is missing in the model while OH is reproduced accurately, indicates that the missing reactivity is an unaccounted source of HO$_2$. Furthermore, the recycling reaction of NO and O$_3$ with the missing HO$_2$ has the potential under most conditions to compensate for the additional OH loss, which has not been considered yet. This preserves the good agreement of simulated and observed OH even when the model accounts for all the observed total OH reactivity.
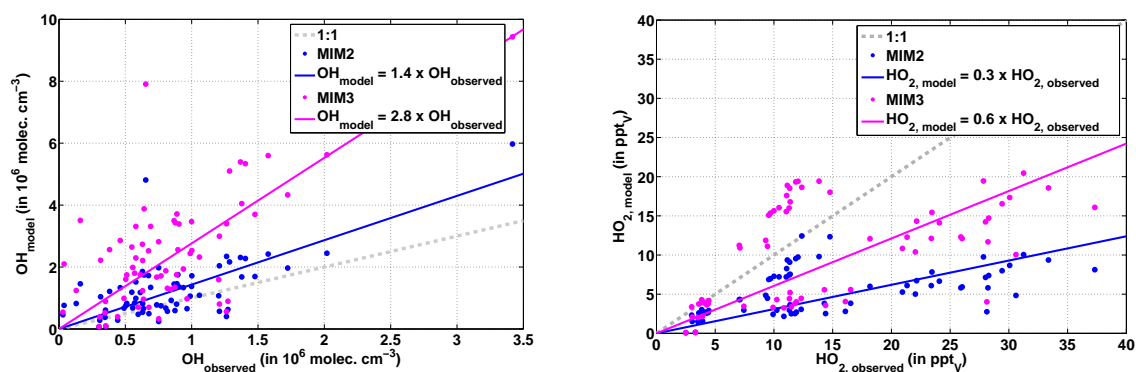
Abbildung 5.3.: Simulated vs. observed OH concentrations and HO_2 mixing ratios, applying the MIM2 chemistry scheme and the recently proposed MIM3 including new additions in the isoprene chemistry.
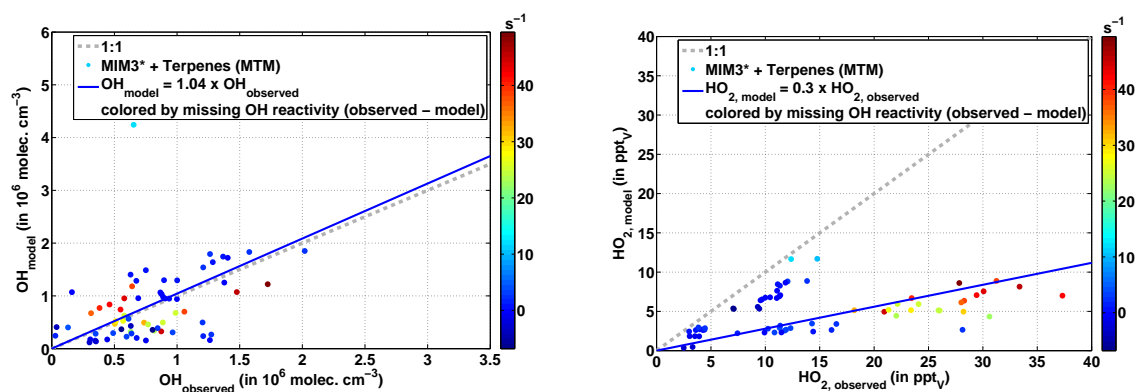
Abbildung 5.4.: Inclusion of the terpene mechanism MTM. HO_2 is still underpredicted in cases when the model reactivity does not match the measured reactivity. This indicates that the missing reactivity is an unaccounted source of HO_2. The OH is reproduced reasonably well, suggesting that the missing source of OH due to the underpredicted HO_2 is compensated by the missing OH reactivity in the simulation.

However, when high total OH reactivities ($> 20 \, \mathrm{s}^{-1}$) were observed, the enhanced HO$_2$ recycling is not sufficient to reproduce the observed OH. Additional mechanisms, e.g. direct OH recycling as discussed for isoprene-dominated, low-NO$_x$ environments, or an additional primary source of OH is required to explain the observed hydroxyl radical concentrations under these conditions.

5.2.1. OH loss tuning

To investigate the hypothesis that the OH reactivity missing in the model using the terpene mechanism acts as a source of HO$_2$, additional reactivity towards OH was introduced by adding the surrogate molecule X which behaves chemically identically to $\alpha-$pinene and its concentration was iteratively tuned for each dataset in such a way that the total OH reactivity in the model agreed with the observed OH reactivity. To match the observed total OH reactivity, up to $3 \, \mathrm{ppb_V}$ of X (typically a factor of 5 to 10 times the measured $\alpha-$pinene) had to be added. Tuning the simulation to the observed total OH reactivity improves the HO$_2$ agreement slightly (HO$_2{}^{mod.}$/HO$_2{}^{obs.}$=0.4), as shown in Figure 5.5. The production of OH from the additional HO$_2$, however, is not sufficient to compensate for the enhanced reactivity in the model, leading to underprediction of hydroxyl radicals in the simulation. The unaccounted OH reactivity in the simulation might still be linked to the missing source of HO$_2$, nevertheless, this shows that $\alpha-$pinene-like chemistry for the compound X does not suffice to provide this connection. A direct HO$_2$/RO$_2$ source like decomposition of transported PAN, which is not represented in the box model simulation, could explain the underprediction of HO$_2$, independent of the unaccounted OH reactivity in the simulation.

5.2.2. Significance and uncertainties

To quantify the significance of model-measurement discrepancies the uncertainties in both, observations and simulations, have to be considered. The uncertainties of HO$_x$ measurements are listed in Table 4.1. The uncertainties of simulated HO$_x$ related to the reaction rate coefficients were determined via Monte-Carlo simulations as described in Section 5.1.1. Monte-Carlo-Analysis using the terpene mechanism yields uncertainties of 14 % and 11 % for the simulated OH and HO$_2$, respectively. Measured and simulated HO$_x$ concentrations including their 1σ-uncertainties are compared in Figure 5.6. Modelled and observed OH within their uncertainties partly agree within a factor of two. Significant discrepancies by more than a factor of two are present for a minor part of the dataset (22 %). For HO$_2$ the underestimation by more than a factor of two in the model is significant for a large part of the dataset (52 %).

The uncertainties in observed trace gas species and photolysis frequencies used to constrain the model can also have a direct impact on the uncertainty of simulated HO$_x$. Even
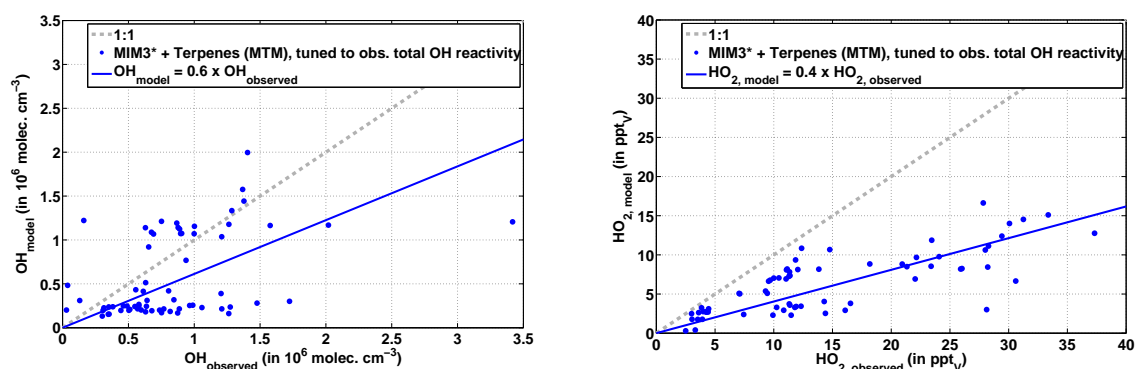
Abbildung 5.5.: Tuning the model to the observed total OH reactivity by introducing an additional $\alpha-$pinene equivalent slightly improves the HO_2 agreement. The production of OH from the additional HO_2 is not sufficient to compensate for the enhanced reactivity in the model.

less obviously these parameters which are kept fixed at the observed values within the simulation, influence the abundance of unmeasured trace gases and intermediate products, therefore also showing an indirect effect on the resulting calculation of HO_x concentrations. Sensitivity studies were conducted by varying the observed trace gas concentrations separately by a factor between 0.5-10 to investigate the overall influence on the simulated HO_x (Table 5.2) with the terpene mechanism.

Substances relevant for primary production of HO_x show the highest impact in this sensitivity study. Doubling the O_3 or water vapour concentration leads to about 25 % increase in simulated OH and about 15 % enhanced HO_2. An even larger effect (OH: +37 %, HO_2: + 26 %) is found for photolysis elevated by a factor of two. Constraining the model with twice the amount of NO observed causes 24 % more hydroxyl radicals in the simulation. The simulated HO_2 decreases by 23 %. Reducing the CO concentration by a factor of two leads to a 8 % increase in simulated OH and a 8 % decrease in simulated HO_2 while doubling the observed CO yields a 13 % decrease in OH and a 13 % increase in HO_2. Doubling formaldehyde or H_2O_2 only has a minor influence on the simulated HO_x. Changing the deposition rates by a factor of two causes at most a 12 % change in HO_x. None of these input parameter variations yield a change in OH and/or HO_2 of a factor of two or more. All photolysis frequencies multiplied by a factor of ten could cause such changes in simulated HO_x. Unless the uncertainties of the species used to constrain the simulation (Table 4.1) exceed the variation intervals, these uncertainties individually can neither explain the discrepancies between observation and modelled HO_2, nor cause a significant disagreement for OH.
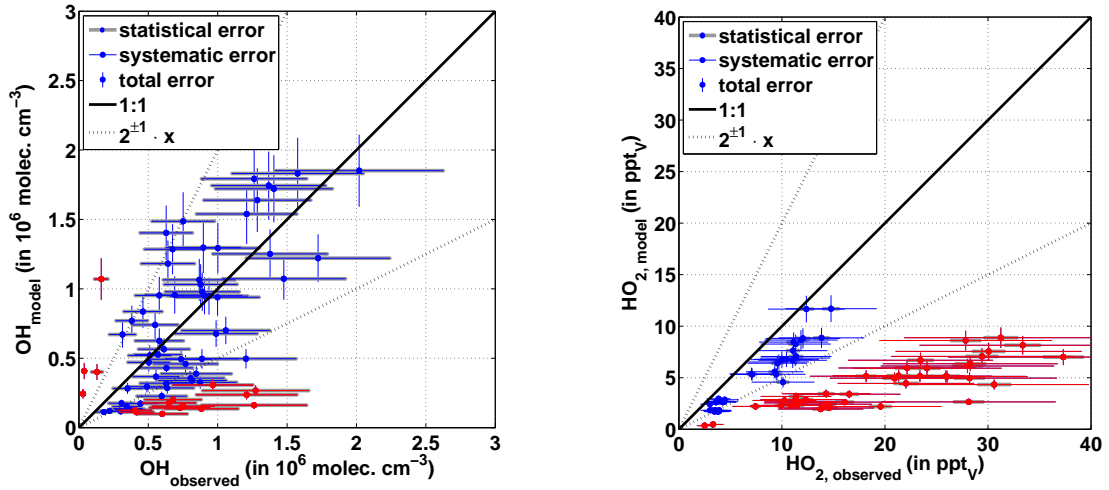
Abbildung 5.6.: Uncertainties of HO$_x$ simulations (using the terpene mechanism) with respect to measurement uncertainties. The solid line represents the 1:1 ratio of observed and simulated HO$_x$. Data points showing significant discrepancies within their uncertainties by more than a factor of $2^{\pm 1}$ (dashed lines) are shown in red.

Free running HCHO, i.e. not constraining the simulation to the HCHO observations, leads to enhanced OH and HO$_2$ concentrations (up to 30 %), which is for a minor part of the dataset sufficient to produce good agreement between measured and simulated HO$_2$, while OH is overestimated in these simulations. Formaldehyde concentrations in the free running model are up to four times higher than observed levels. This suggests a formaldehyde sink not represented in the box model, possibly due to transport processes or uptake by plants (Lowe and Schmidt, 1983; Benning and Wahner, 1998). However, it was shown that changes in the deposition velocity have only a small impact on the simulated HO$_x$. The overprediction of formaldehyde in this case is more likely due to inadequate representation of the HCHO sources in the simulation. Another sensitivity simulation by also constraining the model to estimated 2-methyl-3-buten-2-ol (MBO) concentrations was conducted. Unfortunately, MBO, which is often referred to as "the isoprene of coniferous forests" was not directly measured during HUMPPA–COPEC–2010, though PTR-MS measurements of isoprene were affected by an MBO interference, as described in section 4.1. Previous measurements in this forest showed that MBO accounts only for 1-3 % of the total monoterpene emission rate (Tarvainen et al., 2005). In American pine forests it can be more important. However, the

Tabelle 5.2.: Sensitivity analysis with respect to changes in observed, model constraining parameters. The values presented refer to a dataset around local solar noon (1pm in UTC+2).

	OH		HO$_2$	
	(molec. cm^{-3})	mod/mod$_{\text{reference}}$	(molec. cm^{-3})	mod/mod$_{\text{reference}}$
Observation	$3.42{\times}10^6$		$3.63{\times}10^8$	
Reference simulation	$5.20{\times}10^6$	1	$2.87{\times}10^8$	1
2x NO	$6.47\ {\times}10^6$	1.24	$2.22\ {\times}10^8$	0.77
2x O$_3$	$6.42\ {\times}10^6$	1.23	$3.32\ {\times}10^8$	1.16
2x H$_2$O	$6.62\ {\times}10^6$	1.27	$3.31\ {\times}10^8$	1.15
0.5x CO	$5.63\ {\times}10^6$	1.08	$2.65\ {\times}10^8$	0.92
2x CO	$4.55\ {\times}10^6$	0.88	$3.23\ {\times}10^8$	1.13
2x H$_2$O$_2$	$5.27\ {\times}10^6$	1.01	$2.92\ {\times}10^8$	1.02
2x HCHO	$5.30\ {\times}10^6$	1.02	$3.07\ {\times}10^8$	1.07
0.5x deposition	$5.59{\times}10^6$	1.08	$3.17{\times}10^8$	1.10
2x deposition	$5.83{\times}10^6$	1.12	$3.12{\times}10^8$	1.09
2x photolysis	$7.11\ {\times}10^6$	1.37	$3.63\ {\times}10^8$	1.26
10x photolysis	$1.77\ {\times}10^7$	3.40	$6.88\ {\times}10^8$	2.40

PTR-MS signal was used as an upper limit estimate of MBO for this simulation to investigate the influence on the simulated HO$_x$. This MBO causes, on average, about $0.5\,\text{s}^{-1}$ additional reactivity towards OH, similar to the reactivity by methane. Only about 20 % of the observed HO$_2$ can be explained by the model and the observed OH is underpredicted by 40-60 % in this simulation. Considering the results from the above mentioned sensitivity tests and significance analysis, the discrepancy between measured and simulated HO$_2$ is significant, thus, the chemical mechanism applied in the simulations needs further improvement to reproduce the HO$_2$ for the observed boreal forest environment.

5.2.3. Sources and sinks of HO$_x$

The production rates of the hydroxyl radical in the box model using the terpene mechanism are shown in Figure 5.7, with respect to their contribution to the total OH production derived from measurements. The dataset is again grouped by conditions of different radiation and total OH reactivity (see Table 4.2). When the total OH reactivity is high ($k'_{OH} > 15\,\mathrm{s}^{-1}$), the total production rate of hydroxyl radicals in the simulation accounts only for about 10 % of the observed production. This is mainly due to the strong underestimation of HO$_2$ by the model under these conditions (see Sections 4.4 & 4.7). Photolytic production accounts for one third of the OH formation in the simulation. A similar contribution is found by HO$_2$ recycling via reaction with NO and O$_3$. Ozonolysis of BVOCs and a minor contribution by other species produced in the model account for the remaining OH production. At lower radiation ($J_{O(^1D)} \leq 3 \times 10^{-6}\,\mathrm{s}^{-1}$), the ozonolysis of BVOCs becomes relatively more important and the recycling reaction of HO$_2$ with O$_3$ more relevant in comparison to the reaction with NO. Under conditions of moderate total OH reactivity ($k'_{OH} \leq 15\,\mathrm{s}^{-1}$) and low radiation ($J_{O(^1D)} \leq 3 \times 10^{-6}\,\mathrm{s}^{-1}$) about 33 % of the observed total OH production is represented by the box model simulation. Ozonolysis of observed biogenic VOCs accounts for on average 15 % of the total production rate. Even though the hydroxyl radical production rates due to recycling of HO$_2$ via the reactions with NO and O$_3$ are based on the underestimated HO$_2$ by the box model, they are relevant source terms contributing 13 % to the total OH production. Photolytic sources and production due to other species play a minor role. By assuming observed rather than model calculated HO$_2$, this contribution would increase to 30%.

Almost one quarter of the OH during periods characterized by high radiation values ($J_{O(^1D)} > 3 \times 10^{-6}\,\mathrm{s}^{-1}$) and moderate total OH reactivity ($k'_{OH} \leq 15\,\mathrm{s}^{-1}$) is produced by photolytic sources. Ozonolysis of BVOCs and other sources in the simulation contribute 4 % each to the total observed OH production. HO$_2$ recycling via NO dominates the OH production (37 %). Nonetheless, about 30 % of the total OH observed production is not represented in the simulation, due to the underestimation of HO$_2$ and the associated recycling pathways.

OH reactivity contributions calculated from individually measured compounds compared to directly measured OH reactivity revealed 58 % missing OH reactivity under "normal" boreal conditions and up to about 90 % under "stressed" boreal conditions (i.e. prolonged high temperature) during HUMPPA–COPEC–2010 (Nölscher et al., 2012). About 50 % of missing OH reactivity was reported from the same site during summer in 2008 by Sinha et al. (2010) when more typical boreal conditions at lower temperatures than in 2010 prevailed. The loss of OH in terms of OH reactivity in the simulation is presented in Figure 5.8. Similar to the findings of another modeling study based on different measurements conducted at the field station SMEAR II (Mogensen et al., 2011), the inorganic contribution (CO, O$_3$, H$_2$, H$_2$O$_2$, NO, NO$_2$, HO$_2$, and HONO) is significant (15 %). A large sink for OH is due to organic compounds, most importantly monoterpenes (5 %), methane (4 %), and
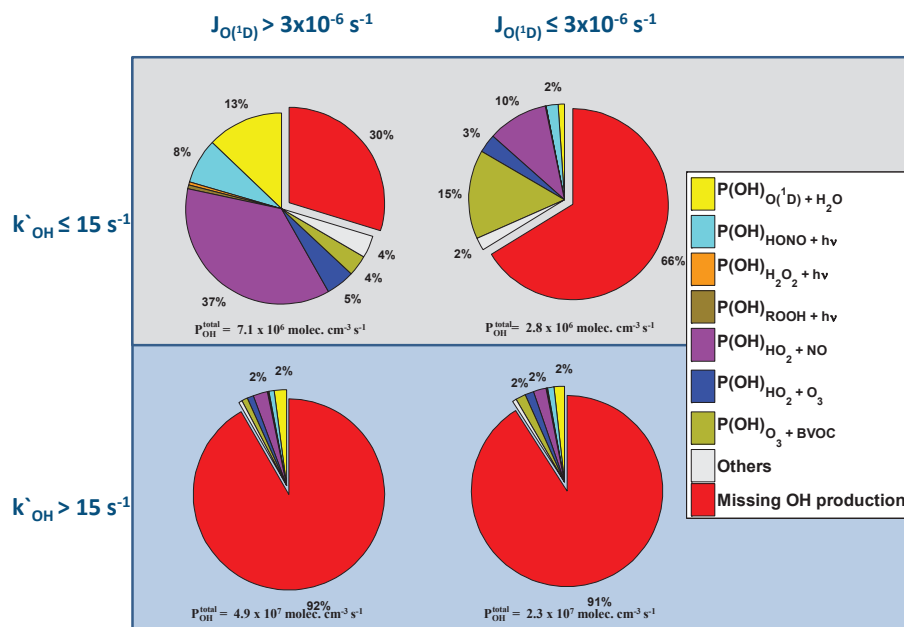
Abbildung 5.7.: Simulated contributions to the OH production during HUMPPA–COPEC–2010. Partitioning at different conditions of radiation and observed total OH reactivity with respect to the total OH production derived from measured OH concentrations and the total OH reactivity.

isoprene (2 %). In contrast to the study by Mogensen et al. (2011), second and higher order organic reaction products by the model contribute an additional 42 % to the total OH reactivity. On average, almost one third of the observed total OH reactivity remains unexplained. The large contribution by second and higher order organic reaction products in the model is mainly caused by aldehydes coming from monoterpene oxidation (~ 30 %) and secondary products of isoprene oxidation (MVK + MACR ~ 4 %). Primary biogenic emissions, e.g. unmeasured monoterpenes and sesquiterpenes, photooxidation products, as well as anthropogenic pollutants occasionally transported to the measurement site are likely candidates causing the "missing" fraction of total OH reactivity.

HO_2 radicals are lost by reaction with other radicals as well as recycled towards OH by reaction with NO and O_3 (Figure 5.9). The biggest contribution to the loss of HO_2 under all conditions is the reaction with nitrogen dioxide yielding peroxynitric acid (HNO_4).
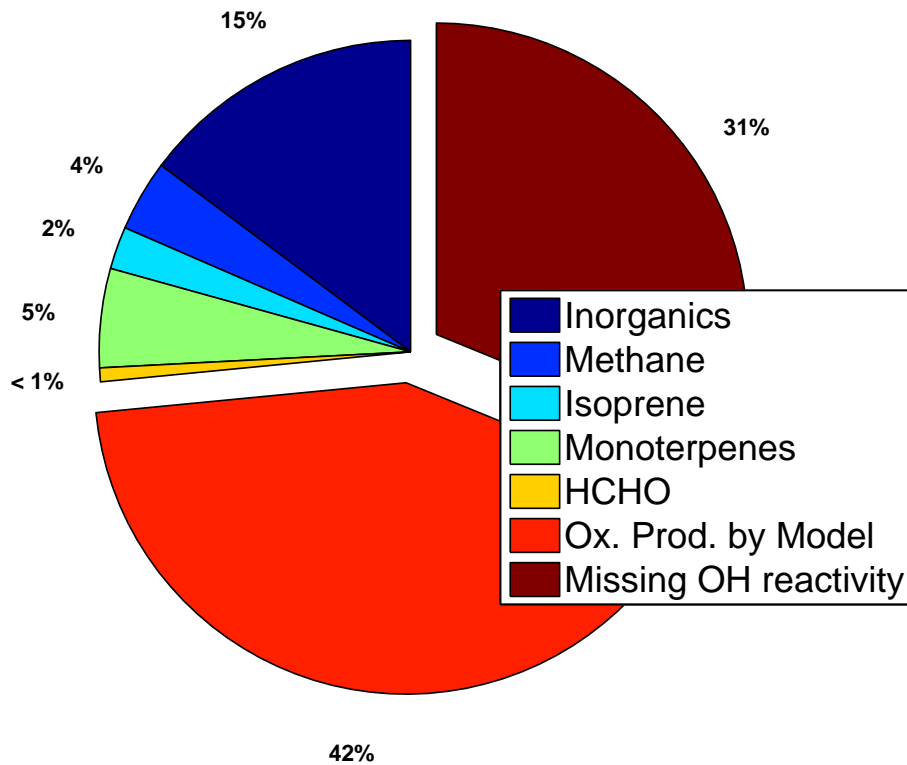
Abbildung 5.8.: Simulated contributions to the observed total OH reactivity during HUMPPA–COPEC–2010.

However, under standard conditions, HNO_4 is rather unstable and decomposes typically within a few seconds. This creates an equilibrium between HNO_4 and $HO_2 + NO_2$ which is strongly temperature dependent (Dentener et al., 2002). In the simulation the production and decomposition of HNO_4 occur at the same rate, thus HNO_4 acts as a reservoir species for the hydroperoxyl radicals.

At conditions of low radiation ($J_{O(^1D)} \leq 3 \times 10^{-6}\,\mathrm{s}^{-1}$) hydroperoxyl radicals reacting with RO_2 and HO_x contribute to the total loss of HO_2 in a similar amount as the recycling reactions with NO and O_3. This is still the case at conditions of enhanced observed OH reactivity and low radiation. The higher absolute HO_2 loss is caused by enhanced recycling as well as enhanced loss by radical-radical reactions.

At high photolysis frequencies ($J_{O(^1D)} > 3 \times 10^{-6}\,\mathrm{s}^{-1}$) both the total HO_2 production and loss increase by about a factor of two compared to nighttime. The HO_2 loss contribu-

tion from the recycling reaction with NO is predominant (41 %) at a total OH reactivity $k'_{OH} \leq 15\,s^{-1}$. This is followed by the reaction with RO_2 contributing about 12 %. Other reactions, e.g. $HO_2 + NO_3$ or $HO_2 + HO_x$, contribute only a few percent. When the total OH reactivity is high, $k'_{OH} > 15\,s^{-1}$, the OH recycling reaction of HO_2 with NO becomes less important (23 %) in the simulation, whereas the reaction with RO_2 contributes about 20 % to the total HO_2 loss. In addition to HNO_4 decomposition, the reaction of OH with carbon monoxide and the reaction of RO_2 with NO are the main sources of HO_2 in the model. The photolysis of formaldehyde contributes less than 1 % to the total HO_2 production under all conditions. Ozonolysis of monoterpenes yields up to 8 % when photolysis is low but is rather unimportant at higher J-values. OH reactions with O_3, HCHO, and H_2O_2 are minor contributors (typically in total about 4 %) in HO_2 production. Differences between conditions of moderate and high total OH reactivity show up in the reactions of OH + CO and RO_2 + NO, forming HO_2. The absolute HO_2 production under conditions of enhanced radiation and high observed total OH reactivity is smaller compared to the case with enhanced radiation and moderate total OH reactivity. Under these conditions, the simulation underestimates the observed HO_2 most, indicating that important species and HO_2 production pathways are missing in the chemical mechanism, very likely including unmeasured BVOCs and their oxidation products. Unfortunately, there were no direct observations of RO_2 during HUMPPA–COPEC–2010. Thus, we are lacking the possibility to constrain the model by RO_2 observations, which would improve our understanding of the underlying processes. The hydroperoxyl radical as well as organic peroxy radicals play an important role in the production of ozone. Ozone is mainly formed and destroyed in the photochemical cycle of NO and NO_2:

$$NO_2 + h\nu \longrightarrow NO + O(^3P) \tag{R5.1}$$

$$O(^3P) + O_2 \xrightarrow{+M} O_3 \tag{R5.2}$$

$$O_3 + NO \longrightarrow NO_2 + O_2 \tag{R5.3}$$

For O_3 Reactions R5.1 - R5.3 represent a "null-cycle", i.e. net ozone production and destruction is zero. However, NO is also consumed in the reaction with peroxy radicals (see Reactions R2.23 & R2.31). Thus, NO_2 is formed without consumption of O_3, leading to a net ozone production in the photolysis of NO_2 (Reaction R5.1). Whereas ozone is produced in radical reactions in polluted environments, it is destroyed by radicals in very clean airmasses, when the reaction of HO_2 with O_3 becomes dominant compared to the reaction with NO. The radical mechanism of ozone production is the major O_3 source in the polluted troposphere (Seinfeld and Pandis, 2006). Therefore, the underestimation of HO_2 in the box model simulations for HUMPPA–COPEC–2010 has a direct impact on the ozone formation in the observed and other boreal forest environments.
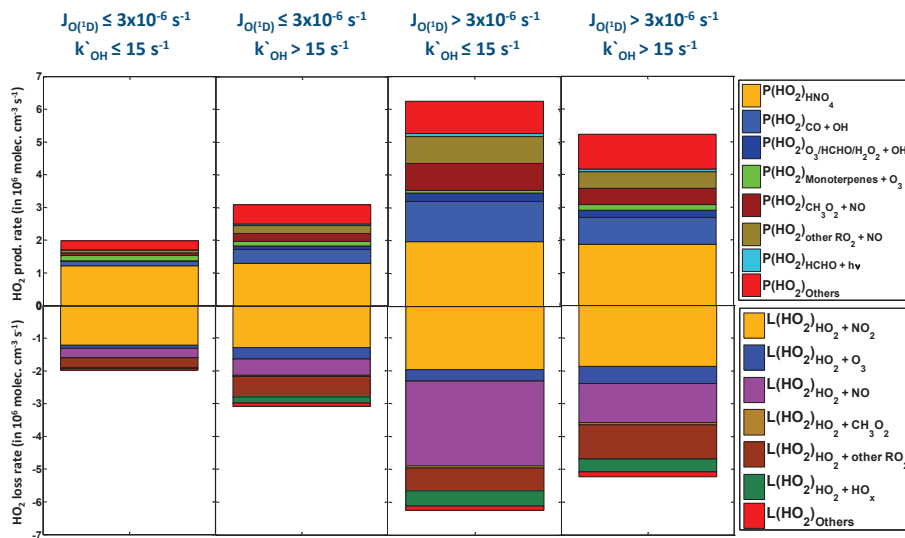
Abbildung 5.9.: Simulated production and loss rates of HO$_2$ during HUMPPA–COPEC–2010 under conditions of different radiation and total observed OH reactivity.

6. Summary and conclusions

Recent efforts to model HO_x concentrations in forest environments characterized by high concentrations of BVOCs and low concentrations of NO_x revealed serious discrepancies with observations of OH and HO_2 (Tan et al., 2001; Lelieveld et al., 2008; Kubistin et al., 2010; Martinez et al., 2010; Pugh et al., 2010b; Whalley et al., 2011). In contrast to well-known OH recycling pathways via HO_2 by reaction with NO and O_3, various mechanisms recycling OH directly in the absence of NO have been proposed and tested in different studies to improve the understanding of HO_x-chemistry influenced by forest emissions (Paulot et al., 2009; Peeters et al., 2009; Hofzumahaus et al., 2009; Crounse et al., 2011). Griffith et al. (2013) measured OH during two subsequent summers in a deciduous forest in northern Michigan during the PROPHET 2008 and CABINEX 2009 campaigns. The authors found good model-to-measurement agreement during the colder summer of CABINEX 2009 campaign, when lower temperatures led to lower observed mixing ratios of isoprene, its oxidation products MVK and MACR, and formaldehyde. During the warmer summer of PROPHET 2008 the model underestimates the OH concentration in the afternoon. Kim et al. (2013) reported reasonable agreement between observed OH and that from steady-state calculations using observations, particularly measurements of HO_2, in a forest environment dominated by emissions of monoterpenes and MBO. Constrained box model simulations underpredicted the observed HO_2 and OH concentrations significantly in this forest. Mao et al. (2012), addressing the impact of measurement artefacts in LIF measurements, showed reasonable agreement between model predictions and observations using their new "chemical removal method" for detection of OH in a California ponderosa pine forest during the BEARPEX09[11] campaign.

Within the framework of this thesis the HORUS instrument was operated for the first time using the IPI-LIF-FAGE technique to measure OH during HUMPPA–COPEC–2010. To identify possible measurement interferences an instrument intercomparison between the CIMS and HORUS-LIF instruments was conducted at the beginning of the campaign on the ground. The hydroxyl radical measurements by the two independent techniques show generally good agreement. During daytime, OH concentrations up to $3.5 \times 10^6 \, \mathrm{molec.\, cm^{-3}}$ were observed above canopy, a factor of two to three times higher than the measurements on ground. Higher OH concentrations above canopy were driven by higher radiation. There is no evidence for differences in the chemical regime on ground and above the canopy on a timescale comparable to, or less than the timescale of mixing processes.

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[11]BEARPEX09 = Biosphere Effects on AeRosols and Photochemistry EXperiment

Comparison of the calculated total OH production rate with the total loss rate calculated from observed OH concentrations and total OH reactivity measurements showed that the known OH sources are almost sufficient to close the budget above the canopy. Detailed analysis of the radical production, loss, and recycling pathways revealed that OH recycling in the observed boreal forest environment occurs mainly by recycling via HO_2 under conditions of high radiation and moderate observed total OH reactivity ($J_{O(^1D)} > 3 \times 10^{-6}\,s^{-1}$, $k'_{OH} \leq 15\,s^{-1}$). Under conditions of enhanced total OH reactivity ($k'_{OH} > 15\,s^{-1}$) recycling mechanisms of OH, not via reaction of HO_2 with NO/O_3, are likely in addition. Furthermore, a source of HO_2 is missing under these conditions.

During some nights both instruments, CIMS (on ground) and IPI-LIF-FAGE (above canopy), detected significant amounts of OH that cannot be explained by known production rates calculated from observations. The missing OH source during nighttime of the order of $1 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$ could partly be related to NO_3. The NO_3 mixing ratio during HUMPPA–COPEC–2010 was always below the lower limit of detection of the CRD instrument (Rinne et al., 2012). However, it was produced at a rate of up to $1 \times 10^6\,molec.\,cm^{-3}\,s^{-1}$ from the reaction of NO_2 with O_3. RO_2 radicals from NO_3-initiated VOC oxidation potentially undergo isomerization reactions or react with HO_2 as well, forming OH. Thus, NO_3 might, at least under some conditions, contribute to the missing OH source during nighttime. Ozonolysis of unmeasured VOCs is also likely to contribute.

The role of potentially undetected VOCs and oxidation products in the chemistry of HO_x can not be understood from observations alone. Hence, box model simulations have been considered for further investigation. The chemistry of the condensed isoprene mechanism ("Mainz Isoprene Mechanism") is shown to be deficient for the observed monoterpene-dominated boreal forest environment. Isoprene levels of typically less than $200\,ppt_V$ contributed at most $10\,\%$ to the total observed OH reactivity thus leading to an overprediction of OH due to the missing sinks by a factor of up to 3 and HO_2 being significantly underpredicted ($HO_2^{mod.}/HO_2^{obs.}$=0.3). Inclusion of the Mainz Terpene Mechanism (MTM) to account for the reactivity towards OH due to observed terpene species and their oxidation products leads to much better agreement between observed and simulated OH concentrations. However, this is due to two compensating effects. On average about one third of the observed total OH reactivity is not reproduced in the simulation, thus leading to underestimation of the total sink of OH. On the other hand, the production of OH is significantly underestimated due to the underpredicted HO_2 available for recycling by reaction with NO and O_3 which was shown to be an important source of OH by direct calculation from observations. Tuning the simulation on the observed total OH reactivity by adding an unknown compound which behaves like $\alpha-$pinene produced a somewhat better $HO_2^{mod.}/HO_2^{obs.}$ agreement. Nevertheless, the additional HO_2 being recycled towards OH was not sufficient to compensate for the resulting enhanced OH loss. The biggest model-observation discrepancies for HO_2 occured when "missing" OH reactivity was highest. Therefore, this provides evidence that the "missing" OH reactivity in the simulation is a source of HO_2. However, a single terpene following the chemical mechanism of $\alpha-$pinene as described in the preliminary terpene mechanism

cannot account for this alone. Additional RO_2/HO_2 sources that are independent of OH, such as the thermal decomposition of transported peroxyalcyl nitrates and the photolysis of glyoxal, are indicated.

HO_2 being underestimated in simulations for terpene dominated environments implies that the net O_3 production in global model simulations using the state-of-the-art chemical reaction schemes is potentially underestimated in boreal regions.

The OH production in this forest environment seems to be understood reasonably well under moderate total OH reactivity conditions (Table 4.2). In periods of high observed total OH reactivity a source of OH is missing. Only a small fraction of the loss of OH can be explained, even through inclusion of higher order oxidation products by application of a box model. HO_2 is underestimated in simulations, indicating missing BVOCs, which could also account for the missing reactivity in the model. Additional recycling processes of OH, not via HO_2 + NO/O_3 are indicated under conditions of high observed total OH reactivity by detailed analysis of the HO_x budget calculated from observations.

Future observations in forest environments should include RO_2 measurements, that could help constrain simulations better and further improve the understanding of the radical cycling processes in this boreal forest (and elsewhere). Particularly, identification of the fraction of alcyl peroxy radical species that can directly recycle OH by reaction with HO_2 would enable a more detailed analysis of radical recycling processes under conditions of enhanced OH reactivity. Observations of additional HO_2 and RO_2 precursor species, such as glyoxal, PAN, and acetone, would enhance the capabilities to investigate the oxidation capacity. Chemical mechanisms used in simulations need to include a comprehensive representation of the most abundant biogenic VOCs, e.g. in this case monoterpenes and their oxidation chemistry in order to reproduce the radical photochemistry when isoprene is not the predominant BVOC.

A. Measurements of trace gas species and meteorological parameters during HUMPPA-COPEC 2010

Tabelle A.1.: Median levels and variability of relevant trace gases under different conditions of observed radiation and total OH reactivity.

	$J_{O(^1D)} > 3 \times 10^{-6}\,s^{-1}$			$J_{O(^1D)} \leq 3 \times 10^{-6}\,s^{-1}$		
$k'_{OH} \leq 15\,s^{-1}$						
	OH	$\approx$	$(1.0 \pm 0.8) \times 10^6$ molec. cm^{-3}	OH	$\approx$	$(3.8 \pm 3.0) \times 10^5$ molec. cm^{-3}
	HO$_2$	$\approx$	(10 ± 1) ppt$_V$	HO$_2$	$\approx$	(10 ± 6) ppt$_V$
	O$_3$	$\approx$	(33 ± 2) ppb$_V$	O$_3$	$\approx$	(35 ± 7) ppb$_V$
	NO	$\approx$	(46 ± 16) ppt$_V$	NO	$\approx$	(3 ± 39) ppt$_V$
	NO$_2$	$\approx$	(280 ± 40) ppt$_V$	NO$_2$	$\approx$	(570 ± 210) ppt$_V$
	CO	$\approx$	(85 ± 1) ppb$_V$	CO	$\approx$	(96 ± 5) ppb$_V$
	C$_5$H$_8$	$\approx$	(145 ± 30) ppt$_V$	C$_5$H$_8$	$\approx$	(62 ± 65) ppt$_V$
	$\alpha-$pinene	$\approx$	(63 ± 15) ppt$_V$	$\alpha-$pinene	$\approx$	(68 ± 67) ppt$_V$
	$\beta-$pinene	$\approx$	(16 ± 4) ppt$_V$	$\beta-$pinene	$\approx$	(20 ± 17) ppt$_V$
	$\beta-$myrcene	$\approx$	(5 ± 1) ppt$_V$	$\beta-$myrcene	$\approx$	(5 ± 4) ppt$_V$
	Δ^3-carene	$\approx$	(30 ± 8) ppt$_V$	Δ^3-carene	$\approx$	(44 ± 44) ppt$_V$
$k'_{OH} > 15\,s^{-1}$						
	OH	$\approx$	$(6.4 \pm 5.6) \times 10^5$ molec. cm^{-3}	OH	$\approx$	$(6.3 \pm 2.0) \times 10^5$ molec. cm^{-3}
	HO$_2$	$\approx$	(27 ± 2) ppt$_V$	HO$_2$	$\approx$	(22 ± 4) ppt$_V$
	O$_3$	$\approx$	(51 ± 1) ppb$_V$	O$_3$	$\approx$	(51.0 ± 0.3) ppb$_V$
	NO	$\approx$	(28 ± 7) ppt$_V$	NO	$\approx$	(17 ± 5) ppt$_V$
	NO$_2$	$\approx$	(320 ± 20) ppt$_V$	NO$_2$	$\approx$	(290 ± 30) ppt$_V$
	CO	$\approx$	(93 ± 1) ppb$_V$	CO	$\approx$	(92 ± 1) ppb$_V$
	C$_5$H$_8$	$\approx$	(112 ± 13) ppt$_V$	C$_5$H$_8$	$\approx$	(110 ± 5) ppt$_V$
	$\alpha-$pinene	$\approx$	(80 ± 4) ppt$_V$	$\alpha-$pinene	$\approx$	(61 ± 8) ppt$_V$
	$\beta-$pinene	$\approx$	(17 ± 1) ppt$_V$	$\beta-$pinene	$\approx$	(14 ± 1) ppt$_V$
	$\beta-$myrcene	$\approx$	(5.0 ± 0.3) ppt$_V$	$\beta-$myrcene	$\approx$	(4.0 ± 0.5) ppt$_V$
	Δ^3-carene	$\approx$	(38 ± 2) ppt$_V$	Δ^3-carene	$\approx$	(27 ± 5) ppt$_V$
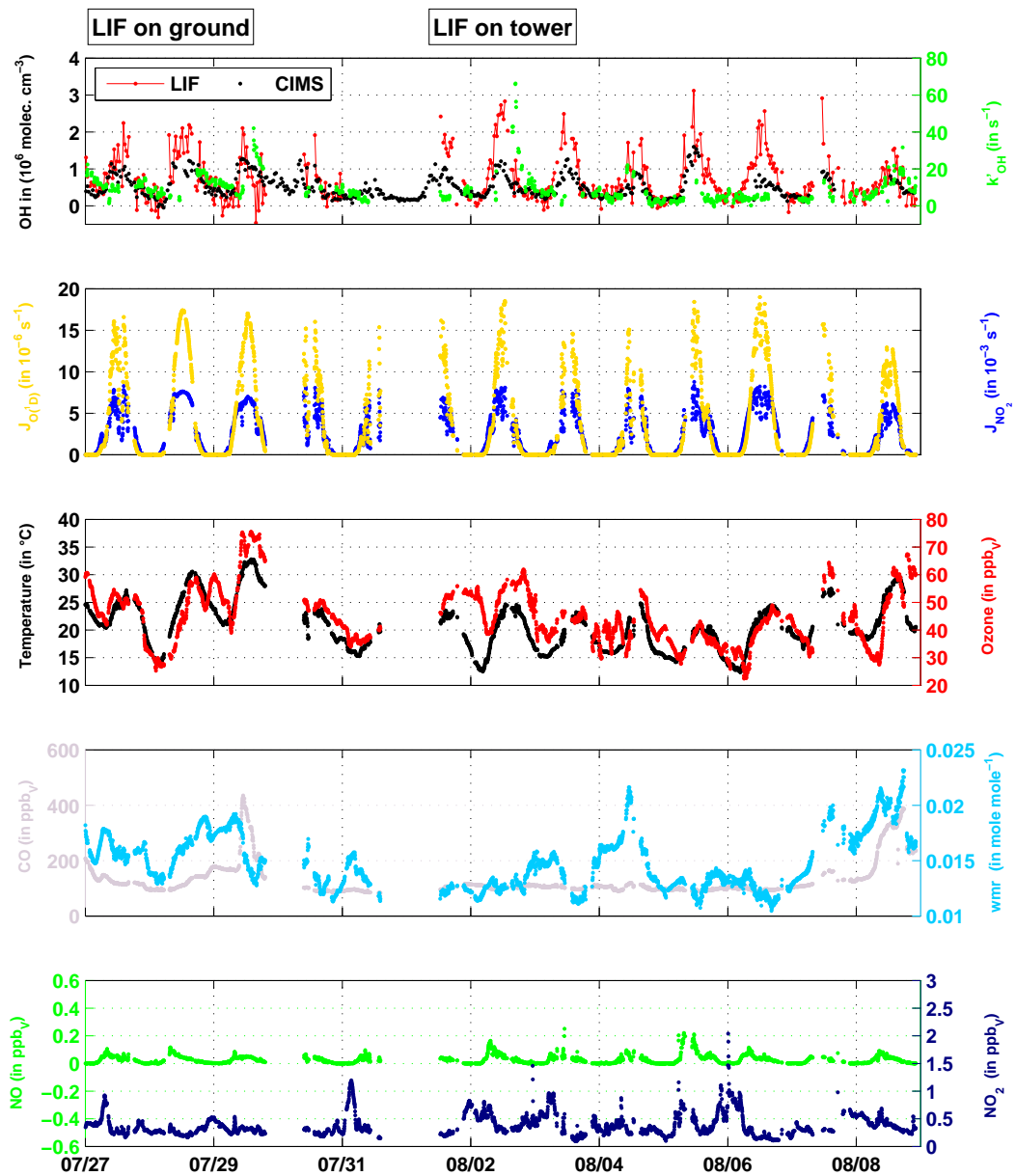
Abbildung A.1.: Timeseries of trace gas species and meteorological parameters during HUMPPA–COPEC–2010.

Abbildung A.1.: (continued): Timeseries of trace gas species and meteorological parameters during HUMPPA–COPEC–2010.

B. Chemical mechanism – MTM

The Chemical Mechanism of MECCA

KPP version: `2.2.1_rs5`

MECCA version: `3.3`

Date: October 9, 2013.

Selected reactions:
"`Tr && G && !S && !Cl && !Br && !I && !Hg`"

Number of aerosol phases: 0

Number of species in selected mechanism:

Gas phase:	394
Aqueous phase:	0
All species:	394

Number of reactions in selected mechanism:

Gas phase (Gnnn):	952
Aqueous phase (Annn):	0
Henry (Hnnn):	0
Photolysis (Jnnn):	102
Heterogeneous (HETnnn):	0
Equilibria (EQnn):	0
Isotope exchange (DGnnn):	0
Dummy (Dnn):	0
All equations:	1054

B. Chemical mechanism – MTM

Table 1: Gas phase reactions

#	labels	reaction	rate coefficient	reference
G1000	StTrG	$O_2 + O(^1D) \rightarrow O(^3P) + O_2$	3.2E-11*EXP(70./temp)	Sander et al. (2003)
G1001	StTrG	$O_2 + O(^3P) \rightarrow O_3$	6.E-34*((temp/300.)**(-2.4))*cair	Sander et al. (2003)
G2100	StTrG	$H + O_2 \rightarrow HO_2$	k_3rd(temp,cair,5.7E-32,1.6,7.5E-11,0., 0.6)	Sander et al. (2003)
G2104	StTrG	$OH + O_3 \rightarrow HO_2 + LOHOX$	1.7E-12*EXP(-940./temp)	Sander et al. (2003)
G2105	StTrG	$OH + H_2 \rightarrow H_2O + H + LOHOX$	2.8E-12*EXP(-1800./temp)	Sander et al. (2006)
G2107	StTrG	$HO_2 + O_3 \rightarrow OH + POHOX$	1.E-14*EXP(-490./temp)	Sander et al. (2003)
G2109	StTrG	$HO_2 + OH \rightarrow H_2O + LOHOX$	4.8E-11*EXP(250./temp)	Sander et al. (2003)
G2110	StTrG	$HO_2 + HO_2 \rightarrow H_2O_2$	k_HO2_HO2	Christensen et al. (2002), Kircher and Sander (1984)*
G2111	StTrG	$H_2O + O(^1D) \rightarrow 2\,OH + 2\,POHOX + 2\,POHPR$	2.2E-10	Sander et al. (2003)
G2112	StTrG	$H_2O_2 + OH \rightarrow H_2O + HO_2 + LOHOX$	2.9E-12*EXP(-160./temp)	Sander et al. (2003)
G3101	StTrG	$N_2 + O(^1D) \rightarrow O(^3P) + N_2$	1.8E-11*EXP(110./temp)	Sander et al. (2003)
G3103	StTrGN	$NO + O_3 \rightarrow NO_2 + O_2$	3.E-12*EXP(-1500./temp)	Sander et al. (2003)
G3106	StTrGN	$NO_2 + O_3 \rightarrow NO_3 + O_2$	1.2E-13*EXP(-2450./temp)	Sander et al. (2003)
G3108	StTrGN	$NO_3 + NO \rightarrow 2\,NO_2$	1.5E-11*EXP(170./temp)	Sander et al. (2003)
G3109	StTrGN	$NO_3 + NO_2 \rightarrow N_2O_5$	k_NO3_NO2	Sander et al. (2003)*
G3110	StTrGN	$N_2O_5 \rightarrow NO_2 + NO_3$	k_NO3_NO2/(3.E-27*EXP(10990./temp))	Sander et al. (2003)*
G3200	TrG	$NO + OH \rightarrow HONO + LONOX$	k_3rd(temp,cair,7.E-31,2.6,3.6E-11,0.1, 0.6)	Sander et al. (2003)
G3201	StTrGN	$NO + HO_2 \rightarrow NO_2 + OH + PONOX$	3.5E-12*EXP(250./temp)	Sander et al. (2003)
G3202	StTrG	$NO_2 + OH \rightarrow HNO_3 + LONOX$	k_3rd(temp,cair,1.48E-30,3.,2.58E-11, 0.,0.6)	Mollner et al. (2010)
G3203	StTrGN	$NO_2 + HO_2 \rightarrow HNO_4$	k_NO2_HO2	Sander et al. (2003)
G3204	TrGN	$NO_3 + HO_2 \rightarrow NO_2 + OH + O_2 + PONOX$	3.5E-12	Sander et al. (2003)
G3205	TrG	$HONO + OH \rightarrow NO_2 + H_2O + LONOX$	1.8E-11*EXP(-390./temp)	Sander et al. (2003)
G3206	StTrGN	$HNO_3 + OH \rightarrow H_2O + NO_3 + LONOX$	k_HNO3_OH	Sander et al. (2003)*
G3207	StTrGN	$HNO_4 \rightarrow NO_2 + HO_2$	k_NO2_HO2/(2.1E-27*EXP(10900./temp))	Sander et al. (2003)*
G3208	StTrGN	$HNO_4 + OH \rightarrow NO_2 + H_2O + LONOX$	1.3E-12*EXP(380./temp)	Sander et al. (2003)
G4101	StTrG	$CH_4 + OH \rightarrow CH_3O_2 + H_2O + POHORG$	1.85E-20*EXP(2.82*log(temp)-987./temp)	Atkinson (2003)
G4102	TrG	$CH_3OH + OH \rightarrow HCHO + HO_2 + POHORG$	7.3E-12*EXP(-620./temp)	Sander et al. (2003)
G4103a	StTrG	$CH_3O_2 + HO_2 \rightarrow CH_3OOH$	4.1E-13*EXP(750./temp)/(1.+1./ 497.7*EXP(1160./temp))	Sander et al. (2003)*

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4103b	StTrG	$CH_3O_2 + HO_2 \rightarrow HCHO + H_2O + O_2$	4.1E-13*EXP(750./temp)/(1.+ 497.7*EXP(-1160./temp))	Sander et al. (2003)*
G4104	StTrGN	$CH_3O_2 + NO \rightarrow HCHO + NO_2 + HO_2$	2.8E-12*EXP(300./temp)	Sander et al. (2003)
G4105	TrGN	$CH_3O_2 + NO_3 \rightarrow HCHO + HO_2 + NO_2$	1.3E-12	Atkinson et al. (1999)
G4106a	StTrG	$CH_3O_2 \rightarrow HCHO + HO_2$	2.*RO2*9.5E-14*EXP(390./temp)/(1.+1./ 26.2*EXP(1130./temp))	Sander et al. (2003)
G4106b	StTrG	$CH_3O_2 \rightarrow .5\,HCHO + .5\,CH_3OH$	2.*RO2*9.5E-14*EXP(390./temp)/(1.+ 26.2*EXP(-1130./temp))	Sander et al. (2003)
G4107	StTrG	$CH_3OOH + OH \rightarrow .6\,CH_3O_2 + .4\,HCHO + .4\,OH + H_2O + .4\,POHORG + POHORG$	k_CH3OOH_OH	see note
G4108	StTrG	$HCHO + OH \rightarrow CO + H_2O + HO_2 + POHORG$	9.52E-18*EXP(2.03*log(temp)+636./temp)	Sivakumaran et al. (2003)
G4109	TrGN	$HCHO + NO_3 \rightarrow HNO_3 + CO + HO_2$	3.4E-13*EXP(-1900./temp)	Sander et al. (2003)*
G4110	StTrG	$CO + OH \rightarrow H + CO_2 + POHORG$	1.57E-13 + cair*3.54E-33	McCabe et al. (2001)
G4111	TrG	$HCOOH + OH \rightarrow CO_2 + HO_2 + H_2O + POHORG$	4.5E-13	IUPAC (2013)
G4112e	TrGC	$HCHO + HO_2 \rightarrow HOCH2O2$	7.7E-15*EXP(625./temp)	IUPAC (2013)
G4113e	TrGC	$HOCH2O2 \rightarrow HCHO + HO_2$	2.E12*EXP(-7000./temp)	IUPAC (2013)
G4114e	TrGC	$HOCH2O2 + HO_2 \rightarrow .5\,HOCH2OOH + .5\,HCOOH + .2\,OH + .2\,HO_2 + .3\,H_2O + .2\,POHORG$	5.6E-15*EXP(2300./temp)	Jenkin et al. (2007)
G4115e	TrGC	$HOCH2O2 + NO \rightarrow NO_2 + HO_2 + HCOOH$	2.8E-12*EXP(300./temp)	Sander et al. (2003)
G4116e	TrGC	$HOCH2O2 + NO_3 \rightarrow NO_2 + HO_2 + HCOOH$	1.2E-12	see note
G4117e	TrGC	$HOCH2O2 \rightarrow HCOOH + .62\,HO_2$	1.4E-12*RO2	see note
G4118e	TrGC	$HOCH2OOH + OH \rightarrow HOCH2O2 + H_2O + POHORG$	0.6*k_CH3OOH_OH + krohro	see note
G4119e	TrGC	$HOCH2OOH + OH \rightarrow OH + HCOOH + H_2O + POHORG + POHORG$	ks*fsoh*fsooh	see note
G4200	TrGC	$C_2H_6 + OH \rightarrow C_2H_5O_2 + H_2O + POHORG$	1.49E-17*temp*temp*EXP(-499./temp)	Atkinson (2003)
G4201e	TrGC	$C_2H_4 + O_3 \rightarrow HCHO + .63\,CO + .13\,HO_2 + 0.37\,HOCH2OOH + .13\,OH + .13\,POHORG$	1.2E-14*EXP(-2630./temp)	Sander et al. (2003)*
G4202	TrGC	$C_2H_4 + OH \rightarrow HOCH_2CH_2O_2 + H_2O + POHORG$	k_3rd(temp,cair,1.E-28,0.8,8.8E-12,0., 0.6)	Sander et al. (2003)
G4203	TrGC	$C_2H_5O_2 + HO_2 \rightarrow C_2H_5OOH$	7.5E-13*EXP(700./temp)	Sander et al. (2003)
G4204	TrGNC	$C_2H_5O_2 + NO \rightarrow CH_3CHO + HO_2 + NO_2$	2.6E-12*EXP(365./temp)	Sander et al. (2003)
G4205	TrGNC	$C_2H_5O_2 + NO_3 \rightarrow CH_3CHO + HO_2 + NO_2$	2.3E-12	Atkinson et al. (1999)
G4206	TrGC	$C_2H_5O_2 \rightarrow .98\,CH_3CHO + .38\,HO_2 + .02\,HOCH_2CH_2O_2$	3.1E-13*RO2	Rickard and Pascoe (2009)*
G4207	TrGC	$C_2H_5OOH + OH \rightarrow .43\,C_2H_5O_2 + .43\,H_2O + .57\,CH_3CHO + .57\,OH + .57\,POHORG + POHORG$	0.6*k_CH3OOH_OH + 8.01E-12	see note

3

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4208ea	TrGC	$CH_3CHO + OH \to CH_3C(O)OO + H_2O + POHORG$	4.4E-12*EXP(365./temp)*0.95	Atkinson et al. (2006)
G4208eb	TrGC	$CH_3CHO + OH \to .84 + .1\ HCHO + .1\ CO + .06\ GLYOX + .16\ OH + H_2O + .16\ POHORG + POHORG$	4.4E-12*EXP(365./temp)*0.05	Atkinson et al. (2006)
G4209	TrGNC	$CH_3CHO + NO_3 \to CH_3C(O)OO + HNO_3$	KNO3AL	Sander et al. (2003)
G4210e	TrGC	$CH_3COOH + OH \to CH_3O_2 + CO_2 + H_2O + POHORG$	4.2E-14*exp(850./temp)	IUPAC (2013)
G4211et1	TrGC	$CH_3C(O)OO + HO_2 \to OH + CH_3O_2 + CO_2 + POHORG$	KAPHO2*0.70	Taraborrelli (2013a)*
G4211et2	TrGC	$CH_3C(O)OO + HO_2 \to CH_3C(O)OOH$	KAPHO2*0.12	Taraborrelli (2013a)*
G4211et3	TrGC	$CH_3C(O)OO + HO_2 \to CH_3COOH + O_3$	KAPHO2*0.18	Taraborrelli (2013a)*
G4212	TrGNC	$CH_3C(O)OO + NO \to CH_3O_2 + CO_2 + NO_2$	8.1E-12*EXP(270./temp)	Tyndall et al. (2001)
G4213	TrGNC	$CH_3C(O)OO + NO_2 \to PAN$	k_CH3CO3_NO2	Tyndall et al. (2001)
G4214	TrGNC	$CH_3C(O)OO + NO_3 \to CH_3O_2 + NO_2 + CO_2$	4.E-12	Canosa-Mas et al. (1996)
G4217	TrGC	$CH_3C(O)OO \to .7\ CH_3O_2 + .7\ CO_2 + .3\ CH_3COOH$	1.00E-11*RO2	Rickard and Pascoe (2009)
G4218	TrGC	$CH_3C(O)OOH + OH \to CH_3C(O)OO + H_2O + POHORG$	0.6*k_CH3OOH_OH	Rickard and Pascoe (2009)*
G4220	TrGNC	$PAN + OH \to HCHO + CO + NO_2 + H_2O + POHORG$	9.50E-13*EXP(-650./temp)	Rickard and Pascoe (2009)
G4221	TrGNC	$PAN \to CH_3C(O)OO + NO_2$	k_PAN_M	Sander et al. (2003)*
G4223e	TrGC	$HOCH_2CHO + OH \to .84 + .16 + .2\ HO_2 + H_2O + POHORG$	8.00E-12	Rickard and Pascoe (2009)
G4224e	TrGNC	$HOCH_2CHO + NO_3 \to + HNO_3$	KNO3AL	Rickard and Pascoe (2009)
G4255et2	TrGC	$\to HOCH_2CO_3$	KDEC*.97	Taraborrelli (2013a)*
G4255et3	TrGC	$\to OH + HCHO + CO + POHORG$	KDEC*.03	Taraborrelli (2013a)*
G4256et2	TrGC	$\to GLYOX + HO_2$	KDEC	Taraborrelli (2013a)
G4225	TrGC	$HOCH_2CO_3 \to .7\ HCHO + .7\ CO_2 + .7\ HO_2 + .3\ HOCH_2CO_2H$	1.00E-11*RO2	Rickard and Pascoe (2009)
G4226ea	TrGC	$HOCH_2CO_3 + HO_2 \to HCHO + HO_2 + OH + CO_2 + POHORG$	KAPHO2*rco3_oh	Taraborrelli (2013a)*
G4226eb	TrGC	$HOCH_2CO_3 + HO_2 \to HOCH_2CO_3H$	KAPHO2*rco3_ooh	Taraborrelli (2013a)*
G4226ec	TrGC	$HOCH_2CO_3 + HO_2 \to HOCH_2CO_2H + O_3$	KAPHO2*rco3_o3	Taraborrelli (2013a)*
G4227	TrGNC	$HOCH_2CO_3 + NO \to NO_2 + HO_2 + HCHO + CO_2$	KAPNO	Rickard and Pascoe (2009)
G4228	TrGNC	$HOCH_2CO_3 + NO_2 \to PHAN$	k_CH3CO3_NO2	Rickard and Pascoe (2009)
G4229	TrGNC	$HOCH_2CO_3 + NO_3 \to NO_2 + HO_2 + HCHO + CO_2$	KRO2NO3*1.60	Rickard and Pascoe (2009)
G4230e	TrGC	$HOCH_2CO_2H + OH \to .09\ HCHO + .09\ CO_2 + .91\ HCOCO_2H + HO_2 + H_2O + POHORG$	kco2h+ks*fsoh*fco2h	Taraborrelli (2013a)
G4231ea	TrGC	$HOCH_2CO_3H + OH \to HOCH_2CO_3 + H_2O + POHORG$	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4231eb	TrGC	$HOCH_2CO_3H + OH \to HCOCO_3H + HO_2 + POHORG$	ks*fsoh*fco2h	Taraborrelli (2013a)
G4232	TrGNC	$PHAN \to HOCH_2CO_3 + NO_2$	k_PAN_M	Rickard and Pascoe (2009)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4233	TrGNC	$PHAN + OH \to HCHO + CO + NO_2 + H_2O$	1.12E-12	Rickard and Pascoe (2009)
G4234e	TrGC	$GLYOX + OH \to 1.2\ CO + .6\ HO_2 + .4 + H_2O + POHORG$	3.1E-12*EXP(340./temp)	IUPAC (2013)
G4235e	TrGNC	$GLYOX + NO_3 \to 1.2\ CO + .6\ HO_2 + .4 + HNO_3$	KNO3AL	Rickard and Pascoe (2009)
G4235et2	TrGNC	$\to 1.5\ CO + .5\ HO_2 + .5\ OH + .5\ CO_2 + .5\ POHORG$	KDEC	Taraborrelli (2013a)
G4236	TrGC	$HCOCO_3 \to .7\ CO + .7\ HO_2 + .7\ CO_2 + .3\ HCOCO_2H$	1.00E-11*RO2	Rickard and Pascoe (2009)
G4237e	TrGC	$HCOCO_3 + HO_2 \to HO_2 + CO + CO_2 + OH + POHORG$	KAPHO2	Feierabend et al. (2008),Taraborrelli (2013a)
G4238	TrGNC	$HCOCO_3 + NO \to HO_2 + CO + NO_2 + CO_2$	KAPNO	Rickard and Pascoe (2009)
G4239	TrGNC	$HCOCO_3 + NO_3 \to HO_2 + CO + NO_2 + CO_2$	KRO2NO3*1.60	Rickard and Pascoe (2009)
G4239t2	TrGNC	$HCOCO_3 + NO_2 \to HO_2 + CO + NO_3 + CO_2$	k_CH3CO3_NO2	Orlando and Tyndall (2001),Taraborrelli (2013a)*
G4240	TrGC	$HCOCO_2H + OH \to CO + HO_2 + CO_2 + H_2O + POHORG$	kco2h+kt*fo*fco2h	Taraborrelli (2013a)
G4241	TrGC	$HCOCO_3H + OH \to .2\ HCOCO_3 + .8\ CO + .8\ OH + .8\ CO_2 + H_2O + POHORG + .8\ POHORG$	0.6*k_CH3OOH_OH+kt*fo*fco2h	Taraborrelli (2013a)
G4242	TrGC	$HOCH_2CH_2O_2 \to .6\ HOCH_2CH_2O + .2\ HOCH_2CHO + .2\ ETHGLY$	2.00E-12*RO2	Rickard and Pascoe (2009)
G4244	TrGC	$HOCH_2CH_2O_2 + HO_2 \to HYETHO2H$	2.00E-13*EXP(1250./temp)	Rickard and Pascoe (2009)
G4243	TrGNC	$HOCH_2CH_2O_2 + NO \to .24875\ HO_2 + .4975\ HCHO + .74625\ HOCH_2CH_2O + .995\ NO_2 + .005\ ETHOHNO3$	KRO2NO	Orlando et al. (1998)
G4245	TrGNC	$ETHOHNO3 + OH \to .93 + .93\ HO_2 + .07\ HOCH_2CHO + .07\ NO_2 + H_2O + POHORG$	ks*(fsoh*fch2ono2+fono2*fpch2oh)+krohro	Taraborrelli (2013a)
G4246a	TrGC	$HYETHO2H + OH \to HOCH_2CH_2O_2 + H_2O + POHORG$	0.6*k_CH3OOH_OH	Rickard and Pascoe (2009)
G4246b	TrGC	$HYETHO2H + OH \to HOCH_2CHO + OH + H_2O + POHORG + POHORG$	ks*fsooh*fpch2oh	Taraborrelli (2013a)
G4246c	TrGC	$HYETHO2H + OH \to + HO_2 + H_2O$	ks*fsoh*fpch2oh+krohro	Taraborrelli (2013a)
G4247a	TrGC	$HOCH_2CH_2O \to HO_2 + HOCH_2CHO$	6.00E-14*EXP(-550./temp)*C(ind_O2)	Orlando et al. (1998)
G4247b	TrGC	$HOCH_2CH_2O \to HO_2 + HCHO + HCHO$	9.50E+13*EXP(-5988./temp)	Orlando et al. (1998)
G4248	TrGC	$ETHGLY + OH \to HOCH_2CHO + HO_2 + H_2O + POHORG$	2*ks*fsoh*fpch2oh+2*krohro	Taraborrelli (2013a)
G4249e	TrGC	$\to 0.6\ HCHO + 0.6\ CO + 0.6\ HO_2 + 0.2\ GLYOX + 0.2\ HOCH_2CHO$	2.00E-12*RO2	Taraborrelli (2013a)
G4250e	TrGC	$+ HO_2 \to 0.85 + 0.15\ HCHO + 0.15\ CO + 0.15\ HO_2 + 0.15\ OH + .15\ POHORG$	KRO2HO2*0.387	Taraborrelli (2013a)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4251e	TrGC	+ NO → NO$_2$ + HCHO + CO + HO$_2$	KRO2NO	Taraborrelli (2013a)
G4252e	TrGC	+ NO$_3$ → HCHO + CO + HO$_2$ + NO$_2$	KRO2NO3	Taraborrelli (2013a)
G4253e	TrGC	+ OH → .71 OH + .31 HCHO + .31 CO + .40 GLYOX + .29 + .71 POHORG + POHORG	0.6*k_CH3OOH_OH+ks*fsooh*fcho*.8*8.E-12	Taraborrelli (2013a)
G4254e	TrGNC	+ NO$_3$ → OH + HCHO + CO + HNO$_3$ + POHORG	KNO3AL	Rickard and Pascoe (2009)
G4257e	TrGC	+ OH → HCHO + CO$_2$ + NO$_2$ + H$_2$O + POHORG	1.E-11	Paulot et al. (2009a),Taraborrelli (2013a)
G4258e	TrGNC	+ NO → NO$_2$ + OH + HCHO + CO$_2$ + POHORG	KAPNO	Taraborrelli (2013a)
G4259e	TrGNC	+ NO$_3$ → NO$_2$ + OH + HCHO + CO$_2$ + POHORG	KRO2NO3*1.60	Taraborrelli (2013a)
G4260e	TrGC	+ HO$_2$ → 2 OH + HCHO + CO$_2$ + 2 POHORG	KAPHO2*rco3_oh	Taraborrelli (2013a)
G4260et2	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Taraborrelli (2013a)*
G4260et3	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*rco3_o3	Taraborrelli (2013a)*
G4261e	TrGC	→ .7 OH + .7 HCHO + .7 CO$_2$ + .3 + .7 POHORG	1.00E-11*RO2	Taraborrelli (2013a)
G4262e	TrGC	+ OH → + H$_2$O + POHORG	2.*0.6*k_CH3OH_OH	Taraborrelli (2013a)
G4263e	TrGC	+ OH → HCOCO$_3$H + OH + H$_2$O + POHORG + POHORG	ks*fsooh*fco2h	Taraborrelli (2013a)
G4265e	TrGC	+ OH → HCOCO$_2$H + OH + H$_2$O + POHORG + POHORG	ks*fsooh*fco2h+kco2h	Taraborrelli (2013a)
G4266e	TrGC	+ OH → .6 HCHO + .6 HO$_2$ + .6 CO + .4 + POHORG	2.8E-12*exp(510./temp)	Baulch et al. (2005),Taraborrelli (2013a)*
G4267e	TrGC	+ OH → CH$_3$COOH + OH + POHORG + POHORG	kt*fftooh*ftoh + krohro	Taraborrelli (2013a)
G4268e	TrGC	+ OH → + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4269e	TrGC	→ CH$_3$CHO + HO$_2$	3.46E12*EXP(-12500./(1.98*temp))	Hermans et al. (2005),Taraborrelli (2013a)
G4270e	TrGC	CH$_3$CHO + HO$_2$ →	3.46E12*EXP(-12500./(1.98*temp)) /(6.34E26*EXP(-14700./(1.98*temp)))	Hermans et al. (2005),Taraborrelli (2013a)
G4271e	TrGC	+ HO$_2$ → .5 + .3 CH$_3$COOH + .2 CH$_3$O$_2$ + .2 HCOOH + .2 OH	5.6E-15*EXP(2300./temp)	Taraborrelli (2013a)
G4272e	TrGC	→ CH$_3$O$_2$ + HCOOH + OH	1.4E-12*RO2	Taraborrelli (2013a)
G4273e	TrGC	+ NO → CH$_3$O$_2$ + HCOOH + OH + NO$_2$	KRO2NO	Taraborrelli (2013a)
G4300	TrGC	C$_3$H$_8$ + OH → .736 iC$_3$H$_7$O$_2$ + .264 C$_2$H$_5$O$_2$ + .264 CO$_2$ + .264 HO$_2$ + H$_2$O + POHORG	1.55E-17*temp*temp*EXP(-61./temp)	Rickard and Pascoe (2009)*

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4301et2	TrGC	C$_3$H$_6$ + O$_3$ → .0855 + .4389 CH$_3$CHO + .4389 H$_2$O$_2$ + .0456 CH$_3$COOH + .285 + .0855 CH$_4$ + .0855 CO$_2$ + .0342 + .0513 CH$_3$OH + .0228 CH$_3$C(O)OO + .57 HCHO + .2709 CO + .0688 HO$_2$ + .1591 HOCH2OOH + .43 CH$_3$CHO + .3766 OH + .3766 POHORG	6.5E-15*EXP(-1900./temp)	Taraborrelli (2013a)
G4302	TrGC	C$_3$H$_6$ + OH → HYPROPO2 + POHORG	k_3rd(temp,cair,8.E-27,3.5,3.E-11,0., 0.5)	Atkinson et al. (1999)
G4303	TrGNC	C$_3$H$_6$ + NO$_3$ → PRONO3BO2	4.6E-13*EXP(-1155./temp)	Atkinson et al. (1999)
G4304	TrGC	iC$_3$H$_7$O$_2$ + HO$_2$ → iC$_3$H$_7$OOH	1.9E-13*EXP(1300./temp)	Atkinson (1997)*
G4305	TrGNC	iC$_3$H$_7$O$_2$ + NO → .96 CH$_3$COCH$_3$ + .96 HO$_2$ + .96 NO$_2$ + .04 iC$_3$H$_7$ONO$_2$	2.7E-12*EXP(360./temp)	Atkinson et al. (1999)
G4306	TrGC	iC$_3$H$_7$O$_2$ → CH$_3$COCH$_3$ + .8 HO$_2$	4.E-14*RO2	Rickard and Pascoe (2009)*
G4307	TrGC	iC$_3$H$_7$OOH + OH → .27 iC$_3$H$_7$O$_2$ + .73 CH$_3$COCH$_3$ + .73 OH + H$_2$O + .73 POHORG + POHORG	1.66E-11 + 0.6*k_CH3OOH_OH	Rickard and Pascoe (2009)*
G4311	TrGC	CH$_3$COCH$_3$ + OH → CH$_3$COCH$_2$O$_2$ + H$_2$O + POHORG	1.33E-13+3.82E-11*EXP(-2000./temp)	Sander et al. (2003)
G4312e	TrGC	CH$_3$COCH$_2$O$_2$ + HO$_2$ → .15 OH + .15 CH$_3$C(O)OO + .15 HCHO + .85 CH$_3$COCH$_2$O$_2$H + .15 POHORG	8.6E-13*EXP(700./temp)	Taraborrelli (2013a)
G4313	TrGNC	CH$_3$COCH$_2$O$_2$ + NO → CH$_3$C(O)OO + HCHO + NO$_2$	2.9E-12*EXP(300./temp)	Sander et al. (2003)
G4314	TrGC	CH$_3$COCH$_2$O$_2$ → .6 CH$_3$C(O)OO + .6 HCHO + .2 MGLYOX + .2 CH$_3$COCH$_2$OH	7.5E-13*EXP(500./temp)*2.*RO2	Tyndall et al. (2001)
G4321	TrGNC	CH$_3$COCH$_2$O$_2$ + NO$_3$ → CH$_3$C(O)OO + HCHO + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)
G4315a	TrGC	CH$_3$COCH$_2$O$_2$H + OH → CH$_3$COCH$_2$O$_2$ + H$_2$O + POHORG	0.6*k_CH3OOH_OH	Rickard and Pascoe (2009)*
G4315b	TrGC	CH$_3$COCH$_2$O$_2$H + OH → MGLYOX + OH + H$_2$O + POHORG + POHORG	ks*fsooh*fco	Taraborrelli (2013a)
G4316e	TrGC	CH$_3$COCH$_2$OH + OH → + H$_2$O + POHORG	1.60E-12*EXP(305./temp)	Taraborrelli (2013a)
G4336ea	TrGC	→ MGLYOX + HO$_2$	0.8485	Taraborrelli (2013a)
G4317e	TrGC	MGLYOX + OH → .4 CH$_3$O$_2$ + .6 CH$_3$C(O)OO + 1.4 CO + POHORG	1.9E-12*EXP(575./temp)	Baeza-Romero et al. (2007),IU-PAC (2013)
G4331	TrGNC	MGLYOX + NO$_3$ → CH$_3$C(O)OO + CO + HNO$_3$	KNO3AL*2.4	Rickard and Pascoe (2009)
G4320	TrGNC	iC$_3$H$_7$ONO$_2$ + OH → CH$_3$COCH$_3$ + NO$_2$ + POHORG	6.2E-13*EXP(-230./temp)	Atkinson et al. (1999)
G4322	TrGC	HYPROPO2 → CH$_3$CHO + HCHO + HO$_2$	8.80E-13*RO2	Rickard and Pascoe (2009)
G4323	TrGC	HYPROPO2 + HO$_2$ → HYPROPO2H	KRO2HO2*0.520	Rickard and Pascoe (2009)
G4324	TrGNC	HYPROPO2 + NO → CH$_3$CHO + HCHO + HO$_2$ + NO$_2$	KRO2NO	Rickard and Pascoe (2009)
G4325	TrGNC	HYPROPO2 + NO$_3$ → CH$_3$CHO + HCHO + HO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4326a	TrGC	HYPROPO2H + OH → HYPROPO2 + POHORG	0.6*k_CH3OOH_OH	Rickard and Pascoe (2009)
G4326b	TrGC	HYPROPO2H + OH → CH_3COCH_2OH + OH + POHORG + POHORG	ks*fsoh*fpch2oh+kt*ftooh*fpch2oh	Taraborrelli (2013a)
G4327	TrGNC	PRONO3BO2 + HO_2 → PR2O2HNO3	KRO2HO2*0.520	Rickard and Pascoe (2009)
G4328	TrGNC	PRONO3BO2 + NO → NOA + HO_2 + NO_2	KRO2NO	Rickard and Pascoe (2009)
G4329	TrGNC	PRONO3BO2 + NO_3 → NOA + HO_2 + NO_2	KRO2NO3	Rickard and Pascoe (2009)
G4330a	TrGNC	PR2O2HNO3 + OH → PRONO3BO2 + POHORG	1.90E-12*EXP(190./temp)	Rickard and Pascoe (2009)
G4330b	TrGNC	PR2O2HNO3 + OH → NOA + OH + POHORG + POHORG	kt*ftooh*fch2ono2	Rickard and Pascoe (2009)
G4332	TrGNC	NOA + OH → MGLYOX + NO_2 + POHORG	ks*fco*fono2+kp*fco	Taraborrelli (2013a)
G4333e	TrGC	HOCH2COCHO + OH → .8609 + .8609 CO + .1391 + .1391 HO_2 + POHORG	1.9E-12*EXP(575./temp)+ks*fsoh*fco	Taraborrelli (2013a)
G4334e	TrGNC	HOCH2COCHO + NO_3 → + CO + HNO_3	KNO3AL*2.4	Taraborrelli (2013a)
G4337e	TrGC	+ OH → $CH_3C(O)OO$ + H_2O + CO_2 + POHORG	4.9E-14*EXP(276./temp)	Mellouki and Mu (2003),Taraborrelli (2013a)
G4338e	TrGC	→ HCHO +	RO2*2.0E-12	Taraborrelli (2013a)
G4339e	TrGC	+ HO_2 → .15 HCHO + .15 + .15 OH + .85 + .15 POHORG	KRO2HO2*0.520	Taraborrelli (2013a)
G4340e	TrGC	+ NO → HCHO + + NO_2	KRO2NO	Taraborrelli (2013a)
G4341e	TrGC	+ OH → HOCH2COCHO + OH + POHORG + POHORG	ks*fsooh*fco	Taraborrelli (2013a)
G4342e	TrGC	+ OH → + POHORG	.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4343e	TrGC	+ OH → + HO_2 + POHORG	0.9295*1.60E-12*EXP(305./temp)	Taraborrelli (2013a)
G4344e	TrGC	→ 0.6 + 0.6 HCHO + 0.2 + 0.2 HOCH2COCHO	2.00E-12*RO2	Taraborrelli (2013a)
G4345e	TrGC	+ NO → HCHO + NO_2	KRO2NO	Taraborrelli (2013a)
G4346e	TrGC	+ HO_2 → 0.85 + 0.15 + .15 HCHO + 0.15 OH + .15 POHORG	KRO2HO2*0.520	Taraborrelli (2013a)
G4347e	TrGC	+ NO_3 → + HCHO + NO_2	KRO2NO3	Taraborrelli (2013a)
G4348e	TrGC	+ OH → + CO + H_2O + POHORG	kt*fo*fco	Taraborrelli (2013a)
G4349e	TrGC	+ OH → + OH + H_2O + POHORG + POHORG	ks*fsooh*fco	Taraborrelli (2013a)
G4350e	TrGC	+ OH → + H_2O + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4351e	TrGC	+ NO_3 → + CO + HNO_3	KNO3AL*2.4	Taraborrelli (2013a)
G4352e	TrGC	+ OH → + CO + POHORG	2*kt*fco*fo	Taraborrelli (2013a)
G4353e	TrGC	+ OH → .72 CO + .72 CH_3CHO + .72 HO_2 + .21 + .07 CH_3CHO + .07 HO_2 + .07 CO_2 + POHORG	7.6E-11	Hatakeyama et al. (1985),Taraborrelli (2013a)*

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4354e	TrGC	+ OH → CO + + POHORG	1E-10*acho	Hatakeyama et al. (1985),Taraborrelli (2013a)*
G4355e	TrGC	+ OH → CO + + POHORG	7.6E-11*acoch3	Hatakeyama et al. (1985),Taraborrelli (2013a)*
G4400	TrGC	nC_4H_{10} + OH → $LC_4H_9O_2$ + H_2O + POHORG	1.81E-17*temp*temp*EXP(114./temp)	Atkinson (2003)*
G4401	TrGC	$LC_4H_9O_2$ → 0.254 CO_2 + 0.5552 MEK + 0.5552 HO_2 + 0.3178 CH_3CHO + 0.4448 $C_2H_5O_2$	2.5E-13*RO2	Rickard and Pascoe (2009)*
G4402	TrGC	$LC_4H_9O_2$ + HO_2 → LC4H9OOH	KRO2HO2*0.625	Rickard and Pascoe (2009)
G4403	TrGNC	$LC_4H_9O_2$ + NO → 0.9172 NO_2 + 0.233 CO_2 + 0.5092 MEK + 0.5092 HO_2 + 0.2915 CH_3CHO + 0.408 $C_2H_5O_2$ + 0.0828 LC4H9NO3	KRO2NO	Rickard and Pascoe (2009)*
G4404	TrGC	LC4H9OOH + OH → 0.2285796 $LC_4H_9O_2$ + 0.7117253 MEK + 0.1193902 CO_2 + 0.0596951 $C_2H_5O_2$ + 0.7714204 OH + H_2O + .7714204 POHORG + POHORG	2.636E-11	Rickard and Pascoe (2009)*
G4405e	TrGC	MVK + O_3 → .87 MGLYOX + 0.5481 CO + 0.1392 HO_2 + 0.1392 OH + 0.3219 HOCH2OOH + .13 HCHO + 0.04680 OH + 0.04680 CO + 0.07280 $CH_3C(O)OO$ + .026 CH_3CHO + .026 CO_2 + .026 HCHO + .026 HO_2 + 0.02402 MGLYOX + 0.02402 H_2O_2 + 0.007176 + 0.1860 POHORG	8.5E-16*EXP(-1520./temp)	Taraborrelli (2013a)
G4406e	TrGC	MVK + OH → LHMVKABO2 + POHORG	2.6E-12*EXP(610./temp)	Taraborrelli (2013a)*
G4413	TrGC	MEK + OH → LMEKO2 + H_2O + POHORG	3.24E-18*temp*temp*EXP(414./temp)	Rickard and Pascoe (2009)*
G4414ea	TrGC	LMEKO2 + HO_2 → LMEKOOH	KRO2HO2*0.625*rcoch2o2_ooh	Taraborrelli (2013a)
G4414eb	TrGC	LMEKO2 + HO_2 → 0.538 HCHO + 0.538 CO_2 + 0.459 $HOCH_2CH_2O_2$ + 0.079 $C_2H_5O_2$ + 0.462 $CH_3C(O)OO$ + 0.462 CH_3CHO + OH + POHORG	KRO2HO2*0.625*rcoch2o2_oh	Taraborrelli (2013a)
G4415	TrGNC	LMEKO2 + NO → 0.538 HCHO + 0.538 CO_2 + 0.459 $HOCH_2CH_2O_2$ + 0.079 $C_2H_5O_2$ + 0.462 $CH_3C(O)OO$ + 0.462 CH_3CHO + NO_2	KRO2NO	Rickard and Pascoe (2009)*
G4416	TrGC	LMEKOOH + OH → 0.40851 $CH_3COCH_2O_2$ + 0.350196 BIACET + 0.807212 OH + 0.048506 $C_2H_5O_2$ + 0.505522 CO_2 + 0.192788 LMEKO2 + H_2O + .807212 POHORG + POHORG	3.786E-11	Rickard and Pascoe (2009)*
G4417	TrGNC	LC4H9NO3 + OH → 0.91423 MEK + 0.08577 $C_2H_5O_2$ + 0.17154 CO_2 + NO_2 + H_2O + POHORG	9.598E-13	Rickard and Pascoe (2009)*

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4418	TrGNC	MPAN + OH → CH3COCH2OH + CO + NO2 + POHORG	3.2E-11	Orlando et al. (2002)
G4419	TrGNC	MPAN → MACO3 + NO2	k_PAN_M	see note
G4420	TrGNC	LMEKO2 → 0.538 HCHO + 0.538 CO2 + 0.459 HOCH2CH2O2 + 0.079 C2H5O2 + 0.462 CH3C(O)OO + 0.462 CH3CHO	1.483E-12*RO2	Rickard and Pascoe (2009)*
G4421e	TrGC	MACR + OH → .45 MACO3 + .55 MACRO2 + POHORG	8.E-12*EXP(380./temp)	Orlando et al. (1999b),Taraborrelli (2013a)
G4422e	TrGC	MACR + O3 → 0.5481 CO + 0.1392 HO2 + 0.1392 OH + 0.3219 HOCH2OOH + .87 MGLYOX + .13 HCHO + .13 OH + .065 + .065 CO + .065 CH3C(O)OO + 0.2692 POHORG	1.36E-15*EXP(-2112./temp)	Taraborrelli (2013a)
G4423	TrGNC	MACR + NO3 → MACO3 + HNO3	KNO3AL*2.0	Rickard and Pascoe (2009)
G4424e	TrGC	MACO3 → .7 + .3 MACO2H	1.00E-11*RO2	Taraborrelli (2013a)
G4425e	TrGC	MACO3 + HO2 → + OH + POHORG	KAPHO2*rco3_oh	Taraborrelli (2013a)
G4425et2	TrGC	MACO3 + HO2 → MACO3H	KAPHO2*rco3_ooh	Taraborrelli (2013a)
G4425et3	TrGC	MACO3 + HO2 → MACO2H + O3	KAPHO2*rco3_o3	Taraborrelli (2013a)
G4426e	TrGNC	MACO3 + NO → + NO2	8.70E-12*EXP(290./temp)	Taraborrelli (2013a)
G4427	TrGNC	MACO3 + NO2 → MPAN	k_CH3CO3_NO2	Rickard and Pascoe (2009)
G4428e	TrGNC	MACO3 + NO3 → + NO2	KRO2NO3*1.60	Taraborrelli (2013a)
G4429e	TrGC	MACRO2 → .7 CH3COCH2OH + .7 HCHO + .7 HO2 + .3 MACROH	9.20E-14*RO2	Taraborrelli (2013a)
G4430e	TrGC	MACRO2 + HO2 → + OH + POHORG	KRO2HO2*0.625*rcoch2o2_oh	Taraborrelli (2013a)
G4430et2	TrGC	MACRO2 + HO2 → MACROOH	KRO2HO2*0.625*rcoch2o2_ooh	Taraborrelli (2013a)
G4431e	TrGNC	MACRO2 + NO → .85 + .85 NO2 + .15	KRO2NO	Taraborrelli (2013a)
G4432e	TrGNC	MACRO2 + NO3 → + NO2	KRO2NO3	Taraborrelli (2013a)
G4433ea	TrGC	MACROOH + OH → MACRO2 + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4433eb	TrGC	MACROOH + OH → + CO + OH + CH3COCH2OH + POHORG + POHORG	kt*fo*ftch2oh*falk	Taraborrelli (2013a)
G4433ec	TrGC	MACROOH + OH → CO + MGLYOX + HO2 + POHORG	ks*fsoh*fpch2oh + krohro	Taraborrelli (2013a)
G4434e	TrGC	MACROH + OH → CH3COCH2OH + CO + HO2 + POHORG	kt*fo*ftch2oh*falk	Taraborrelli (2013a)
G4434et2	TrGC	→ .885 CH3COCH2OH + .885 CO + .115 MGLYOX + .115 HCHO + HO2	KDEC	Taraborrelli (2013a)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4435e	TrGC	MACO2H + OH → CH3COCH2OH + HO2 + CO2 + POHORG	(kadt+kadp)*aco2h+kco2h	Taraborrelli (2013a)
G4436e	TrGC	MACO3H + OH → CH3COCH2OH + CO2 + OH + POHORG + POHORG	0.6*k_CH3OOH_OH+(kadt+kadp)*aco2h	Taraborrelli (2013a)
G4437e	TrGC	LHMVKABO2 → .024 CO2H3CHO + .072 + .072 HCHO + .5280 CH3C(O)OO + .5280 HOCH2CHO + .176 BIACETOH + .2 HO12CO3C4	1.014E-12*RO2	Taraborrelli (2013a)*
G4438e	TrGC	LHMVKABO2 + HO2 → OH + HOCH2CHO + CH3C(O)OO + POHORG	KRO2HO2*0.625*.88*rcoch2o2_oh	Taraborrelli (2013a)
G4438et2	TrGC	LHMVKABO2 + HO2 → LHMVKABOOH	KRO2HO2*0.625*(.12+.88*rcoch2o2_ooh)	Taraborrelli (2013a)
G4439ea	TrGNC	LHMVKABO2 + NO → .12 + .88 HOCH2CHO + .88 CH3C(O)OO + .12 HCHO + NO2	KRO2NO*(1.-0.11)	Taraborrelli (2013a)*
G4439eb	TrGNC	LHMVKABO2 + NO →	KRO2NO*0.11	Taraborrelli (2013a)
G4440e	TrGNC	LHMVKABO2 + NO3 → .12 MGLYOX + .88 HOCH2CHO + .88 CH3C(O)OO + .12 HCHO + .12 HO2 + NO2	KRO2NO3	Taraborrelli (2013a)*
G4441e	TrGC	LHMVKABOOH + OH → .12 CO2H3CHO + .88 BIACETOH + POHORG + POHORG	0.6*k_CH3OOH_OH+.12*ks*fsooh*fpch2oh+ .88*kt*ftooh*fpch2oh*fco	Taraborrelli (2013a)*
G4449e	TrGC	CO2H3CHO + OH → CO2H3CO3 + POHORG	kt*fo*falk	Taraborrelli (2013a)
G4449et2	TrGC	CO2H3CHO + OH → + HO2 + H2O + POHORG	kt*fco*ftoh*fcho	Taraborrelli (2013a)
G4450	TrGNC	CO2H3CHO + NO3 → CO2H3CO3 + HNO3	KNO3AL*4.0	Rickard and Pascoe (2009)
G4451e	TrGC	CO2H3CO3 → + CO2	1.00E-11*RO2	Taraborrelli (2013a)
G4452e	TrGC	CO2H3CO3 + HO2 → OH + + CO2 + POHORG	KAPHO2*rco3_oh	Taraborrelli (2013a)
G4452et2	TrGC	CO2H3CO3 + HO2 → + O3	KAPHO2*rco3_o3	Taraborrelli (2013a)
G4452et3	TrGC	CO2H3CO3 + HO2 → CO2H3CO3H	KAPHO2*rco3_ooh	Taraborrelli (2013a)
G4453e	TrGNC	CO2H3CO3 + NO → + NO2 + CO2	KAPNO	Taraborrelli (2013a)
G4454e	TrGC	CO2H3CO3 + NO3 → + NO2 + CO2	KRO2NO3*1.60	Taraborrelli (2013a)
G4455	TrGC	CO2H3CO3H + OH → 0.5127 CO2H3CO3 + 0.4873 CH3C(O)OO + 0.4873 CO + 0.4873 CO2 + 0.4873 OH + POHORG + 0.4873 POHORG	kt*fco2h*fco*ftoh+0.6*k_CH3OOH_OH	Taraborrelli (2013a)*
G4455t2	TrGC	+ OH → + HO2 + POHORG	kt*fco2h*fco*ftoh+kco2h	Taraborrelli (2013a)
G4456a	TrGC	HO12CO3C4 + OH → BIACETOH + HO2 + POHORG	kt*ftoh*falk*fco	Taraborrelli (2013a)
G4456b	TrGC	HO12CO3C4 + OH → CO2H3CHO + HO2 + POHORG	ks*fsoh*falk	Taraborrelli (2013a)
G4457e	TrGC	→ .65 CH3O2 + .65 CO + .65 HCHO + .35 OH + .35 CH3COCH2O2 + CO2 + .35 POHORG	KDEC	Taraborrelli (2013a)

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#	labels	reaction	rate coefficient	reference
G4458e	TrGC	LHMVKABO2 → .88 MGLYOX + .88 HCHO + .12 + .12 CH$_3$C(O)OO + OH + POHORG	KHSD	Taraborrelli (2013a)
G4459e	TrGNC	MACRO2 → MGLYOX + HCHO + OH + POHORG		Taraborrelli (2013a)
G4460e	TrGNC	+ OH → .7 MGLYOX + .7 HCOOH + .7 NO$_3$ + .3 CO2H3CHO + .3 NO$_2$ + H$_2$O + POHORG	5.6E-12	Taraborrelli (2013a)
G4461e	TrGC	+ OH → .08 CH$_3$COOH + .08 HCHO + .15 NO$_3$ + .07 HCOOH + .07 MGLYOX + .85 CH$_3$COCH$_2$OH + .85 NO$_3$ + .93 CO$_2$ + H$_2$O + POHORG	5.E-11	Taraborrelli (2013a)
G4462e	TrGC	→ .9 + .1 CH$_3$C(O)OO + .01 GLYOX + .18 CO + .09 HO$_2$ + OH + POHORG	k16HS	Taraborrelli (2013a)*
G4463e	TrGC	→ + OH + POHORG	K16HS	Taraborrelli (2013a)
G4500e	TrGC	C$_5$H$_8$ + O$_3$ → .3508 MACR + 0.01518 MACO2H + .2440 MVK + .7085 HCHO + .11 HOCH2OOH + .1275 C$_3$H$_6$ + .1575 CH$_3$C(O)OO + .0510 CH$_3$O$_2$ + 0.2625 HO$_2$ + .27 OH + .09482 H$_2$O$_2$ + .255 CO$_2$ + .522 CO + 0.07182 HCHO + .03618 + .01782 CO + .27 POHORG	1.03E-14*EXP(-1995./temp)	Taraborrelli (2013a)*
G4501e	TrGC	C$_5$H$_8$ + OH → .63 + .30 + .07 + POHORG	2.7E-11*EXP(390./temp)*(1.-iseg)	Taraborrelli (2013a)*
G4502	TrGNC	C$_5$H$_8$ + NO$_3$ → NISOPO2	3.15E-12*EXP(-450./temp)	Rickard and Pascoe (2009)
G4503e	TrGC	+ O$_2$ → LISOPACO2	5.530E-13	Taraborrelli (2013a)*
G4504e	TrGC	+ O$_2$ → ISOPBO2	3.E-12	Taraborrelli (2013a)*
G4505e	TrGC	+ O$_2$ →	6.780E-13	Taraborrelli (2013a)*
G4506e	TrGC	+ O$_2$ → ISOPDO2	3.E-12	Taraborrelli (2013a)*
G4507e	TrGC	LISOPACO2 → + O$_2$	3.1E12*exp(-7900./temp)*.6+ 7.8E13*exp(-8600./temp)*.4	Taraborrelli (2013a)*
G4508e	TrGC	ISOPBO2 → + O$_2$	3.7E14*exp(-9570./temp) +4.2E14*exp(-9970./temp)	Taraborrelli (2013a)*
G4509e	TrGC	→ + O$_2$	5.65E12*exp(-8410./temp)*.42+ 1.4E14*exp(-9110./temp)*.58	Taraborrelli (2013a)*
G4510e	TrGC	ISOPDO2 → + O$_2$	5.0E14*exp(-10120./temp) +8.25E14*exp(-10220./temp)	Taraborrelli (2013a)*
G4511e	TrGC	LISOPACO2 → + HO$_2$	K16HS	Taraborrelli (2013a)
G4512e	TrGC	→ + HO$_2$	K16HS	Taraborrelli (2013a)
G4513et3	TrGC	LISOPACO2 → .9 LHC4ACCHO + .8 HO$_2$ + .1 ISOPAOH	2.4E-12*RO2	Rickard and Pascoe (2009)
G4514t2	TrGC	LISOPACO2 + HO$_2$ → LISOPACOOH	.706*KRO2HO2	Rickard and Pascoe (2009)

#	labels	reaction	rate coefficient	reference
G4515et2	TrGNC	LISOPACO2 + NO → 0.95 LHC4ACCHO + 0.95 HO$_2$ + 0.95 NO$_2$ + .05 LISOPACNO3	KRO2NO	Lockwood et al. (2010),Taraborrelli (2013a)
G4506et3	TrGNC	LISOPACO2 + NO$_3$ → LHC4ACCHO + HO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)
G4507et3	TrGC	→ .9 LHC4ACCHO + .8 HO$_2$ + .1 ISOPAOH	2.4E-12*RO2	Rickard and Pascoe (2009)
G4511et3	TrGC	+ HO$_2$ → LISOPACOOH	.706*KRO2HO2	Rickard and Pascoe (2009)
G4512et3	TrGNC	+ NO → 0.95 LHC4ACCHO + 0.95 HO$_2$ + 0.95 NO$_2$ + .05 LISOPACNO3	KRO2NO	Lockwood et al. (2010),Taraborrelli (2013a)
G4513et4	TrGNC	+ NO$_3$ → LHC4ACCHO + HO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)
G4514e	TrGC	LISOPACOOH + OH → LISOPACO2 + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4514et2	TrGC	LISOPACOOH + OH → + HO$_2$ + POHORG	ks*fallyl*fsoh	Taraborrelli (2013a)
G4514et3	TrGC	LISOPACOOH + OH → LHC4ACCHO + OH + POHORG + POHORG	ks*fsooh*fallyl+ krohro	Taraborrelli (2013a)
G4514et4	TrGC	LISOPACOOH + OH → + OH + POHORG + POHORG	(kadt+kads)*ach2oh*ach2ooh	Taraborrelli (2013a)
G4515	TrGC	ISOPAOH + OH → LHC4ACCHO + HO$_2$ + POHORG	(kadt+kads)*ach2oh*ach2oh+ ks*fsoh*fallyl+krohro	Taraborrelli (2013a)
G4516e	TrGNC	LISOPACNO3 + OH → + POHORG	9.5E-11	Paulot et al. (2009a),Taraborrelli (2013a)
G4517e	TrGC	ISOPBO2 → .8 MVK + .8 HCHO + .8 HO$_2$ + .2 ISOPBOH	8.E-13*RO2	Rickard and Pascoe (2009)
G4518	TrGC	ISOPBO2 + HO$_2$ → ISOPBOOH	.706*KRO2HO2	Rickard and Pascoe (2009)
G4519e	TrGNC	ISOPBO2 + NO → .947 MVK + .947 HCHO + .947 HO$_2$ + .947 NO$_2$ + .053 ISOPBNO3	KRO2NO	Lockwood et al. (2010),Taraborrelli (2013a)
G4520e	TrGNC	ISOPBO2 + NO$_3$ → MVK + .75 HCHO + .75 HO$_2$ + .25 CH$_3$O$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)
G4521ea	TrGC	ISOPBOOH + OH → + OH + POHORG + POHORG	(kads+kadp)*ach2ooh	Paulot et al. (2009b),Taraborrelli (2013a)
G4521eb	TrGC	ISOPBOOH + OH → ISOPBO2 + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4521ec	TrGC	ISOPBOOH + O$_3$ → 0.1368 MACROOH + 0.1368 H$_2$O$_2$ + 0.2280 HO$_2$ + 0.4332 CH$_3$COCH$_2$OH + 0.2280 CO$_2$ + 0.6384 OH + 0.2052 CO + .57 HCHO + .43 MACROOH + 0.06880 HO$_2$ + 0.06880 OH + 0.2709 CO + 0.1591 HOCH2OOH + 0.7072 POHORG	1.E-17	Taraborrelli (2013a)*
G41911	TrGC	ISOPBOOH + OH → MGLYOX + HOCH$_2$CHO + POHORG	krohro+ks*falk*fsoh	Taraborrelli (2013a)
G4522e	TrGC	ISOPBOOH + OH → MVK + .75 HCHO + .75 HO$_2$ + .25 CH$_3$O$_2$ + POHORG	ks*falk*fsoh+(kadp+kads)*ach2oh	Taraborrelli (2013a)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4523e	TrGNC	ISOPBNO3 + OH → + POHORG	1.3E−11	Paulot et al. (2009a),Taraborrelli (2013a)
G4524	TrGC	ISOPDO2 → .8 MACR + .8 HCHO + .8 HO$_2$ + .1 HCOC5 + .1 ISOPDOH	2.9E-12*RO2	Rickard and Pascoe (2009)
G4525	TrGC	ISOPDO2 + HO$_2$ → ISOPDOOH	.706*KRO2HO2	Rickard and Pascoe (2009)
G4526e	TrGNC	ISOPDO2 + NO → .85 MACR + .85 HCHO + .85 HO$_2$ + .85 NO$_2$ + .15 ISOPDNO3	KRO2NO	Lockwood et al. (2010),Taraborrelli (2013a)
G4527	TrGNC	ISOPDO2 + NO$_3$ → MACR + HCHO + HO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)
G4528ea	TrGC	ISOPDOOH + OH → + OH + POHORG + POHORG	(kadt+kadp)*ach2ooh	Paulot et al. (2009b),Taraborrelli (2013a)
G4528eb	TrGC	ISOPDOOH + OH → ISOPDO2 + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4528ec	TrGC	ISOPDOOH + OH → HCOC5 + OH + POHORG + POHORG	kt*ftooh*fallyl*fpch2oh	Taraborrelli (2013a)
G4528ed	TrGC	ISOPDOOH + OH → CH$_3$COCH$_2$OH + GLYOX + OH + POHORG + POHORG	ks*fpch2oh*fsoh	Taraborrelli (2013a)
G45222	TrGC	ISOPDOOH + O$_3$ → 1.393 OH + 1.393 POHORG + BIACETOH + .67 HCHO + 0.05280 HO$_2$ + 0.2079 CO + 0.1221 HOCH2OOH	1.E-17	Taraborrelli (2013a)*
G4529e	TrGC	ISOPDOH + OH → HCOC5 + HO$_2$ + POHORG	2.*krohro+(kt*ftoh*fallyl+ks*fsoh)*fpch2oh+(kadt+kadp)*ach2oh	Taraborrelli (2013a)
G4530e	TrGNC	ISOPDNO3 + OH → + POHORG	1.3E−11	Paulot et al. (2009a),Taraborrelli (2013a)
G4531	TrGC	NISOPO2 → .8 NC4CHO + .6 HO$_2$ + .2 LISOPACNO3	1.3E-12*RO2	Rickard and Pascoe (2009)
G4532	TrGNC	NISOPO2 + HO$_2$ → NISOPOOH	.706*KRO2HO2	Rickard and Pascoe (2009)
G4533	TrGNC	NISOPO2 + NO → NC4CHO + HO$_2$ + NO$_2$	KRO2NO	Rickard and Pascoe (2009)
G4534	TrGNC	NISOPO2 + NO$_3$ → NC4CHO + HO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)
G4535	TrGNC	NISOPOOH + OH → NC4CHO + OH + POHORG + POHORG	1.03E-10	Rickard and Pascoe (2009)
G4536	TrGNC	NC4CHO + OH → LNISO3 + POHORG	4.16E-11	Rickard and Pascoe (2009)
G4537e	TrGNC	NC4CHO + O$_3$ → .27 NOA + .027 HCOCO$_2$H + .0162 GLYOX + .0162 H$_2$O$_2$ + .1458 + .0405 HCOOH + .0405 CO + .8758 OH + .8758 POHORG + .365 MGLYOX + .73 NO$_2$ + 0.7705 HCHO + .4055 CO$_2$ + .73 GLYOX	2.40E-17	Taraborrelli (2013a)*
G4538	TrGNC	NC4CHO + NO$_3$ → LNISO3 + HNO$_3$	KNO3AL*4.25	Rickard and Pascoe (2009)
G4539	TrGNC	LNISO3 + HO$_2$ → LNISOOH	.5*.706*KRO2HO2 + .5*KAPHO2	Rickard and Pascoe (2009)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4540e	TrGNC	LNISO3 + NO → NOA + .5 + .5 CO + .5 HO$_2$ + NO$_2$ + .5 CO$_2$	.5*KAPNO +.5*KRO2NO	Rickard and Pascoe (2009)
G4541e	TrGNC	LNISO3 + NO$_3$ → NOA + .5 + .5 CO + .5 HO$_2$ + NO$_2$ + .5 CO$_2$	1.3*KRO2NO3	Rickard and Pascoe (2009)
G4542	TrGNC	LNISOOH + OH → LNISO3 + POHORG	2.65E-11	Rickard and Pascoe (2009)
G4543e	TrGC	LHC4ACCHO + OH → LC578O2 + POHORG	(kadtertprim+kads)*acho*ach2oh	Taraborrelli (2013a)
G4543et2	TrGC	LHC4ACCHO + OH → LHC4ACCO3 + POHORG	kcho	Taraborrelli (2013a)
G4543et3	TrGC	LHC4ACCHO + OH → + HO$_2$ + POHORG	ks*fsoh*fallyl	Taraborrelli (2013a)
G4544	TrGC	LHC4ACCHO + O$_3$ → .2225 CH$_3$C(O)OO + .89 CO + .0171875 HOCH$_2$CO$_2$H + .075625 H$_2$O$_2$ + .0171875 HCOCO$_2$H + .2775 CH$_3$COCH$_2$OH + .6675 HO$_2$ + .2603125 GLYOX + .2225 HCHO + .89 OH + .2603125 HOCH$_2$CHO + .5 MGLYOX + .89 POHORG	2.40E-17	Rickard and Pascoe (2009)
G4545	TrGNC	LHC4ACCHO + NO$_3$ → LHC4ACCO3 + HNO$_3$	KNO3AL*4.25	Rickard and Pascoe (2009)
G4546e	TrGC	LC578O2 → .25 CH$_3$COCH$_2$OH + .75 MGLYOX + .25 + .75 HOCH$_2$CHO + .75 HO$_2$	9.20E-14*RO2	Rickard and Pascoe (2009)
G4547e	TrGC	LC578O2 + HO$_2$ → MGLYOX + HOCH$_2$CHO + OH + POHORG	KRO2HO2*0.706*rcoch2o2_oh	Rickard and Pascoe (2009)
G4547et2	TrGC	LC578O2 + HO$_2$ → LC578OOH	KRO2HO2*0.706*rcoch2o2_ooh	Rickard and Pascoe (2009)
G4548e	TrGNC	LC578O2 + NO → .25 CH$_3$COCH$_2$OH + .75 MGLYOX + .25 + .75 HOCH$_2$CHO + .75 HO$_2$ + NO$_2$	KRO2NO	Rickard and Pascoe (2009)
G4549e	TrGNC	LC578O2 + NO$_3$ → .25 CH$_3$COCH$_2$OH + .75 MGLYOX + .25 + .75 HOCH$_2$CHO + .75 HO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009)
G4586e	TrGC	LC578O2 → .25 CH$_3$COCH$_2$OH + .75 MGLYOX + .25 HOCH$_2$CHO + .75 HOCH$_2$CHO + HO$_2$ + OH + POHORG	KHSB	Taraborrelli (2013a)
G4550e	TrGC	LC578OOH + OH → LC578O2 + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)*
G4550et2	TrGC	LC578OOH + OH → + HO$_2$ + POHORG	kt*fo*ftch2oh*falk+ kt*ftoh*fpch2oh*fpch2oh+ ks*fsoh*fpch2oh	Taraborrelli (2013a)*
G4551e	TrGC	LHC4ACCO3 → .3 LHC4ACCO2H + .7 OH + .35 MACRO2 + .35 LHMVKABO2 + .7 CO$_2$ + .7 POHORG	1.00E-11*RO2	Taraborrelli (2013a)*
G4552e	TrGC	LHC4ACCO3 + HO$_2$ → 2 OH + .5 MACRO2 + .5 LHMVKABO2 + CO$_2$ + 2 POHORG	KAPHO2*rco3_oh	Taraborrelli (2013a)*
G4552et2	TrGC	LHC4ACCO3 + HO$_2$ → LHC4ACCO3H	KAPHO2*rco3_ooh	Taraborrelli (2013a)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4552et3	TrGC	LHC4ACCO3 + HO$_2$ → LHC4ACCO2H + O$_3$	KAPHO2*rco3_o3	Taraborrelli (2013a)
G4553e	TrGNC	LHC4ACCO3 + NO → .5 MACRO2 + .5 LHMVKABO2 + NO$_2$ + CO$_2$	KAPNO	Taraborrelli (2013a)*
G4554	TrGNC	LHC4ACCO3 + NO$_2$ → LC5PAN1719	k_CH3CO3_NO2	Rickard and Pascoe (2009)
G4555e	TrGNC	LHC4ACCO3 + NO$_3$ → .5 MACRO2 + .5 LHMVKABO2 + NO$_2$ + CO$_2$	1.6*KRO2NO3	Taraborrelli (2013a)*
G4556e	TrGC	LHC4ACCO2H + OH → OH + .5 MACRO2 + .5 LHMVKABO2 + CO$_2$ + POHORG + POHORG	2.52E-11	Taraborrelli (2013a)
G4557	TrGC	LHC4ACCO3H + OH → LHC4ACCO3 + POHORG	2.88E-11	Rickard and Pascoe (2009)
G4558	TrGNC	LC5PAN1719 → LHC4ACCO3 + NO$_2$	k_PAN_M	Rickard and Pascoe (2009)
G4559	TrGNC	LC5PAN1719 + OH → .5 MACROH + .5 HO12CO3C4 + CO + NO$_2$ + POHORG	2.52E-11	Rickard and Pascoe (2009)
G4560a	TrGC	HCOC5 + OH → C59O2 + POHORG	3.81E-11	Rickard and Pascoe (2009)
G4560eb	TrGC	HCOC5 + O$_3$ → BIACETOH + .335 H$_2$O$_2$ + 0.67 HCHO + 0.2079 CO + 0.1221 HOCH2OOH + 0.05280 OH + 0.0528 POHORG	7.51E-16*EXP(-1521./temp)	Taraborrelli (2013a)
G4561	TrGC	C59O2 → CH$_3$COCH$_2$OH +	9.20E-14*RO2	Taraborrelli (2013a)
G4562e	TrGC	C59O2 + HO$_2$ → OH + CH$_3$COCH$_2$OH + + POHORG	KRO2HO2*0.706*rcoch2o2_oh	Taraborrelli (2013a)
G4562et2	TrGC	C59O2 + HO$_2$ → C59OOH	KRO2HO2*0.706*rcoch2o2_ooh	Taraborrelli (2013a)
G4563	TrGNC	C59O2 + NO → CH$_3$COCH$_2$OH + + NO$_2$	KRO2NO	Taraborrelli (2013a)
G4564	TrGNC	C59O2 + NO$_3$ → CH$_3$COCH$_2$OH + + NO$_2$	KRO2NO3	Taraborrelli (2013a)
G4565	TrGC	C59OOH + OH → C59O2 + POHORG	9.7E-12	Taraborrelli (2013a)
G4566e	TrGC	+ OH → LC578O2 + H$_2$O + POHORG	5.78E-11*EXP(-400/temp)	Paulot et al. (2009b),Taraborrelli (2013a)
G4567e	TrGC	ISOPBO2 → MVK + HCHO + OH + POHORG	KHSB	Taraborrelli (2013a)
G4568e	TrGC	ISOPDO2 → MACR + HCHO + OH + POHORG	KHSD	Taraborrelli (2013a)
G4577ea	TrGC	+ OH → .6 + .4 + POHORG	kadt*acho*ach2ooh	Taraborrelli (2013a)
G4577eb	TrGC	+ OH → .6 + .4 + POHORG	kads*acho*ach2ooh	Taraborrelli (2013a)
G4577e	TrGC	+ OH → + POHORG	kt*fo*falk+0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4577et2	TrGC	+ OH → OH + + POHORG + POHORG	ks*fsooh*fallyl	Taraborrelli (2013a)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4577et3	TrGC	+ O$_3$ → .4672 OH + .2336 + .2336 CO + .2336 CH$_3$C(O)OO + .4672 + .1728 MGLYOX + .1901 OH + .0864 GLYOX + .02765 + .02765 H$_2$O$_2$ + .02592 CH$_3$OOH + .02592 CO$_2$ + .01037 + .01555 HOCH2OOH + .01555 CO + .006912 + .2628 OH + .1314 MGLYOX + .1314 OH + .1314 + 0.2628 GLYOX + .0972 CH$_3$COCH$_2$O$_2$H + .00972 HCOCO2H + .005832 GLYOX + .005832 H$_2$O$_2$ + .05249 OH + .05249 + .01458 HCHO + .01458 CO$_2$ + .01458 HCOOH + .01458 CO+ 1.104 POHORG	2.4E-17	Taraborrelli (2013a)*
G4578e	TrGC	→ .78 CH$_3$COCH$_2$O$_2$H + .78 + .22 CO2H3CHO + .22 HCHO + .22 OH + .22 POHORG	8.00E-13*RO2	Taraborrelli (2013a)
G4579e	TrGC	+ NO → .78 CH$_3$COCH$_2$O$_2$H + .78 + .22 CO2H3CHO + .22 HCHO + .22 OH + .22 POHORG + NO$_2$	KRO2NO	Taraborrelli (2013a)
G4580e	TrGC	+ HO$_2$ →	KRO2HO2*0.706	Taraborrelli (2013a)
G4580ea	TrGC	→ CH$_3$COCH$_2$O$_2$H + GLYOX + OH + POHORG	KHSB	Taraborrelli (2013a)
G4581e	TrGC	→ OH + + POHORG	K15HSDHB	Taraborrelli (2013a)
G4581et2	TrGC	+ OH → + OH + POHORG + POHORG	ks*fsooh*fpch2oh	Taraborrelli (2013a)
G4581et3	TrGC	+ OH → CH$_3$COCH$_2$O$_2$H + OH + 2 CO + 2 HO$_2$ + POHORG + POHORG	kt*ftoh*fpch2oh*fpch2oh	Taraborrelli (2013a)
G4581et4	TrGC	+ OH → + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G4581et6	TrGC	→ MGLYOX + + HO$_2$	2.90E-12*RO2	Taraborrelli (2013a)
G4581et7	TrGC	+ NO → MGLYOX + + HO$_2$ + NO$_2$	KRO2NO	Taraborrelli (2013a)
G4581et8	TrGC	+ HO$_2$ → .5 CH$_3$C(O)OO + .5 CO + .5 MGLYOX + HO$_2$ +	KRO2HO2*0.706	Taraborrelli (2013a)*
G4581et9	TrGC	→ MGLYOX + OH + + POHORG	KHSD	Taraborrelli (2013a)
G4581et10	TrGC	→ .625 MGLYOX + 2 CO + 1.625 HO$_2$ + .375 CH$_3$C(O)OO + .375 CO$_2$ + OH + POHORG	K15HSDHB	Taraborrelli (2013a)*
G4582e	TrGC	LHC4ACCO3 → + HO$_2$	K16HS	Taraborrelli (2013a)
G4583e	TrGC	+ OH → + POHORG	2*kt*fo*falk+(kadt+kads)*acho*acho	Taraborrelli (2013a)
G4584e	TrGC	+ HO$_2$ → OH + POHORG + MGLYOX +	KRO2HO2*0.706*rcoch2o2_oh	Taraborrelli (2013a)
G4584et2	TrGC	+ HO$_2$ →	KRO2HO2*0.706*rcoch2o2_ooh	Taraborrelli (2013a)
G4585e	TrGC	+ NO → NO$_2$ + MGLYOX +	KRO2NO	Taraborrelli (2013a)
G4585et2	TrGC	→ MGLYOX +	8.00E-13*RO2	Taraborrelli (2013a)
G4585et3	TrGC	+ OH → MGLYOX + 2 CO + .5 OH + POHORG + .5 POHORG	2.*kt*fo*ftch2oh*falk+ kt*ftoh*fcho*fpch2oh	Taraborrelli (2013a)*

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G4587e	TrGC	+ NO → .21 NOA + .21 HOCH$_2$CHO + .21 HO$_2$ + .49 HO12CO3C4 + .49 HCHO + .49 NO$_2$ + .045 + .045 HCHO + .255 CH$_3$COCH$_2$OH + .255 + .225 H$_2$O$_2$ + NO$_2$	KRO2NO	Taraborrelli (2013a)
G4587et2	TrGC	→ .21 NOA + .21 HOCH$_2$CHO + .21 HO$_2$ + .49 HO12CO3C4 + .49 HCHO + .49 NO$_2$ + .045 + .045 HCHO + .255 CH$_3$COCH$_2$OH + .255 + .225 H$_2$O$_2$	8.00E-13*RO2+KRO2HO2*0.706*c(ind_HO2)	Taraborrelli (2013a)
G4587et3	TrGC	+ NO → .6 CH$_3$COCH$_2$OH + .6 HOCH$_2$CHO + .26 + .14 + .4 HCHO + .4 HO$_2$ + 1.6 NO$_2$	KRO2NO	Taraborrelli (2013a)
G4587et4	TrGC	→ .6 CH$_3$COCH$_2$OH + .6 HOCH$_2$CHO + .26 + .14 + .4 HCHO + .4 HO$_2$ + .6 NO$_2$	2.9E-12*RO2+KRO2HO2*0.706*c(ind_HO2)	Taraborrelli (2013a)
G4588e	TrGNC	LISOPACNO3 + O$_3$ → .8704 OH + .365 HO$_2$ + .73 MGLYOX + .4325 + .135 CH$_3$COCH$_2$OH + .0675 GLYOX + .4325 NO$_2$ + .0891 H$_2$O$_2$ + .135 NOA + .0675 + .3866 HOCH$_2$CHO + .0405 CH$_3$OH + .0405 CO + .0054 + .8704 POHORG	4.E-16	Taraborrelli (2013a)
G4599e	TrGC	LISOPACOOH + O$_3$ → 1.3272 OH + 0.36986 HO$_2$ + .0432 H$_2$O$_2$ + 0.23002 CO + .2025 CH$_3$OOH + .01215 HOCH2OOH + 0.3704 HCHO + .00405 CH$_3$OH + .0405 CO$_2$ + .1825 + .365 MGLYOX + .3866 + .135 CH$_3$COCH$_2$OH + .0675 GLYOX + .00324 + .3866 HOCH$_2$CHO + .135 CH$_3$COCH$_2$H + .0675 + .0054 + 1.3272 POHORG	4.829E-16	Taraborrelli (2013a)
G4598et3	TrGC	+ OH → .62 CO2H3CHO + .62 OH + .62 CO$_2$ + .38 MGLYOX + .38 HCOCO$_3$H + .38 HO$_2$ + POHORG + .62 POHORG	kadt*acho*aco2h	Taraborrelli (2013a)*
G4598et4	TrGC	+ OH → .62 + 1.24 CO + 1.24 HO$_2$ + .38 + .38 CO + .38 HO$_2$ + .38 OH + .38 CO$_2$ + POHORG + .38 POHORG	kads*acho*aco2h	Taraborrelli (2013a)*
G41311	TrGC	→ .7143 MACR + .2857 MVK + HCHO + HO$_2$	2.40E-12*RO2	Taraborrelli (2013a)
G41341	TrGC	+ NO → .7143 MACR + .2857 MVK + HCHO + HO$_2$ + NO$_2$	KRO2NO	Taraborrelli (2013a)
G41351t2	TrGC	+ HO$_2$ → .7143 MACR + .2857 MVK + HCHO + HO$_2$	KRO2HO2*0.706	Taraborrelli (2013a)
G41361	TrGC	+ NO$_3$ → .7143 MACR + .2857 MVK + HCHO + HO$_2$ + NO$_2$	KRO2NO3	Taraborrelli (2013a)
G41378	TrGC	→	9.39E9*EXP(-7322/temp)	Taraborrelli (2013a)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G41341t2	TrGC	→ .7143 MACR + .2857 MVK + HCHO + OH + POHORG	.7143*KHSD+.2857*KHSB	Taraborrelli (2013a)
G413112	TrGC	→ + HO$_2$	8.00E-13*RO2	Taraborrelli (2013a)
G413416	TrGC	+ NO → + HO$_2$ + NO$_2$	KRO2NO	Taraborrelli (2013a)*
G413519	TrGC	+ HO$_2$ →	KRO2HO2*0.706	Taraborrelli (2013a)
G413618	TrGC	+ NO$_3$ → + HO$_2$ + NO$_2$	KRO2NO3	Taraborrelli (2013a)
G413417	TrGC	→ + OH + POHORG	KHSB	Taraborrelli (2013a)
G413619	TrGC	+ OH → + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013a)
G413621	TrGC	+ OH → + MGLYOX + 2 CO + 2 HO$_2$ + POHORG	kt*ftoh*falk*fpch2oh	Taraborrelli (2013a)*
G413622	TrGC	+ OH → .8405 HCHO + .8405 OH + .8405 CO2H3CHO + .1595 + .1595 HO$_2$ + POHORG + .8405 POHORG	ks*fsoh*falk+ks*fsooh*falk	Taraborrelli (2013a)
G4136	TrGC	+ OH → CH$_3$C(O)OO + CO$_2$ + 2 HCHO + POHORG	kt*fo*ftch2oh	Taraborrelli (2013a)*
G413610	TrGC	+ OH → GLYOX + CH$_3$C(O)OO + HCHO + POHORG	ks*fcho*fsooh	Taraborrelli (2013a)
G41361t2	TrGC	+ OH → MGLYOX + GLYOX + HO$_2$ + POHORG	ks*fco*fsooh	Taraborrelli (2013a)
G45mbo1	TrGC	+ OH →	8.1E-12*EXP(610/TEMP)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo2	TrGC	+ O$_3$ → HCHO + .16 CH$_3$COCH$_3$ + .16 HO$_2$ + .16 CO + .16 OH + .84	1.0E-17*0.57	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo3	TrGC	+ O$_3$ → + .63 CO + .37 HOCH2OOH + .16 OH + .16 HO$_2$	1.0E-17*0.43	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo4	TrGC	+ NO$_3$ →	4.6E-14*EXP(-400/TEMP)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo5	TrGC	+ HO$_2$ →	KRO2HO2*0.706	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo6	TrGC	+ NO →	KRO2NO*(0.064+0.026)/2.	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo7	TrGC	+ NO → HOCH$_2$CHO + CH$_3$COCH$_3$ + HO$_2$ + NO$_2$	KRO2NO*(0.936+0.974)/2.*.67	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo8	TrGC	+ NO → + HCHO + HO$_2$ + NO$_2$	KRO2NO*(0.936+0.974)/2.*.33	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo9	TrGC	→ HOCH$_2$CHO + CH$_3$COCH$_3$ + HO$_2$	8.8E-13*RO2*.67	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo10	TrGC	→ + HCHO + HO$_2$	8.8E-13*RO2*.33	Rickard and Pascoe (2009), Taraborrelli (2013b)

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#	labels	reaction	rate coefficient	reference
G45mbo11	TrGC	+ OH → + OH	.67*2.93E-11+.33*2.05E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G45mbo12	TrGC	+ OH →	.6*k_CH3OOH_OH	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo13	TrGC	+ hν → HOCH$_2$CHO + CH$_3$COCH$_3$ + HO$_2$ + OH	1.14*jx(ip_CH3OOH)*.67	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo14	TrGC	+ hν → + HCHO + HO$_2$ + OH	1.14*jx(ip_CH3OOH)*.33	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo15	TrGC	+ OH → + NO$_2$	.67*1.75E-12+.33*2.69E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G45mbo16	TrGC	+ OH → + HO$_2$	3.79E-12	Rickard and Pascoe (2009)
G45mbo17	TrGC	+ hν → HCHO + HO$_2$ +	J_ACETOL	Rickard and Pascoe (2009)
G45mbo18	TrGC	+ OH → CO +	1.38E-11	Rickard and Pascoe (2009)
G45mbo19	TrGC	+ hν → CO + HO$_2$ +	jx(ip_MGLYOX)	Rickard and Pascoe (2009)
G45mbo20	TrGC	+ OH →	1.4E-11	Rickard and Pascoe (2009)
G45mbo21	TrGC	+ hν → CH$_3$COCH$_3$ + HO$_2$ + HO$_2$ + CO	J_ACETOL	Rickard and Pascoe (2009)
G45mbo22	TrGC	+ HO$_2$ → CH$_3$COCH$_3$ + HO$_2$ + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo23	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*rco3_o3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo24	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo25	TrGC	+ NO → CH$_3$COCH$_3$ + HO$_2$ + NO$_2$	KAPNO	Rickard and Pascoe (2009)
G45mbo26	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009)
G45mbo27	TrGC	+ NO$_3$ → CH$_3$COCH$_3$ + HO$_2$ + NO$_2$	KRO2NO3*1.74	Rickard and Pascoe (2009)
G45mbo28	TrGC	→ CH$_3$COCH$_3$ + HO$_2$	1.00E-11*RO2*0.7	Rickard and Pascoe (2009)
G45mbo29	TrGC	→	1.00E-11*RO2*0.3	Rickard and Pascoe (2009)
G45mbo30	TrGC	+ OH → CH$_3$COCH$_3$ + HO$_2$	1.72E-12	Rickard and Pascoe (2009)
G45mbo31	TrGC	+ hν → CH$_3$COCH$_3$ + HO$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)
G45mbo32	TrGC	OH + →	4.80E-12	Rickard and Pascoe (2009)
G45mbo33	TrGC	→ + NO$_2$	K_PAN_M	Rickard and Pascoe (2009)
G45mbo34	TrGC	+ OH → CH$_3$COCH$_3$ + CO + NO$_2$	4.75E-13	Rickard and Pascoe (2009)
G45mbo35	TrGC	+ HO$_2$ →	KRO2HO2*0.706	Rickard and Pascoe (2009), Taraborrelli (2013b)

#	labels	reaction	rate coefficient	reference
G45mbo36	TrGC	+ NO → .65 + .65 CH$_3$COCH$_3$ + .65 HO$_2$ + .35 + .35 HCHO + .35 NO$_2$ + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo37	TrGC	+ NO$_3$ →.65 + .65 CH$_3$COCH$_3$ + .65 HO$_2$ + .35 + .35 HCHO + .35 NO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo38	TrGC	→ .65 + .65 CH$_3$COCH$_3$ + .65 HO$_2$ + .35 + .35 HCHO + .35 NO$_2$	8.8E-13*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo39	TrGC	+ OH → .65 + .35 + OH	.65*4.89E-12+.35*2.52E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo40	TrGC	+ OH →	.6*k_CH3OOH_OH	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo41	TrGC	+ hν → + CH$_3$COCH$_3$ + HO$_2$ + OH	1.14*jx(ip_CH3OOH)*.65	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo42	TrGC	+ hν → + HCHO + NO$_2$ + OH	1.14*jx(ip_CH3OOH)*.35	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo43	TrGC	+ OH → CH$_3$COCH$_3$ + HCHO + CO$_2$ + NO$_2$	1.23E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G45mbo44	TrGC	+ OH →	4.26E-12	Rickard and Pascoe (2009)
G45mbo45	TrGC	+ HO$_2$ → + NO$_2$ + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo46	TrGC	+ HO$_2$ →	KAPHO2*(rco3_o3+rco3_ooh)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo47	TrGC	+ NO → + NO$_2$ + NO$_2$	KAPNO	Rickard and Pascoe (2009)
G45mbo48	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009)
G45mbo49	TrGC	+ NO$_3$ → + NO$_2$ + NO$_2$	KRO2NO3*1.74	Rickard and Pascoe (2009)
G45mbo50	TrGC	→ + NO$_2$	1.00E-11*RO2	Rickard and Pascoe (2009)
G45mbo51	TrGC	+ OH →	4.50E-12	Rickard and Pascoe (2009)
G45mbo52	TrGC	→ + NO$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)
G45mbo53	TrGC	+ OH → + CO + NO$_2$ + NO$_2$	1.27E-12	Rickard and Pascoe (2009)
G45mbo54	TrGC	→ + NO$_2$	K_PAN_M	Rickard and Pascoe (2009)
G45mbo55	TrGC	→	1.60E-17*C(ind_H2O)*(0.08+0.15)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo56	TrGC	→ + H$_2$O$_2$	1.60E-17*C(ind_H2O)*0.77	Rickard and Pascoe (2009), Taraborrelli (2013b)
G45mbo57	TrGC	+ CO →	1.20E-15	Rickard and Pascoe (2009)
G45mbo58	TrGC	+ NO → + NO$_2$	1.00E-14	Rickard and Pascoe (2009)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G45mbo59	TrGC	+ NO$_2$ → + NO$_3$	1.00E-15	Rickard and Pascoe (2009)
G45mbo60	TrGC	+ SO$_2$ → + H$_2$SO$_4$	7.00E-14	Rickard and Pascoe (2009)
G410apin1	TrGC	+ OH →	1.47E-11*EXP(467/TEMP)*(.50+.25)	Vereecken et al. (2007), Taraborrelli (2013b)*
G410apin2	TrGC	+ OH → + HO$_2$	1.47E-11*EXP(467/TEMP)*.25*.60	Vereecken et al. (2007), Taraborrelli (2013b)*
G410apin3	TrGC	+ OH →	1.47E-11*EXP(467/TEMP)*.25*.40	Vereecken et al. (2007), Taraborrelli (2013b)*
G410apin4	TrGC	+ NO → + HO$_2$	KRO2NO*0.770	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin5	TrGC	+ NO →	KRO2NO*0.230	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin6	TrGC	+ HO$_2$ →	KRO2HO2*0.914	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin7	TrGC	→ + HO$_2$	RO2*(.33*9.20E-14+.67*8.80E-13)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin9	TrGC	+ OH → .33 + .67	.33*1.83E-11+.67*3.28E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin10	TrGC	+ hν → + HO$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin11	TrGC	+ OH → .33 + .67 + NO$_2$	.33*5.50E-12+.67*3.64E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin12	TrGC	+ OH →	(kads+kadt)*acoch3	Vereecken et al. (2007), Taraborrelli (2013b)
G410apin13	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)	Vereecken et al. (2007), Taraborrelli (2013b)
G410apin14	TrGC	+ NO → + HO$_2$ + NO$_2$	KRO2NO	Vereecken et al. (2007), Taraborrelli (2013b)
G410apin15	TrGC	+ HO$_2$ →	KRO2HO2*0.914	Vereecken et al. (2007), Taraborrelli (2013b)
G410apin16	TrGC	→ + HO$_2$	RO2*9.20E-14	Vereecken et al. (2007), Taraborrelli (2013b)
G410apin17	TrGC	+ OH → LCARBON	1E-11	Vereecken et al. (2007), Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apin18	TrGC	+ hν → LCARBON + OH	1.14*jx(ip_CH3OOH)	Vereecken et al. (2007), Taraborrelli (2013b)
G410apin18t2	TrGC	+ OH →	4.20E-11*0.772	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin19	TrGC	+ OH →	4.20E-11*0.228	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin20	TrGC	→ + CO + HO$_2$	jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin21	TrGC	+ NO$_3$ → + HNO$_3$	3.80E-14	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apin	TrGC	→ 0.3 + 0.7	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint2	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint3	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*rco3_o3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint4	TrGC	+ HO$_2$ → + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint5	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint6	TrGC	+ NO → + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint7	TrGC	+ NO$_3$ → + NO$_2$	KRO2NO3*1.60	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint8	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint9	TrGC	+ OH → + CO + NO$_2$	3.66E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint10	TrGC	→	1.30E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint11	TrGC	+ NO →	KRO2NO*0.157	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint12	TrGC	+ HO$_2$ →	KRO2HO2*0.890	Rickard and Pascoe (2009), Taraborrelli (2013b)

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#	labels	reaction	rate coefficient	reference
G410apint13	TrGC	+ NO → + NO$_2$	KRO2NO*0.843	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint14	TrGC	+ hν → + NO$_2$	J_IC3H7NO3+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint15	TrGC	+ OH → + NO$_2$	2.88E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint16	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint17	TrGC	+ OH →	1.90E-12*EXP(190/TEMP)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint18	TrGC	+ OH → + OH	1.30E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint19	TrGC	→	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint20	TrGC	+ NO → + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint21	TrGC	+ HO$_2$ →	KRO2HO2*0.890	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint22	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint23	TrGC	+ OH →	1.05E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint24	TrGC	→ + CH$_3$COCH$_3$	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint25	TrGC	+ NO →	KRO2NO*0.118	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint26	TrGC	+ NO → + CH$_3$COCH$_3$ + NO$_2$	KRO2NO*0.882	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint27	TrGC	+ HO$_2$ →	KRO2HO2*0.890	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint28	TrGC	+ hν → + CH$_3$COCH$_3$ + OH	1.14*jx(ip_CH3OOH)+2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint29	TrGC	+ OH →	2.05E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)

#	labels	reaction	rate coefficient	reference
G410apint30	TrGC	+ OH →	6.65E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint31	TrGC	+ hν → + HO$_2$	J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint32	TrGC	+ OH →	2.64E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint33	TrGC	+ hν → + CO + HO$_2$	jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint34	TrGC	+ NO$_3$ → + HNO$_3$	KNO3AL*8.5	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint35	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint36	TrGC	+ OH →	9.73E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint37	TrGC	→	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint38	TrGC	+ NO → + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint39	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint40	TrGC	+ HO$_2$ →	KAPHO2*(rco3_ooh+rco3_o3)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint41	TrGC	+ HO$_2$ → + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint42	TrGC	→	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint43	TrGC	+ HO$_2$ →	KRO2HO2*0.859	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint44	TrGC	+ NO → + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint45	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint46	TrGC	+ OH → + CO + NO$_2$	6.60E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint47	TrGC	$\rightarrow$ + OH	1.14*jx(ip_CH3OOH)+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint48	TrGC	+ OH $\rightarrow$	1.02E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint49	TrGC	+ hν $\rightarrow$ + OH	1.14*jx(ip_CH3OOH)+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint50	TrGC	+ OH $\rightarrow$	1.29E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint51	TrGC	$\rightarrow$ + CH_3COCH_3	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint52	TrGC	+ NO $\rightarrow$ + CH_3COCH_3 + NO_2	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint53	TrGC	+ HO_2 $\rightarrow$	KRO2HO2*0.859	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint54	TrGC	+ hν $\rightarrow$ + CH_3COCH_3 + OH	1.14*jx(ip_CH3OOH)+ jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint55	TrGC	+ OH $\rightarrow$	3.45E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint56	TrGC	+ HO_2 $\rightarrow$	KRO2HO2*0.914	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint57	TrGC	+ NO $\rightarrow$	KRO2NO*0.050	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint58	TrGC	+ NO $\rightarrow$ + NO_2	KRO2NO*0.950	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint59	TrGC	$\rightarrow$	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint60	TrGC	+ OH $\rightarrow$	2.75E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint61	TrGC	+ hν $\rightarrow$ + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint62	TrGC	+ OH $\rightarrow$ + CH_3COCH_3 + NO_2	2.25E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint63	TrGC	+ hν $\rightarrow$ + NO_2	J_IC3H7NO3+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint64	TrGC	+ HO_2 $\rightarrow$	KRO2HO2*0.914	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint65	TrGC	+ NO $\rightarrow$	KRO2NO*0.125	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint66	TrGC	+ NO $\rightarrow$ + CH_3COCH_3 + NO_2	KRO2NO*0.875	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint67	TrGC	$\rightarrow$ + CH_3COCH_3	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint68	TrGC	+ OH $\rightarrow$	8.01E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint69	TrGC	+ hν $\rightarrow$ + CH_3COCH_3 + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint70	TrGC	+ OH $\rightarrow$ + CH_3COCH_3 + NO_2	7.03E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint71	TrGC	+ hν $\rightarrow$ + CH_3COCH_3 + NO_2	J_IC3H7NO3+ jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint72	TrGC	+ NO_3 $\rightarrow$ + HNO_3	KNO3AL*5.5	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint73	TrGC	+ OH $\rightarrow$	6.70E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint74	TrGC	+ hν $\rightarrow$ + $CH_3C(O)OO$	2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint75	TrGC	+ HO_2 $\rightarrow$	KAPHO2*(rco3_ooh+rco3_o3)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint76	TrGC	+ HO_2 $\rightarrow$ + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint77	TrGC	+ NO $\rightarrow$ + NO_2	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint78	TrGC	+ NO_2 $\rightarrow$	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint79	TrGC	$\rightarrow$	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint80	TrGC	+ OH $\rightarrow$	4.75E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)

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#	labels	reaction	rate coefficient	reference
G410apint81	TrGC	$+ h\nu \rightarrow\ + OH$	1.14*jx(ip_CH3OOH)+2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint82	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.770	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint83	TrGC	$+ NO \rightarrow\ + HCHO + NO_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint84	TrGC	$\rightarrow\ + HCHO$	2.00E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint85	TrGC	$+ OH \rightarrow\ + CO + NO_2$	8.83E-13	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint86	TrGC	$\rightarrow\ + NO_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint87	TrGC	$+ OH \rightarrow$	1.01E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint88	TrGC	$+ h\nu \rightarrow\ + HCHO + OH$	1.14*jx(ip_CH3OOH)+ 2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint89	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.820	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint90	TrGC	$+ NO \rightarrow\ + CH_3C(O)OO + NO_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint91	TrGC	$\rightarrow\ + CH_3C(O)OO$	8.80E-13*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint92	TrGC	$+ OH \rightarrow\ + OH$	1.20E-10	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint93	TrGC	$+ h\nu \rightarrow\ + CH_3C(O)OO + OH$	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint94	TrGC	$\rightarrow CH_3C(O)OO +$	8.80E-13*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint95	TrGC	$+ NO \rightarrow CH_3C(O)OO +\ + NO_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint96	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.706	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint97	TrGC	$+ h\nu \rightarrow CH_3C(O)OO +\ + OH$	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint98	TrGC	$+ OH \rightarrow$	7.49E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint99	TrGC	$+ OH \rightarrow$	4.29E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint100	TrGC	$+ h\nu \rightarrow\ + HO_2 + CO$	jx(ip_HOCH2CHO)*2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint101	TrGC	$+ NO_3 \rightarrow\ + HNO_3$	2*KNO3AL*2.4	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint102	TrGC	$\rightarrow\ + HCHO + HO_2$	8.80E-13*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint103	TrGC	$+ NO \rightarrow$	KRO2NO*0.098	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint104	TrGC	$+ NO \rightarrow\ + HCHO + HO_2 + NO_2$	KRO2NO*0.902	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint105	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.770	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint106	TrGC	$+ h\nu \rightarrow\ + HCHO + HO_2 + NO_2$	2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint107	TrGC	$+ OH \rightarrow\ + NO_2$	7.11E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint108	TrGC	$+ h\nu \rightarrow\ + HCHO + HO_2 + OH$	1.14*jx(ip_CH3OOH)+2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint109	TrGC	$+ OH \rightarrow\ + OH$	8.69E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint110	TrGC	$+ h\nu \rightarrow\ + HOCH_2CO_3$	J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint111	TrGC	$+ OH \rightarrow\ + HO_2$	3.22E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint112	TrGC	$\rightarrow CH_3C(O)OO + HCHO + CO$	2.00E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint113	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.625	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint114	TrGC	$+ NO \rightarrow CH_3C(O)OO + HCHO + CO + NO_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint115	TrGC	+ OH → + OH	ks*fco*fsooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint116	TrGC	+ OH →	.6*k_CH3OOH_OH	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint117	TrGC	+ $h\nu$ → + OH + HO_2	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint118	TrGC	+ $h\nu$ → $CH_3C(O)OO$ + CO + OH + HCHO	J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint119	TrGC	+ $h\nu$ → $CH_3C(O)OO$ + $HCOCO_3$	2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint120	TrGC	+ OH → + CO	1.33E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint121	TrGC	+ $h\nu$ → + CO + HO_2	jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint122	TrGC	+ NO_3 → + CO + HNO_3	KNO3AL*5.5	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint123	TrGC	+ OH →	6.65E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint124	TrGC	+ $h\nu$ → + HO_2 + CO	jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint125	TrGC	+ $h\nu$ → $CH_3C(O)OO$ +	2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint126	TrGC	+ NO_3 → + HNO_3	KNO3AL*5.5	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint127	TrGC	→	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint128	TrGC	+ NO → + NO_2	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint129	TrGC	+ NO_2 →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint130	TrGC	+ HO_2 →	KAPHO2*(rco3_ooh+rco3_o3)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint131	TrGC	+ HO_2 → + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint132	TrGC	+ $h\nu$ → + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint133	TrGC	+ $h\nu$ →	4.23E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint134	TrGC	→ + NO_2	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint135	TrGC	+ OH → + CO + NO_2	3.12E-13	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint136	TrGC	→ 0.7 + 0.3	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint137	TrGC	+ NO → + NO_2	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint138	TrGC	+ NO_2 →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint139	TrGC	+ HO_2 →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint140	TrGC	+ HO_2 → + O_3	KAPHO2*rco3_o3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint141	TrGC	+ HO_2 → + CO_2 + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint142	TrGC	→ + NO_2	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint143	TrGC	+ OH → GLYOX + CO + NO_2	2.10E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint144	TrGC	+ OH →	2.14E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint145	TrGC	+ $h\nu$ → + HO_2	jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint146	TrGC	+ O_3 →	1.01E-15*EXP(-732/TEMP)*.50*.18	Capouet et al. (2008)
G410apint147	TrGC	+ O_3 →	1.01E-15*EXP(-732/TEMP)*.50*.16	Capouet et al. (2008)
G410apint148	TrGC	+ O_3 → OH + + CO + HO_2	1.01E-15*EXP(-732/TEMP)*.50*.66	Capouet et al. (2008)
G410apint149	TrGC	+ O_3 →	1.01E-15*EXP(-732/TEMP)*.50*.12	Capouet et al. (2008)
G410apint150	TrGC	+ O_3 → OH +	1.01E-15*EXP(-732/TEMP)*.50*(.22+.66)	Capouet et al. (2008)*
G410apint151	TrGC	→ + H_2O_2	1.00E-17*c(ind_H2O)	Rickard and Pascoe (2009), Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint152	TrGC	+ CO →	1.20E-15	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint153	TrGC	+ NO → + NO$_2$	1.00E-14	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint154	TrGC	+ NO$_2$ → + NO$_3$	1.00E-15	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint155	TrGC	+ SO$_2$ → + H$_2$SO$_4$	7.00E-14	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint156	TrGC	→	1.00E-17*c(ind_H2O)*(0.08+0.15)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint157	TrGC	→ + H$_2$O$_2$	1.00E-17*c(ind_H2O)*0.77	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint158	TrGC	+ CO →	1.20E-15	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint159	TrGC	+ NO → + NO$_2$	1.00E-14	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint160	TrGC	+ NO$_2$ → + NO$_3$	1.00E-15	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint161	TrGC	+ SO$_2$ → + H$_2$SO$_4$	7.00E-14	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint162	TrGC	→ + HCHO	2.00E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint163	TrGC	+ NO → + HCHO + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint164	TrGC	+ HO$_2$ →	KRO2HO2*0.914	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint165	TrGC	→ + HCHO + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint166	TrGC	+ OH → + OH	5.47E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint167	TrGC	+ hν → + HCHO + OH	J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint168	TrGC	+ OH → + CO	5.47E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint169	TrGC	+ hν → + CO + HO$_2$	jx(ip_MGLYOX)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint170	TrGC	→ .56 + .14 + 0.3	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint171	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint172	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*rco3_o3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint173	TrGC	+ HO$_2$ → .80 + 0.20 + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint174	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint175	TrGC	+ NO → 0.80 + 0.20 + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint176	TrGC	+ OH → 0.80 + 0.20	2.69E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint177	TrGC	+ hν → 0.80 + 0.20 + HO$_2$	jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint178	TrGC	→ 0.80 + 0.20 + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint179	TrGC	+ OH →	3.00E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint180	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint181	TrGC	+ OH → CH$_3$COCH$_3$ + + CO + NO$_2$	2.52E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint182	TrGC	→ 0.7 + 0.3	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint183	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint184	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*rco3_o3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint185	TrGC	+ HO$_2$ → + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint186	TrGC	+ NO → + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint187	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint188	TrGC	+ OH →	7.29E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint189	TrGC	→	1.30E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint190	TrGC	+ HO$_2$ →	KRO2HO2*0.859	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint191	TrGC	+ NO → + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint192	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint193	TrGC	+ OH →	1.04E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint194	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint195	TrGC	+ OH → + CO + NO$_2$	6.77E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint196	TrGC	→	9.20E-14*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint197	TrGC	+ NO → + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint198	TrGC	+ HO$_2$ →	KRO2HO2*0.859	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint199	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint200	TrGC	+ OH →	1.09E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint201	TrGC	→ CH$_3$COCH$_3$ +	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint202	TrGC	+ NO → CH$_3$COCH$_3$ + + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)*

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint203	TrGC	+ HO$_2$ →	KRO2HO2*0.859	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint204	TrGC	+ hν → CH$_3$COCH$_3$ + + OH	1.14*jx(ip_CH3OOH)+jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint205	TrGC	+ OH →	1.86E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint206	TrGC	+ NO$_3$ → + HNO$_3$	KNO3AL*8.5	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint207	TrGC	+ OH →	2.63E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint208	TrGC	→ + CO + HO$_2$	jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint209	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint210	TrGC	+ HO$_2$ → + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint211	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*rco3_o3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint212	TrGC	+ NO → + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint213	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint214	TrGC	+ NO$_3$ → + NO$_2$	KRO2NO3*1.74	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint215	TrGC	→	1.00E-11*RO2*0.7	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint216	TrGC	→	1.00E-11*RO2*0.3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint217	TrGC	+ HO$_2$ →	KRO2HO2*0.820	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint218	TrGC	+ NO → + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint219	TrGC	→	1.30E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint220	TrGC	+ OH →	9.65E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint221	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint222	TrGC	+ OH →	6.57E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint223	TrGC	+ OH → + CO + NO$_2$	2.96E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint224	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint225	TrGC	+ OH →	1.27E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint226	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint227	TrGC	+ HO$_2$ →	KRO2HO2*0.820	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint228	TrGC	+ NO → CH$_3$COCH$_3$ + + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint229	TrGC	→ CH$_3$COCH$_3$ +	6.70E-15*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint230	TrGC	+ OH →	3.31E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint231	TrGC	+ hν → CH$_3$COCH$_3$ + + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint232	TrGC	+ HO$_2$ →	KRO2HO2*0.625	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint233	TrGC	+ NO → + HO$_2$ + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint234	TrGC	→ + HO$_2$	8.80E-13*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint235	TrGC	+ OH →	7.46E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint236	TrGC	+ hν → + HO$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint237	TrGC	→	1.30E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint238	TrGC	+ HO$_2$ →	KRO2HO2*0.706	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint239	TrGC	+ NO → + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint240	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint241	TrGC	+ OH → + OH	1.01E-10	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint242	TrGC	→ GLYOX +	8.80E-13*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint243	TrGC	+ NO → GLYOX + + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint244	TrGC	+ HO$_2$ →	KRO2HO2*0.706	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint245	TrGC	+ OH →	1.33E-10	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint246	TrGC	+ hν → + CO + HO$_2$	jx(ip_HOCH2CHO)*2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint247	TrGC	+ NO$_3$ → + HNO$_3$	2*KNO3AL*5.5	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint248	TrGC	+ hν → GLYOX + + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint249	TrGC	+ OH → + OH	9.23E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint250	TrGC	→	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint251	TrGC	+ HO$_2$ →	KAPHO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint252	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint253	TrGC	+ NO → + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint254	TrGC	→ + HCHO	2.00E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint255	TrGC	+ HO$_2$ →	KRO2HO2*0.625	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint256	TrGC	+ NO → + HCHO + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint257	TrGC	+ OH → + CO + CO	2.64E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint258	TrGC	+ hν → + HO$_2$ + CO + CO	jx(ip_MGLYOX)+2.15*jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint259	TrGC	+ OH →	8.33E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint260	TrGC	+ hν → + HCHO + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint261	TrGC	+ OH →	7.55E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint262	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)+J_ACETOL	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint263	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint264	TrGC	+ OH → + CO + NO$_2$	7.19E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint265	TrGC	+ OH →	3.39E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint266	TrGC	+ hν → + HO$_2$ + CO	jx(ip_HOCH2CHO)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint267	TrGC	+ hν → + HO$_2$ + CO	jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint268	TrGC	+ NO$_3$ → + HNO$_3$	2*KNO3AL*4.0	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint269	TrGC	→	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint270	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint271	TrGC	+ HO$_2$ → + OH	KAPHO2*(1-rco3_ooh)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint272	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint273	TrGC	+ NO → + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint274	TrGC	+ OH →	1.63E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint275	TrGC	+ hν → + OH	1.14*jx(ip_CH3OOH)+jx(ip_MGLYOX)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint276	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint277	TrGC	+ OH → + CO + NO$_2$	1.27E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410apint278	TrGC	→ 0.7 HOCH$_2$CH$_2$O$_2$ + 0.3	1.00E-11*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint279	TrGC	+ NO → HOCH$_2$CH$_2$O$_2$ + NO$_2$	KAPNO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint280	TrGC	+ HO$_2$ →	KAPHO2*rco3_ooh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint281	TrGC	+ HO$_2$ → HOCH$_2$CH$_2$O$_2$ + OH	KAPHO2*rco3_oh	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint282	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*rco3_o3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint283	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint284	TrGC	+ OH → HOCH$_2$CH$_2$O$_2$	1.39E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint285	TrGC	+ OH →	1.73E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint286	TrGC	+ hν → HOCH$_2$CH$_2$O$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint287	TrGC	→ + NO$_2$	k_PAN_M	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410apint288	TrGC	+ OH → HOCH$_2$CHO + CO + NO$_2$	4.51E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint289	TrGC	+ NO$_3$ →	1.2E-12*EXP(490./temp)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint290	TrGC	→ + NO$_2$	(.65*6.70E-15+.35*2.50E-13)*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint291	TrGC	+ NO → + NO$_2$ + NO$_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint292	TrGC	+ HO$_2$ →	KRO2HO2*0.914	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint293	TrGC	+ NO$_3$ → + NO$_2$ + NO$_2$	KRO2NO3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint294	TrGC	+ hν → + NO$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint295	TrGC	+ OH →	.65*6.87E-12+.35*1.23E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)*
G410bpin	TrGC	+ OH →	1.47E-11*EXP(467/TEMP)*(0.8326*0.3+0.068)/(0.8326+0.068)	Vereecken and Peeters (2012)*
G410bpint2	TrGC	+ OH →	1.47E-11*EXP(467/TEMP)*0.8326*0.7/(0.8326+0.068)	Vereecken and Peeters (2012)*
G410bpint3	TrGC	+ HO$_2$ →	KRO2HO2*0.914	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint4	TrGC	+ NO →	KRO2NO*0.240	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint5	TrGC	+ NO → + HCHO + HO$_2$ + NO$_2$	KRO2NO*0.760	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint6	TrGC	→ + HCHO + HO$_2$	9.20E-14*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint7	TrGC	+ OH →	1.33E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint8	TrGC	+ hν → + HCHO + HO$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint9	TrGC	+ OH → + HCHO + NO$_2$	4.70E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410bpint10	TrGC	+ NO → + CH$_3$COCH$_3$ + NO$_2$	KRO2NO*0.892	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint11	TrGC	+ NO →	KRO2NO*0.108	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint12	TrGC	+ HO$_2$ →	KRO2HO2*0.914	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint13	TrGC	→ + CH$_3$COCH$_3$	1.60E-13*RO2	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint14	TrGC	→	5.68E10*exp(-8745/TEMP)	Vereecken and Peeters (2012), Taraborrelli (2013b)*
G410bpint15	TrGC	+ NO → + NO$_2$	KRO2NO*0.890	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint16	TrGC	+ NO →	KRO2NO*0.110	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint17	TrGC	+ HO$_2$ →	KRO2HO2*0.820	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint18	TrGC	→	2.50E-13*RO2	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint19	TrGC	→ + HO$_2$	5.7E10*exp(-2949/TEMP)	Vereecken and Peeters (2012), Taraborrelli (2013b)*
G410bpint20	TrGC	→ + OH	9.17E10*exp(-8706/TEMP)	Vereecken and Peeters (2012), Taraborrelli (2013b)*
G410bpint21	TrGC	+ NO → + NO$_2$	KRO2NO*0.747	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint22	TrGC	+ NO →	KRO2NO*0.253	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint23	TrGC	+ HO$_2$ →	KRO2HO2*0.914	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint24	TrGC	→	8.80E-13*RO2	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint25	TrGC	+ NO → + NO$_2$	KRO2NO*0.893	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint26	TrGC	+ NO →	KRO2NO*0.107	Vereecken and Peeters (2012), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410bpint27	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.914	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint28	TrGC	$\rightarrow$	5.00E-12*RO2	Vereecken and Peeters (2012), Taraborrelli (2013b)
G410bpint29	TrGC	$+ OH \rightarrow$	1.55E-11	Lewis et al. (2005), Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint30	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.890	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint31	TrGC	$+ NO \rightarrow + NO_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint32	TrGC	$\rightarrow$	2.00E-12*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint33	TrGC	$+ OH \rightarrow + OH$	2.63E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint34	TrGC	$+ h\nu \rightarrow + OH$	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint35	TrGC	$+ OH \rightarrow$	3.07E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint36	TrGC	$+ O_3 \rightarrow + .63$ CO $+ .37$ HOCH2OOH $+ .16$ OH $+ .16$ HO$_2$	1.5E-17*.051/(1-.027)	Nguyen et al. (2009), Taraborrelli (2013b)
G410bpint37	TrGC	$+ O_3 \rightarrow$	1.5E-17*.368/(1-.027)	Nguyen et al. (2009), Taraborrelli (2013b)
G410bpint38	TrGC	$+ O_3 \rightarrow + OH$	1.5E-17*.283/(1-.027)	Nguyen et al. (2009), Taraborrelli (2013b)
G410bpint40	TrGC	$+ O_3 \rightarrow + CO_2$	1.5E-17*(.104+.167)/(1-.027)	Nguyen et al. (2009), Taraborrelli (2013b)*
G410bpint41	TrGC	$+ OH \rightarrow$	3.04E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint42	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.859	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint43	TrGC	$+ NO \rightarrow$	KRO2NO*0.138	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint44	TrGC	$+ NO \rightarrow + NO_2$	KRO2NO*0.862	Rickard and Pascoe (2009), Taraborrelli (2013b)

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410bpint45	TrGC	$\rightarrow$	2.50E-13*RO2	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint46	TrGC	$+ OH \rightarrow + OH$	1.62E-11	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint47	TrGC	$+ h\nu \rightarrow + OH$	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint48	TrGC	$+ OH \rightarrow + NO_2$	1.84E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint49	TrGC	$\rightarrow + NO_2$	J_IC3H7NO3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint50	TrGC	$+ OH \rightarrow$	3.94E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint51	TrGC	$\rightarrow + H_2O_2$	6.00E-18*c(ind_H2O)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint52	TrGC	$+ CO \rightarrow$	1.2E-15	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint53	TrGC	$+ NO \rightarrow + NO_2$	1.E-14	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint54	TrGC	$+ NO_2 \rightarrow + NO_3$	1.E-15	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint55	TrGC	$+ SO_2 \rightarrow + H_2SO_4$	7.E-14	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint56	TrGC	$+ NO_3 \rightarrow$	2.51E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint57	TrGC	$+ HO_2 \rightarrow$	KRO2HO2*0.914	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint58	TrGC	$+ NO \rightarrow + HCHO + NO_2 + NO_2$	KRO2NO	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint59	TrGC	$+ NO_3 \rightarrow + HCHO + NO_2 + NO_2$	KRO2NO3	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint60	TrGC	$\rightarrow + HCHO + NO_2$	9.20E-14*RO2*0.7	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint61	TrGC	$\rightarrow$	9.20E-14*RO2*0.3	Rickard and Pascoe (2009), Taraborrelli (2013b)*

Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410bpint62	TrGC	+ OH →	9.58E-12	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410bpint63	TrGC	+ hν → + HCHO + NO$_2$ + OH	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009), Taraborrelli (2013b)
G410apint296	TrGC	+ OH →	8.7E-11*(.50+.25)	Wolfe et al. (2011), Taraborrelli (2013b)*
G410apint297	TrGC	+ OH → + HO$_2$	8.7E-11*.25*.60	Wolfe et al. (2011), Taraborrelli (2013b)
G410apint298	TrGC	+ OH →	8.7E-11*.25*.40	Wolfe et al. (2011), Taraborrelli (2013b)
G410apint299	TrGC	+ O$_3$ →	2.E-16*.50*.18	Wolfe et al. (2011), Taraborrelli (2013b)
G410apint300	TrGC	+ O$_3$ →	2.E-16*.50*.16	Wolfe et al. (2011), Taraborrelli (2013b)
G410apint301	TrGC	+ O$_3$ → OH + + CO + HO$_2$	2.E-16*.50*.66	Wolfe et al. (2011), Taraborrelli (2013b)
G410apint302	TrGC	+ O$_3$ →	2.E-16*.50*.12	Wolfe et al. (2011), Taraborrelli (2013b)
G410apint303	TrGC	+ O$_3$ → OH +	2.E-16*.50*(.22+.66)	Wolfe et al. (2011), Taraborrelli (2013b)*
G410apint304	TrGC	+ NO$_3$ →	9.5E-12	Wolfe et al. (2011), Taraborrelli (2013b)
G410myrc	TrGC	+ OH → + POHORG	9.19E-12*exp(1071./temp)*0.64	Hites and Turner (2009), Orlando et al. (2000), Taraborrelli (2013b)
G410myrct2	TrGC	+ OH → + POHORG	9.19E-12*exp(1071./temp)*0.36	Hites and Turner (2009), Orlando et al. (2000), Taraborrelli (2013b)
G410myrct3	TrGC	+ O$_3$ → .25 CH$_3$COCH$_3$ + .75 OH + .75 CH$_3$COCH$_2$O$_2$ + + .75 POHORG	4.7E-16	Atkinson and Arey (2003), Taraborrelli (2013b)
G410myrct4	TrGNC	+ NO$_3$ →	1.1E-11	Atkinson and Arey (2003), Taraborrelli (2013b)
G410myrct5	TrGC	→ CH$_3$COCH$_3$ + HO$_2$ +	8.E-13*RO2	Taraborrelli (2013b)
G410myrct6	TrGC	+ HO$_2$ →	KRO2HO2	Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410myrct7	TrGCN	+ NO → .80 CH$_3$COCH$_3$ + .80 HO$_2$ + .80 + .80 NO$_2$ + .20	KRO2NO	Taraborrelli (2013b)*
G410myrct8	TrGCJ	+ hν → CH$_3$COCH$_3$ + OH + HO$_2$ + + POHORG	1.14*jx(ip_CH3OOH)	Taraborrelli (2013b)
G410myrct9	TrGC	+ OH → + POHORG	1.55E-10	Baker et al. (2004), Taraborrelli (2013b)
G410myrct10	TrGC	+ NO$_3$ → CH$_3$COCH$_3$ + + NISOPO2	4.7E-13	Baker et al. (2004), Taraborrelli (2013b)
G410myrct11	TrGC	+ OH → iC$_3$H$_7$ONO$_2$ + + POHORG	1.55E-10	see note
G410myrct12	TrGC	→	1.E-12*RO2	Taraborrelli (2013b)
G410myrct13	TrGC	+ HO$_2$ →	KRO2HO2	Taraborrelli (2013b)
G410myrct14	TrGC	+ NO → .8 + .8 NO$_2$ + .2	KRO2NO	Taraborrelli (2013b)
G410myrct15	TrGC	→ + HO$_2$	K16HS	Taraborrelli (2013b)
G410myrct16	TrGC	→ CH$_3$COCH$_3$ + + .43 MVK + .27 MACR + .7 HCHO + .29 LHC4ACCHO + HO$_2$	KDEC	Taraborrelli (2013b)
G410myrct17	TrGC	+ OH → CH$_3$COCH$_3$ + HO$_2$ + + ISOPBNO3 + POHORG	kadt+kads	Taraborrelli (2013b)
G410myrct18	TrGC	+ hν → + OH + POHORG	1.14*jx(ip_CH3OOH)	Taraborrelli (2013b)
G410myrct19	TrGC	+ OH → + .43 ISOPBOOH + .27 ISOPDOOH + .29 LISOPACOOH + CH$_3$COCH$_3$ + HO$_2$ + POHORG	kadt+kads	Taraborrelli (2013b)
G410myrct20	TrGCJ	+ hν → OH + + HO$_2$ + POHORG	J_HPALD	Taraborrelli (2013b)
G410myrct21	TrGC	+ OH → + HO$_2$ + CH$_3$COCH$_3$ + POHORG	kadt+kads	Taraborrelli (2013b)
G410myrct22	TrGC	+ OH → + + HCHO + GLYOX + HO$_2$ + POHORG	(kadt+kads)*acho*ach2ooh	Taraborrelli (2013b)
G410myrct23	TrGC	+ O$_3$ → .25 CH$_3$COCH$_3$ + .75 OH + .75 CH$_3$COCH$_2$O$_2$ + .75 POHORG	4.7E-16	Taraborrelli (2013b)
G410myrct24	TrGC	+ OH → + + POHORG	1.55E-10	Baker et al. (2004), Taraborrelli (2013b)
G410myrct25	TrGC	+ NO$_3$ → + NISOPO2	4.7E-13	Baker et al. (2004), Taraborrelli (2013b)
G410myrct26	TrGC	→	1.E-12*RO2	Taraborrelli (2013b)
G410myrct27	TrGC	+ HO$_2$ → + .43 ISOPBOOH + .27 ISOPDOOH + .29 LISOPACOOH	KRO2HO2	Taraborrelli (2013b)
G410myrct28	TrGC	+ NO → .8 + .8 NO$_2$ + .2 + .2 ISOPBNO3	KRO2NO	Taraborrelli (2013b)
G410myrct29	TrGC	→ + HO$_2$	K16HS	Taraborrelli (2013b)
G410myrct30	TrGC	→ + .43 MVK + .27 MACR + .7 HCHO + .29 LHC4ACCHO + HO$_2$	KDEC	Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410myrct31	TrGCJ	+ hν → + OH + + HO$_2$ + POHORG	J_HPALD	Taraborrelli (2013b)
G410myrct32	TrGC	+ OH → + .3 + .2 + .3 + .2 + POHORG	(kadt+kads)*acho*ach2ooh	Taraborrelli (2013b)
G410myrct33	TrGC	→	1.E-12*RO2	Taraborrelli (2013b)
G410myrct34	TrGC	+ HO$_2$ →	KRO2HO2	Taraborrelli (2013b)
G410myrct35	TrGC	+ NO → .8 + .8 NO$_2$ + .2 CH$_3$COCH$_3$ + .2 + .2 ISOPBNO3	KRO2NO	Taraborrelli (2013b)
G410myrct36	TrGC	→ + HO$_2$	K16HS	Taraborrelli (2013b)
G410myrct37	TrGC	→ CH$_3$COCH$_3$ + + .43 MVK + .27 MACR + .7 HCHO + .29 LHC4ACCHO + HO$_2$ + OH + POHORG	KDEC	Taraborrelli (2013b)
G410myrct38	TrGCJ	+ hν → + OH + POHORG	1.14*jx(ip_CH3OH)	Taraborrelli (2013b)
G410myrct39	TrGCJ	+ hν → CH$_3$COCH$_3$ + HO$_2$ + + .43 ISOPBOOH + .27 ISOPDOOH + .29 LISOPACOOH + OH + POHORG	1.14*jx(ip_CH3OH)	Taraborrelli (2013b)
G410myrct40	TrGCJ	+ hν → CH$_3$COCH$_3$ + OH + + OH + + HO$_2$ + 2 POHORG	J_HPALD	Taraborrelli (2013b)
G410myrct41	TrGC	+ OH → CH$_3$COCH$_3$ + OH + + .3 + .2 + .3 + .2 + POHORG + POHORG	(kadt+kads)*acho*ach2ooh	Taraborrelli (2013b)
G410myrct42	TrGC	+ OH → + H$_2$O + POHORG	4.4E-12*EXP(365./temp)	Taraborrelli (2013b)*
G410myrct43	TrGC	+ hν → HCHO + HO$_2$ + HO$_2$ + CO	jx(ip_CH3CHO)	Taraborrelli (2013b)
G410myrct44	TrGC	+ NO$_3$ → HNO$_3$ +	KNO3AL	Taraborrelli (2013b)
G410myrct45	TrGC	→ HCHO + HO$_2$ + CO$_2$	1.00E-11*0.7*RO2	Taraborrelli (2013b)
G410myrct46	TrGC	→	1.00E-11*0.3*RO2	Taraborrelli (2013b)
G410myrct47	TrGC	+ HO$_2$ → OH + HCHO + HO$_2$ + CO$_2$ + POHORG	KAPHO2*0.44	Taraborrelli (2013b)
G410myrct48	TrGC	+ HO$_2$ →	KAPHO2*0.41	Taraborrelli (2013b)
G410myrct49	TrGC	+ HO$_2$ → + O$_3$	KAPHO2*0.15	Taraborrelli (2013b)
G410myrct50	TrGC	+ NO$_2$ →	k_CH3CO3_NO2	Taraborrelli (2013b)
G410myrct51	TrGC	+ NO → NO$_2$ + HCHO + HO$_2$ + CO$_2$	KAPNO	Taraborrelli (2013b)
G410myrct52	TrGC	+ NO$_3$ → NO$_2$ + HCHO + HO$_2$ + CO$_2$	KRO2NO3*1.60	Taraborrelli (2013b)
G410myrct53	TrGC	+ OH → HCHO + HO$_2$ + CO$_2$ + POHORG	4.2E-14*exp(850./temp)	Taraborrelli (2013b)*
G410myrct54	TrGC	+ hν → HCHO + HO$_2$ + OH + CO$_2$ + POHORG	1.14*jx(ip_CH3OH)	Taraborrelli (2013b)
G410myrct55	TrGC	+ OH → + H$_2$O + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013b)
G410myrct56	TrGC	→ + NO$_2$	k_PAN_M	Taraborrelli (2013b)
G410myrct57	TrGC	+ OH → HCHO + CO + NO$_2$ + POHORG	9.50E-13*EXP(-650./temp)	Taraborrelli (2013b)
G410afarn	TrGC	+ OH → + POHORG	2.7E-11*EXP(390./temp)	Taraborrelli (2013b)*
G410afarnt2	TrGC	+ OH → + POHORG	2.*1.9E-11*exp(450./temp)	Taraborrelli (2013b)*

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410afarnt3	TrGC	+ O$_3$ → + .25 CH$_3$COCH$_3$ + .75 OH + .75 CH$_3$COCH$_2$O$_2$ + .75 POHORG	6.51E-15*exp(-829./temp)	Taraborrelli (2013b)*
G410afarnt4	TrGC	+ O$_3$ → + + .75 OH + .75 POHORG	6.51E-15*exp(-829./temp)	Taraborrelli (2013b)*
G410afarnt5	TrGNC	+ NO$_3$ →	2E-12+2*9.37E-12	Taraborrelli (2013b)*
G410afarnt6	TrGC	→	8.E-13*RO2	Taraborrelli (2013b)
G410afarnt7	TrGC	+ HO$_2$ →	KRO2HO2	Taraborrelli (2013b)
G410afarnt8	TrGC	+ NO → .75 + .75 NO$_2$ + .25	KRO2NO	Taraborrelli (2013b)
G410afarnt9	TrGCJ	+ hν → + OH + POHORG	1.14*jx(ip_CH3OH)	Taraborrelli (2013b)
G410afarnt10	TrGC	+ OH → + + POHORG	2.7E-11*EXP(390./temp)	Taraborrelli (2013b)
G410afarnt11	TrGC	+ OH → .5 + .5 + + POHORG	2.*1.9E-11*exp(450./temp)	Taraborrelli (2013b)
G410afarnt12	TrGC	→ .5 + .5 + .5 + .5 CH$_3$COCH$_3$ + HO$_2$	KDEC	Taraborrelli (2013b)
G410afarnt13	TrGC	→	1.E-12*RO2	Taraborrelli (2013b)
G410afarnt14	TrGC	+ HO$_2$ →	KRO2HO2	Taraborrelli (2013b)
G410afarnt15	TrGC	+ NO → .75 + .75 NO$_2$ + .25	KRO2NO	Taraborrelli (2013b)
G410afarnt16	TrGC	→ + HO$_2$ +	K16HS	Taraborrelli (2013b)
G410afarnt17	TrGC	→ +	KDEC	Taraborrelli (2013b)
G410afarnt18	TrGC	+ OH → + HO$_2$ + ISOPBNO3 + POHORG	kadt+kads	Taraborrelli (2013b)
G410afarnt19	TrGC	+ hν → + OH + POHORG	1.14*jx(ip_CH3OH)	Taraborrelli (2013b)
G410afarnt20	TrGC	+ OH → + + POHORG	kadt+kads	Taraborrelli (2013b)
G410afarnt21	TrGC	+ O$_3$ → + + .75 OH + .75 POHORG	2.*6.51E-15*exp(-829./temp)	Taraborrelli (2013b)*
G410afarnt22	TrGC	+ OH → + POHORG	1.9E-11*exp(450./temp)	Taraborrelli (2013b)*
G410afarnt23	TrGC	+ OH → + POHORG	2.7E-11*EXP(390./temp)	Taraborrelli (2013b)*
G410afarnt24	TrGC	+ O$_3$ → + + .75 OH + .75 POHORG	6.51E-15*exp(-829./temp)	Taraborrelli (2013b)*
G410afarnt25	TrGNC	+ NO$_3$ →	2E-12	Taraborrelli (2013b)*
G410afarnt26	TrGNC	+ NO$_3$ →	9.37E-12	Taraborrelli (2013b)*
G410afarnt27	TrGC	→	8.E-13*RO2	Taraborrelli (2013b)
G410afarnt28	TrGC	+ HO$_2$ →	KRO2HO2	Taraborrelli (2013b)
G410afarnt29	TrGC	+ NO → .75 + .75 NO$_2$ + .25	KRO2NO	Taraborrelli (2013b)
G410afarnt30	TrGCJ	+ hν → + OH + POHORG	1.14*jx(ip_CH3OH)	Taraborrelli (2013b)
G410afarnt31	TrGC	+ OH → + HO$_2$ + + POHORG	2.7E-11*EXP(390./temp)	Taraborrelli (2013b)*
G410afarnt32	TrGC	+ OH → + POHORG	1.9E-11*exp(450./temp)	Taraborrelli (2013b)*
G410afarnt33	TrGC	→ + + HO$_2$	KDEC	Taraborrelli (2013b)
G410afarnt34	TrGC	→	1.E-12*RO2	Taraborrelli (2013b)
G410afarnt35	TrGC	+ HO$_2$ →	KRO2HO2	Taraborrelli (2013b)
G410afarnt36	TrGC	+ NO → .75 + .75 NO$_2$ + .25	KRO2NO	Taraborrelli (2013b)

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Table 1: Gas phase reactions (... continued)

#	labels	reaction	rate coefficient	reference
G410afarnt37	TrGC	→ + + HO2 +	K16HS	Taraborrelli (2013b)
G410afarnt38	TrGC	→ +	KDEC	Taraborrelli (2013b)
G410afarnt39	TrGC	+ OH → + HO2 + ISOPBNO3 + POHORG	kadt+kads	Taraborrelli (2013b)
G410afarnt40	TrGC	+ hν → + OH + POHORG	1.14*jx(ip_CH3OOH)	Taraborrelli (2013b)
G410afarnt41	TrGC	+ OH → + + POHORG	kadt+kads	Taraborrelli (2013b)
G410afarnt42	TrGC	+ O3 → + .75 OH + .75 POHORG	6.51E-15*exp(-829./temp)	Taraborrelli (2013b)
G410afarnt43	TrGC	+ OH → + POHORG	1.37E-10	Smith et al. (1996), Taraborrelli (2013b)*
G410afarnt44	TrGC	+ O3 → .25 CH3COCH3 + .125 + .25 GLYOX + .25 CH3COCH2O2 + .125 H2O2 + .75 OH + .75 CH3COCH2O2 + .75 + .75 POHORG	3.9E-16	Grosjean et al. (1996), Taraborrelli (2013b)*
G410afarnt45	TrGC	+ NO3 →	7E-12	Smith et al. (1996), Taraborrelli (2013b)
G410afarnt46	TrGC	→ CH3COCH3 + + HO2	8.E-13*RO2	Taraborrelli (2013b)
G410afarnt47	TrGC	+ HO2 →	KRO2HO2	Taraborrelli (2013b)
G410afarnt48	TrGC	+ NO → .25 + .75 CH3COCH3 + .75 + .75 HO2 + .75 NO2	KRO2NO	Taraborrelli (2013b)
G410afarnt49	TrGC	+ OH → + POHORG	0.6*k_CH3OOH_OH	Taraborrelli (2013b)
G410afarnt50	TrGC	+ OH → + HO2 + POHORG	kt*ftoh*falk*falk	Taraborrelli (2013b)
G410afarnt51	TrGCJ	+ hν → CH3COCH3 + + OH + POHORG	1.14*jx(ip_CH3OOH)	Taraborrelli (2013b)
G410afarnt52	TrGCJ	+ hν → CH3COCH3 + CH3COCH2O2 + + OH + POHORG	1.14*jx(ip_CH3OOH)+2.77*jx(ip_HOCH2CHO)	Taraborrelli (2013b)*
G410afarnt53	TrGC	+ OH → + HO2 + POHORG	kt*ftoh*falk*fch2ono2	Taraborrelli (2013b)
G410afarnt54	TrGC	+ hν → CH3COCH3 + NO2 + CH3COCH2O2 +	2.84*J_IC3H7NO3	Taraborrelli (2013b)
G410afarnt55	TrGC	+ OH → CH3COCH2O2 + + POHORG	2.E-11	Fruekilde et al. (1997), Taraborrelli (2013b)*
G410afarnt56	TrGCJ	+ hν → CH3COCH2O2 + + HO2	jx(ip_CH3CHO)+jx(ip_CH3COCH3)	Taraborrelli (2013b)

*Notes:

Rate coefficients for three-body reactions are defined via the function k_3rd(T, M, k_0^{300}, n, k_{inf}^{300}, m, f_c). In the code, the temperature T is called temp and the concentration of "air molecules" M is called cair. Using the auxiliary variables $k_0(T)$, $k_{inf}(T)$, and k_{ratio}, k_3rd is defined as:

$$k_0(T) = k_0^{300} \times \left(\frac{300K}{T}\right)^n \quad (1)$$

$$k_{inf}(T) = k_{inf}^{300} \times \left(\frac{300K}{T}\right)^m \quad (2)$$

$$k_{ratio} = \frac{k_0(T)M}{k_{inf}(T)} \quad (3)$$

$$k\_3rd = \frac{k_0(T)M}{1+k_{ratio}} \times f_c^{\left(\frac{1}{1+(\log_{10}(k_{ratio}))^2}\right)} \quad (4)$$

A similar function, called k_3rd_iupac here, is used by Atkinson et al. (2005) for three-body reactions. It has the same function parameters as k_3rd and it is defined as:

$$k_0(T) = k_0^{300} \times \left(\frac{300K}{T}\right)^n \quad (5)$$

$$k_{inf}(T) = k_{inf}^{300} \times \left(\frac{300K}{T}\right)^m \quad (6)$$

$$k_{ratio} = \frac{k_0(T)M}{k_{inf}(T)} \quad (7)$$

$$N = 0.75 - 1.27 \times \log_{10}(f_c) \quad (8)$$

$$k\_3rd\_iupac = \frac{k_0(T)M}{1+k_{ratio}} \times f_c^{\left(\frac{1}{1+(\log_{10}(k_{ratio})/N)^2}\right)} \quad (9)$$

G2110: The rate coefficient is: k_HO2_HO2 = (1.5E-12*EXP(19./temp)+1.7E-33*EXP(1000./temp)*cair)* (1.+1.4E-21*EXP(2200./temp)*C(ind_H2O)). The value for the first (pressure-independent) part is from Christensen et al. (2002), the water term from Kircher and Sander (1984).

G3109: The rate coefficient is: k_NO3_NO2 = k_3rd(temp,cair,2.E-30,4.4,1.4E-12,0.7,0.6).

G3110: The rate coefficient is defined as backward reaction divided by equilibrium constant.

G3206: The rate coefficient is: k_HNO3_OH = 2.4E-14 * EXP(460./temp) + 1./ (1./ (6.5E-34 * EXP(1335./temp)*cair) + 1./ (2.7E-17 * EXP(2199./temp)))

G3207: The rate coefficient is defined as backward reaction divided by equilibrium constant.

G4107: The rate coefficient is: k_CH3OOH_OH = 3.8E-12*EXP(200./temp).

G4109: The same temperature dependence assumed as for CH3CHO+NO3.

G4206: The product C2H5OH, which reacts only with OH, is substituted by its degradation products ≈ 0.1 HOCH2CH2O2 + 0.9 CH3CHO + 0.9 HO2.

G4207: The rate constant 8.01E-12 is for the H abstraction in alpha to the −OOH group (Rickard and Pascoe, 2009) and 0.6*k_CH3OOH_OH is for the C2H5O2 channel. The branching ratios are calculated from the terms of the rate coefficient at 298K.

G4218: The rate coefficient is the same as for the CH3O2 channel in G4107 (CH3OOH+OH).

G4221: The rate coefficient isk_PAN_M = k_CH3CO3_NO2/9.E-29*EXP(-14000./temp), i.e. the rate coefficient is defined as backward reaction divided by equilibrium constant.

G4300: The product NC3H7O2 is substituted with its degradation products C2H5O2 + CO2 + HO2.

G4304: The value for the generic RO2 + HO2 reaction from Atkinson (1997) is used here.

G4306: The MCM (Rickard and Pascoe, 2009) products are 0.2 IPROPOL + 0.2 CH3COCH3 + 0.6 IC3H7O. IPROPOL and IC3H7O are substituted with their degradation products. We assume IPROPOL to be oxidized entirely to CH3COCH3 + HO2 by OH. IC3H7O + O2 produces the same products.

G4307: Analogous to G4207 for both rate coefficient and branching ratios.

G4400: LC4H9O2 represents 0.127 NC4H9O2 + 0.873 SC4H9O2.

G4401: NC4H9O and SC4H9O are substituted with 2 CO2 + C2H5O2 and 0.636 MEK + HO2 and 0.364 CH3CHO + C2H5O2, repectively. The stoichiometric coefficients on the right side are weighted averages.

G4403: The alkyl nitrate yield is the weighted average yield for the two isomers forming from NC4H9O2 and SC4H9O2.

G4404: The product distribution is the weighted average of the single isomer hydroperoxides. It is calculated from the rate constants of single channels and the ratio of the isomers NC4H9O2 and SC4H9O2. The overall rate constant for this reaction is calculated as weighted average of the channels rate constants. The relative weight of the products from NC4H9OOH and SC4H9OOH are then 0.0887 and 0.9113. The channels producing RO2 are given the rate coefficient 0.6*k_CH3OOH_OH as for G4107. For NC4H9OOH the products are 0.327 NC4H9O2 + 0.673 C3H7CHO + 0.673 OH. C3H7CHO is then substituted with 2 CO2 + C2H5O2. Hence, 0.327 NC4H9O2 + 1.346 CO2 + 0.673 C2H5O2 + 0.673 OH. For SC4H9OOH the products are 0.219 SC4H9O2 + 0.781 MEK + 0.781 OH.

G4413: LMEKO2 represents 0.459 MEKAO2 + 0.462 MEKBO2 + 0.079 MEKCO2.

G4415: Alkyl nitrate formation is neglected. The products of MEKAO and MEKCO are substituted with

HCHO + CO$_2$ + HOCH$_2$CH$_2$O$_2$ and HCHO + CO$_2$ + C$_2$H$_5$O$_2$.

G4416: LMEKOOH is assumed having the composition 0.459 MEKAOOH + 0.462 MEKBOOH + 0.079 MEK-COOH. MEKAOOH + OH gives 0.89 CO2C3CHO + 0.89 OH + 0.11 MEKAO2 + H$_2$O. CO2C3CHO is substituted with CH$_3$COCH$_2$O$_2$ + CO$_2$ and the products become 0.89 CH$_3$COCH$_2$O$_2$ + 0.89 CO$_2$ + 0.89 OH + 0.11 MEKAO2 + H$_2$O. MEKBOOH + OH gives 0.758 BIACET + 0.758 OH + 0.242 MEKBO2 + H$_2$O. MEKCOOH + OH gives 0.614 EGLYOX + 0.614 OH + 0.386 MEKCO2 + H$_2$O. EGLYOX is substituted with C$_2$H$_5$O$_2$ + 2 CO$_2$ and the products become 0.614 C$_2$H$_5$O$_2$ + 1.228 CO$_2$ + 0.614 OH + 0.386 MEKCO2

+ H$_2$O.

G4417: The rate coefficient is the combination of the ones for the two isomers weighted by the relative abundances for NC4H9NO3 and SC4H9NO3, respectively. Product distribution is calculated accordingly. NC4H9NO3 + OH gives C3H7CHO + NO$_2$ + H$_2$O with C3H7CHO being substituted with 2 CO$_2$ + C$_2$H$_5$O$_2$. After substitution is obtained 2 CO$_2$ + C$_2$H$_5$O$_2$ + NO$_2$ + H$_2$O. SC4H9NO3 + OH gives MEK + NO$_2$ + H$_2$O For the product distribution NC4H9NO3 and SC4H9NO3 account for 0.08577 and 0.91423, respectively.

G4419: The same value as for PAN is assumed.

G4420: Products are as in G4415. Only the main channels for each isomer are considered. Rate constant is the weighted average for the isomers.

G4455: CH3COCOCO3H assumed to photolyse quickly and give CH3CO3 + CO + CO2 + OH

G45222: HYBIACETOOA approximated to yield BIACETOH only, CH3COCHOOHCH2OH's main reaction with OH yields BIACETOH recycling OH =¿ substitution with BIACETOH

G413621: PEROXYRINGC2OOHC3OD substituted

G4136: CH3COCH2OOCH2CO3 -¿ CH3CO3 + CO2 + 2 HCHO

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Table 2: Photolysis reactions

#	labels	reaction	rate coefficient	reference
J1000	StTrGJ	O$_2$ + h$\nu \rightarrow$ O(^{3}P) + O(^{3}P)	jx(ip_O2)	see note
J1001a	StTrGJ	O$_3$ + h$\nu \rightarrow$ O(^{1}D)	jx(ip_O1D)	see note
J1001b	StTrGJ	O$_3$ + h$\nu \rightarrow$ O(^{3}P)	jx(ip_O3P)	see note
J2101	StTrGJ	H$_2$O$_2$ + h$\nu \rightarrow$ 2 OH + 2 POHOX	JX(ip_H2O2)	see note
J3101	StTrGNJ	NO$_2$ + h$\nu \rightarrow$ NO + O(^{3}P)	jx(ip_NO2)	see note
J3103a	StTrGNJ	NO$_3$ + h$\nu \rightarrow$ NO$_2$ + O(^{3}P)	jx(ip_NO2O)	see note
J3103b	StTrGNJ	NO$_3$ + h$\nu \rightarrow$ NO	jx(ip_NOO2)	see note
J3104a	StTrGNJ	N$_2$O$_5$ + h$\nu \rightarrow$ NO$_2$ + NO$_3$	jx(ip_N2O5)	see note
J3200	TrGJ	HONO + h$\nu \rightarrow$ NO + OH + PONOX	JX(ip_HONO)	see note
J3201	StTrGNJ	HNO$_3$ + h$\nu \rightarrow$ NO$_2$ + OH + PONOX	JX(ip_HNO3)	see note
J3202	StTrGNJ	HNO$_4$ + h$\nu \rightarrow$ .667 NO$_2$ + .667 HO$_2$ + .333 NO$_3$ + .333 OH + .333 PONOX	JX(ip_HNO4)	see note
J4100e	StTrGJ	CH$_3$OOH + h$\nu \rightarrow$ HCHO + OH + HO$_2$ + POHORG	1.14*jx(ip_CH3OOH)	see note
J4101a	StTrGJ	HCHO + h$\nu \rightarrow$ H$_2$ + CO	jx(ip_COH2)	see note
J4101b	StTrGJ	HCHO + h$\nu \rightarrow$ H + CO + HO$_2$	jx(ip_CHOH)	see note
J4104e	StTrGJ	HOCH2OOH + h$\nu \rightarrow$ OH + HO$_2$ + HCOOH + POHORG	1.14*jx(ip_CH3OOH)	see note
J4200e	TrGCJ	C$_2$H$_5$OOH + h$\nu \rightarrow$ CH$_3$CHO + HO$_2$ + OH + POHORG	1.14*jx(ip_CH3OOH)	see note
J4201	TrGCJ	CH$_3$CHO + h$\nu \rightarrow$ CH$_3$O$_2$ + HO$_2$ + CO	jx(ip_CH3CHO)	see note
J4202e	TrGCJ	CH$_3$C(O)OOH + h$\nu \rightarrow$ CH$_3$O$_2$ + OH + CO$_2$ + POHORG	1.14*jx(ip_CH3CO3H)	see note
J4204e	TrGNCJ	PAN + h$\nu \rightarrow$ .6 CH$_3$C(O)OO + .6 NO$_2$ + .4 CH$_3$O$_2$ + .4 CO$_2$ + .4 NO$_3$	jx(ip_PAN)	see note
J4205ae	TrGCJ	HOCH2CHO + h$\nu \rightarrow$ HCHO + 2 HO$_2$ + CO	jx(ip_HOCH2CHO)*0.70	Taraborrelli (2013a)
J4205be	TrGCJ	HOCH2CHO + h$\nu \rightarrow$ 1.16 OH + .84 + .1 HCHO + .1 CO + .06 GLYOX + 1.16 POHORG	jx(ip_HOCH2CHO)*0.15	Taraborrelli (2013a)
J4205ce	TrGCJ	HOCH2CHO + h$\nu \rightarrow$ CH$_3$OH + CO	jx(ip_HOCH2CHO)*0.15	Taraborrelli (2013a)
J4206e	TrGCJ	+ h$\nu \rightarrow$ OH + HCHO + CO + HO$_2$ + POHORG	1.14*jx(ip_CH3OOH)*jx(ip_HOCH2CHO)	Taraborrelli (2013a)
J4206et2	TrGCJ	HOCH2CO3H + h$\nu \rightarrow$ HCHO + HO$_2$ + OH + CO$_2$ + POHORG	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)[*]
J4207	TrGCJ	PHAN + h$\nu \rightarrow$ HOCH2CO3 + NO$_2$	jx(ip_PAN)	see note
J4208	TrGCJ	GLYOX + h$\nu \rightarrow$ 2 CO + 2 HO$_2$	jx(ip_GLYOX)	see note
J4209	TrGNCJ	HCOCO2H + h$\nu \rightarrow$ 2 HO$_2$ + CO + CO$_2$	jx(ip_MGLYOX)	Rickard and Pascoe (2009)[*]

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Table 2: Photolysis reactions (... continued)

#	labels	reaction	rate coefficient	reference
J4210e	TrGNCJ	$HCOCO_3H + h\nu \rightarrow HO_2 + CO + OH + CO_2 + POHORG$	1.14*jx(ip_CH3OOH)+jx(ip_HOCH2CHO)	Rickard and Pascoe (2009)*
J4211e	TrGCJ	$HYETHO2H + h\nu \rightarrow HOCH_2CH_2O + OH + POHORG$	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)*
J4212	TrGCJ	$ETHOHNO3 + h\nu \rightarrow HO_2 + 2\ HCHO + NO_2$	J_IC3H7NO3	see note
J4213e	TrGCJ	$+ h\nu \rightarrow OH + HCHO + CO_2 + OH + 2\ POHORG$	2*1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4214e	TrGC	$+ h\nu \rightarrow OH + HCHO + HO_2 + CO_2 + POHORG$	1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4215e	TrGC	$+ h\nu \rightarrow .4\ CO_2 + .8\ H + .34\ CO + .34\ OH + .34\ HO_2 + .16\ HCHO + .16\ O(^3P) + .1\ HCOOH + CO + .34\ POHORG$	J_ketene* 0.36	Taraborrelli (2013a)
J4216e	TrGC	$+ h\nu \rightarrow CH_3O_2 + HCOOH + OH + POHORG$	1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4217e	TrGCJ	$+ h\nu \rightarrow HO_2 + CO + HCHO + NO_2$	1.59*J_IC3H7NO3+jx(ip_CH3COCH3)	Taraborrelli (2013a)
J4300e	TrGCJ	$iC_3H_7OOH + h\nu \rightarrow CH_3COCH_3 + HO_2 + OH + POHORG$	1.14*jx(ip_CH3OOH)	von Kuhlmann (2001)*
J4301	TrGCJ	$CH_3COCH_3 + h\nu \rightarrow CH_3C(O)OO + CH_3O_2$	jx(ip_CH3COCH3)	see note
J4302	TrGCJ	$CH_3COCH_2OH + h\nu \rightarrow CH_3C(O)OO + HCHO + HO_2$	J_ACETOL	see note
J4303	TrGCJ	$MGLYOX + h\nu \rightarrow CH_3C(O)OO + CO + HO_2$	jx(ip_MGLYOX)	see note
J4304e	TrGCJ	$CH_3COCH_2O_2H + h\nu \rightarrow CH_3C(O)OO + HCHO + OH + POHORG$	1.14*jx(ip_CH3OOH)+J_ACETOL	Taraborrelli (2013a)
J4305e	TrGCJ	$+ h\nu \rightarrow\ + HCHO + OH + POHORG$	1.14*jx(ip_CH3OOH)+J_ACETOL	Taraborrelli (2013a)
J4306	TrGNCJ	$iC_3H_7ONO_2 + h\nu \rightarrow CH_3COCH_3 + NO_2 + HO_2$	J_IC3H7NO3	von Kuhlmann et al. (2003)*
J4307	TrGCJ	$NOA + h\nu \rightarrow CH_3C(O)OO + HCHO + NO_2$	J_IC3H7NO3+jx(ip_CH3COCH3)	see note
J4309e	TrGCJ	$HYPROPO2H + h\nu \rightarrow CH_3CHO + HCHO + HO_2 + OH + POHORG$	1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4310e	TrGNCJ	$PR2O2HNO3 + h\nu \rightarrow NOA + HO_2 + OH + POHORG$	1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4311e	TrGCJ	$HOCH2COCHO + h\nu \rightarrow\ + CO + HO_2$	jx(ip_MGLYOX)	Taraborrelli (2013a)
J4312e	TrGCJ	$+ h\nu \rightarrow .5\ CH_3CHO + .8\ CO_2 + .4\ CH_3C(O)OO + .3\ HO_2 + .1\ CH_3COOH + .1\ OH + .2\ CO + .1\ POHORG$	JX(IP_MGLYOX)	Taraborrelli (2013a)
J4313e	TrGCJ	$+ h\nu \rightarrow\ + HCHO + OH + POHORG$	1.14*jx(ip_CH3OOH)+J_ACETOL	Taraborrelli (2013a)
J4314e	TrGCJ	$+ h\nu \rightarrow\ + CO + HO_2$	JX(IP_MGLYOX)	Taraborrelli (2013a)
J4315e	TrGCJ	$+ h\nu \rightarrow\ + HO_2 + CO$	2*JX(IP_MGLYOX)	Taraborrelli (2013a)
J4316e	TrGC	$+ h\nu \rightarrow CH_3C(O)OO + OH + POHORG + CO_2$	JX(IP_MGLYOX)+1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4317e	TrGC	$+ h\nu \rightarrow C_2H_4 + CO$	J_ketene*0.36*2.	Taraborrelli (2013a)*
J4400e	TrGCJ	$LC_4H_9OOH + h\nu \rightarrow OH + 0.254\ CO_2 + 0.5552\ MEK + 0.5552\ HO_2 + 0.3178\ CH_3CHO + 0.4448\ C_2H_5O_2 + POHORG$	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)*
J4401	TrGCJ	$MVK + h\nu \rightarrow C_3H_6 + CO$	jx(ip_MVK)	Taraborrelli (2013a)*

Table 2: Photolysis reactions (... continued)

#	labels	reaction	rate coefficient	reference
J4403	TrGCJ	$MEK + h\nu \rightarrow CH_3C(O)OO + C_2H_5O_2$	0.42*jx(ip_CHOH)	von Kuhlmann et al. (2003)*
J4404e	TrGCJ	$LMEKOOH + h\nu \rightarrow 0.538\ HCHO + 0.538\ CO_2 + 0.459\ HOCH_2CH_2O_2 + 0.079\ C_2H_5O_2 + 0.462\ CH_3C(O)OO + 0.462\ CH_3CHO + OH + POHORG$	1.14*jx(ip_CH3OOH)+J_ACETOL	Rickard and Pascoe (2009)*
J4405	TrGCJ	$BIACET + h\nu \rightarrow 2\ CH_3C(O)OO$	2.15*jx(ip_MGLYOX)	see note
J4406	TrGNCJ	$LC_4H_9NO_3 + h\nu \rightarrow NO_2 + 0.254\ CO_2 + 0.5552\ MEK + 0.5552\ HO_2 + 0.3178\ CH_3CHO + 0.4448\ C_2H_5O_2$	J_IC3H7NO3	see note
J4407e	TrGNCJ	$MPAN + h\nu \rightarrow .6\ MACO3 + .6\ NO_2 + .4\ + .4\ NO_3$	jx(ip_PAN)	Taraborrelli (2013a)*
J4409e	TrGCJ	$CO2H3CO3H + h\nu \rightarrow\ + OH + CO_2 + POHORG$	1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4410	TrGCJ	$CO2H3CO3H + h\nu \rightarrow CH_3C(O)OO + HO_2 + HCOCO_3H$	J_ACETOL	Rickard and Pascoe (2009)*
J4410t2	TrGCJ	$+ h\nu \rightarrow CH_3C(O)OO + HCOCO_2H + POHORG$	J_ACETOL	Taraborrelli (2013a)
J4411	TrGCJ	$MACR + h\nu \rightarrow .5\ MACO3 + .5\ + .5\ CO + HO_2$	jx(ip_MACR)	see note
J4412e	TrGCJ	$MACROOH + h\nu \rightarrow\ + OH + POHORG$	1.14*jx(ip_CH3OOH)+ 2.77*jx(ip_HOCH2CHO)	see note
J4414	TrGCJ	$MACROH + h\nu \rightarrow CH_3COCH_2OH + CO + HO_2 + HO_2$	2.77*jx(ip_HOCH2CHO)	see note
J4415e	TrGCJ	$MACO3H + h\nu \rightarrow\ + OH + POHORG$	1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4416e	TrGCJ	$LHMVKABOOH + h\nu \rightarrow .12\ + .88\ CH_3C(O)OO + .88\ HOCH_2CHO + .12\ HCHO + OH + POHORG$	1.14*jx(ip_CH3OOH)+J_ACETOL	Taraborrelli (2013a)
J4418e	TrGCJ	$CO2H3CHO + h\nu \rightarrow\ + CO + HO_2$	jx(ip_HOCH2CHO)+J_ACETOL	Taraborrelli (2013a)
J4419	TrGCJ	$HO12CO3C4 + h\nu \rightarrow CH_3C(O)OO + HOCH_2CHO + HO_2$	J_ACETOL	Rickard and Pascoe (2009)*
J4420e	TrGCJ	$BIACETOH + h\nu \rightarrow CH_3C(O)OO +$	2.15*jx(ip_MGLYOX)	Taraborrelli (2013a)
J4421e	TrGC	$+ h\nu \rightarrow .5\ OH + .25\ + .25\ CH_3C(O)OO + .5\ + .5\ CO + .5\ POHORG$	J_KETENE	Taraborrelli (2013a)
J4422e	TrGC	$+ h\nu \rightarrow .0192\ + .1848\ H_2O_2 + .2208\ MGLYOX + .36\ OH + .36\ CO + .56\ CH_3C(O)OO + .2\ CH_3CHO + .2\ CO_2 + .2\ HCHO + .2\ HO_2 + .36\ POHORG$	J_KETENE*0.5	Taraborrelli (2013a)
J4422et2	TrGC	$+ h\nu \rightarrow\ + CO$	J_KETENE*0.5	Taraborrelli (2013a)
J4423e	TrGCJ	$+ h\nu \rightarrow CH_3C(O)OO + CO + CO + HO_2$	jx(ip_MGLYOX)	Taraborrelli (2013a)
J4424e	TrGCJ	$+ h\nu \rightarrow CH_3C(O)OO +$	2.15*jx(ip_MGLYOX)	Taraborrelli (2013a)
J4424et2	TrGC	$+ h\nu \rightarrow CH_3C(O)OO + CO + CO_2 + HO_2$	3.15*jx(ip_MGLYOX)	Taraborrelli (2013a)
J4502et2	TrGCJ	$LISOPACOOH + h\nu \rightarrow LHC4ACCHO + HO_2 + OH + POHORG$	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)*

Table 2: Photolysis reactions (... continued)

#	labels	reaction	rate coefficient	reference
J4503et2	TrGNCJ	LISOPACNO3 + hν → LHC4ACCHO + HO$_2$ + NO$_2$	0.59*J_IC3H7NO3	see note
J4504e	TrGCJ	ISOPBOOH + hν → MVK + HCHO + HO$_2$ + OH + POHORG	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)*
J4505e	TrGNCJ	ISOPBNO3 + hν → MVK + HCHO + HO$_2$ + NO$_2$	2.84*J_IC3H7NO3	see note
J4506e	TrGCJ	ISOPDOOH + hν → MACR + HCHO + HO$_2$ + OH + POHORG	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)*
J4507	TrGNCJ	ISOPDNO3 + hν → MACR + HCHO + HO$_2$ + NO$_2$	J_IC3H7NO3	see note
J4508e	TrGNCJ	NISOPOOH + hν → NC4CHO + HO$_2$ + OH + POHORG	1.14*jx(ip_CH3OOH)	Rickard and Pascoe (2009)*
J4509	TrGNCJ	NC4CHO + hν → NOA + 2 CO + 2 HO$_2$	jx(ip_MACR)	see note
J4510e	TrGNCJ	LNISOOH + hν → NOA + OH + .5 + .5 CO + .5 HO$_2$ + .5 CO$_2$ + POHORG	1.14*jx(ip_CH3OOH)	Taraborrelli et al. (2009)*
J4511e	TrGCJ	LHC4ACCHO + hν → .5 LHC4ACCO3 + .5 HO$_2$ + .5 OH + .25 MACRO2 + .25 LHMVKABO2 + .5 POHORG	jx(ip_MACR)	Taraborrelli (2013a)*
J4512e	TrGCJ	LC578OOH + hν → .25 CH$_3$COCH$_2$OH + .75 MGLYOX + .25 + .75 HOCH$_2$CHO + .75 HO$_2$ + OH + POHORG	1.14*jx(ip_CH3OOH)+ 2.77*jx(ip_HOCH2CHO)	Taraborrelli (2013a)
J4513e	TrGCJ	LHC4ACCO3H + hν → OH + .5 MACRO2 + .5 LHMVKABO2 + OH + 2 POHORG + CO$_2$	J_HPALD	Taraborrelli (2013a)*
J4514	TrGNCJ	LC5PAN1719 + hν → .6 LHC4ACCO3 + .6 NO$_2$ + .2 MACRO2 + .2 LHMVKABO2 + .4 CO$_2$ + .4 NO$_3$	jx(ip_PAN)	see note
J4515e	TrGCJ	HCOC5 + hν → +	0.5*jx(ip_MVK)	Taraborrelli (2013a)
J4516e	TrGCJ	C59OOH + hν → CH$_3$COCH$_2$OH + + OH + POHORG	J_ACETOL+1.14*jx(ip_CH3OOH)	Taraborrelli (2013a)
J4517e	TrGCJ	+ hν → LHC4ACCO3 + OH + POHORG	J_HPALD	Taraborrelli (2013a)
J4518e	TrGCJ	+ hν → .62 + .38 + OH + CO$_2$ + POHORG	J_HPALD	Taraborrelli (2013a)
J4519e	TrGCJ	+ hν → CH$_3$COCH$_2$O$_2$H + OH + 2 CO + HO$_2$ + POHORG	2.77*JX(IP_HOCH2CHO)	Taraborrelli (2013a)
J4520e	TrGCJ	+ hν → .5 CH$_3$COCH$_2$O$_2$H + .5 + .5 CO2H3CHO + .5 HCHO + 1.5 OH + 1.5 POHORG	2.*1.14*JX(IP_CH3OOH)	Taraborrelli (2013a)
J4523e	TrGCJ	+ hν → MGLYOX + + OH + POHORG	1.14*JX(IP_CH3OOH)	Taraborrelli (2013a)
J4524e	TrGCJ	+ hν → CO2H3CHO + CO + HO$_2$ + OH + POHORG	2.*2.77*JX(IP_HOCH2CHO)	Taraborrelli (2013a)*
J4525	TrGCJ	+ hν → + HO$_2$ + OH + POHORG	1.14*JX(IP_CH3OOH)	Taraborrelli (2013a)
J4526	TrGCJ	+ hν → HCHO + OH + HO$_2$ + CO2H3CHO + POHORG	1.14*JX(IP_CH3OOH)	Taraborrelli (2013a)*
J4525e	TrGCJ	+ hν → .5 + .5 + CO + HO$_2$ + OH + POHORG	jx(ip_NO2)*0.1*0.5	Taraborrelli (2013a)
J4526e	TrGCJ	+ hν → CH$_3$C(O)OO + HCHO + GLYOX + HO$_2$	1.14*JX(IP_CH3OOH)+J_ACETOL	Taraborrelli (2013a)
J4527e	TrGCJ	+ hν → CH$_3$C(O)OO + HCHO + HCHO + CO + HO$_2$	jx(ip_HOCH2CHO)	Taraborrelli (2013a)

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*Notes:

J-values are calculated with an external module and then supplied to the MECCA chemistry.

Values that originate from the Master Chemical Mechanism (MCM) by Rickard and Pascoe (2009) are translated according in the following way:
J(11) → jx(ip_COH2)
J(12) → jx(ip_CHOH)
J(15) → jx(ip_HOCH2CHO)
J(18) → jx(ip_MACR)
J(22) → jx(ip_ACETOL)
J(23)+J(24) → jx(ip_MVK)
J(31)+J(32)+J(33) → jx(ip_GLYOX)
J(34) → jx(ip_MGLYOX)
J(41) → jx(ip_CH3OOH)
J(53) → J(iC$_3$H$_7$ONO$_2$)
J(54) → J(iC$_3$H$_7$ONO$_2$)
J(55) → J(iC$_3$H$_7$ONO$_2$)
J(56)+J(57) → jx(ip_NOA)

J4207: It is assumed that J(PHAN) is the same as J(PAN).

J4212: It is assumed that J(ETHOHNO3) is the same as J(iC$_3$H$_7$ONO$_2$).

J4302: Following von Kuhlmann et al. (2003), we use J(CH$_3$COCH$_2$OH) = 0.11*jx(ip_CHOH). As an additional factor, the quantum yield of 0.65 is taken from Orlando et al. (1999a).

J4306: Following von Kuhlmann et al. (2003), we use J(iC$_3$H$_7$ONO$_2$) = 3.7*jx(ip_PAN).

J4307: NOA contains the cromophores of both CH$_3$COCH$_3$ and a nitrate group. It is assumed here that the J values are additive, i.e.: J(NOA) = J(CH$_3$COCH$_3$) + J(iC$_3$H$_7$ONO$_2$).

J4401: Romero et al(2005)

J4406: It is assumed that J(LC4H9NO3) is the same as J(iC$_3$H$_7$ONO$_2$).

J4407: It is assumed that J(MPAN) is the same as J(PAN).

J4405: It is assumed that J(BIACET) is 2.15 times larger than J(MGLYOX), consistent with the photolysis rate coefficients used in the MCM (Rickard and Pascoe, 2009).

J4414: It is assumed that J(MACROH) is 2.77 times larger than J(HOCH$_2$CHO), consistent with the photolysis rate coefficients used in the MCM (Rickard and Pascoe, 2009).

J4505: It is assumed that J(ISOPBNO3) = 2.84 × J(iC$_3$H$_7$ONO$_2$), consistent with the photolysis rate coefficients used in the MCM (Rickard and Pascoe, 2009).

J4509: It is assumed that J(NC4CHO) is the same as J(MACR).

J4514: It is assumed that J(LC5PAN1719) is the same as J(PAN).

J4526: decomposition of a dialkoxy radical

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C. Data sheets

C.1. Pen-ray line source – LOT-QuantumDesign, Europe
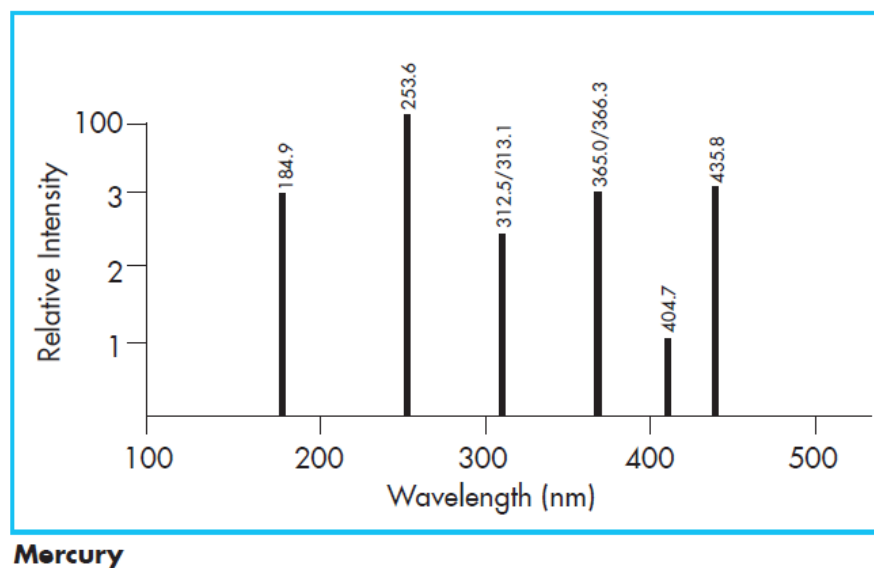
Abbildung C.1.: Discontinuous spectrum of the pen-ray line source used for calibration of the HORUS instrument (Taken from manual, LOT-QuantumDesign, Europe, www.lot-qd.com)

C.2. NIST NO standard

Abbildung C.2.: National Institute of Standards & Technology - NO standard used for actinic flux density calibration of the mercury lamp that was applied for calibration of the HORUS instrument.

C.3. Dew Point Generator - **LI-610 &** H$_2$O-**Monitor** - **LI-7000**

CERTIFICATE of CALIBRATION

LI-610 Portable Dew Point Generator

Serial Number: **DPG-629B**

Standards Used:
Precision Thermistor Serial Number: **#2**
Multimeter: **Hewlett Packard Model 3468A Serial Number: 2137A16238**
Platinum RTD Probe Serial Number: **Minco Model S7297PA1L120S Serial Number: 1194**
Standard Resistor: **Julie Research Model NB-102 Serial Number: 1156**

The copper condenser block temperature is used to calibrate the LI-610. The temperature of the condenser block can be measured with greater accuracy and resolution than the dew point of the output air stream as measured by a dew point hygrometer.

The water temperature inside the condenser block is established by the block temperature, and air brought to saturation at the water temperature will have a dew point equal to the water temperature. Design testing has confirmed that air leaving the LI-610 is saturated at flow rates up to 2 liters min^{-1}, with a dew point equal to the block and water temperature.

The platinum Resistance-Temperature-Detector (RTD) mounted on the copper condenser block is calibrated at two temperatures: 0 °C and 49.90 °C. The slight non-linearity of the RTD is corrected electronically. A precision thermistor is used to calibrate the condenser block at 0 °C and 49.90 °C, as it offers much greater sensitivity than the RTD.
See the instruction manual for more information on calibration standards.

    Cooling Block Temperature errors after calibration:
    At 0 °C   **.00** °C.
    At 25 °C   **-0.02** °C.
    At 49.90 °C   **.00** °C.

This certifies that the dew point generated will be within ± .2 °C of the setting when operated according to the instructions.

    Date of Calibration: November 20, 2003

    Calibration Technician: _____

LI-COR
Biosciences

LI-COR, inc. ● Environmental ● 4421 Superior Street ● P.O. Box 4425 ● Lincoln, NE 68504
Phone: 402-467-3576 ● FAX: 402-467-2819 ● Toll-free 1-800-447-3576 (U.S. & Canada)
E-mail: envsales@licor.com ● www.licor.com

Abbildung C.3.: Certificate of Calibration, Dew Point Generator Licor, LI-610. Calibrated against NIST-traceable standard.
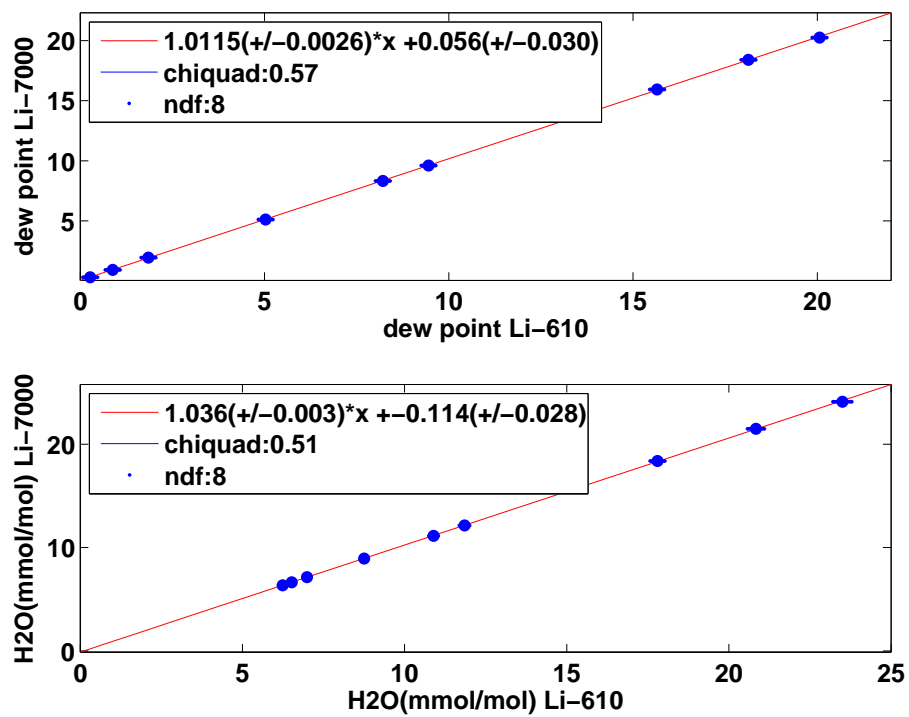
Abbildung C.4.: Calibration of the H_2O-Monitor - Licor, LI-7000, using the Dew Point Generator Licor, LI-610. Date of calibration: 10th of June, 2010.

C.4. Gas Flow Calibrator – DryCal, BIOS, USA

Abbildung C.5.: Certificate of Calibration, DryCal, DC-LC-1 & HC-LC-1,BIOS Internatio-
nal, USA. Calibrated against NIST-traceable standard.

TPF CONTROL

CALIBRATION CERTIFICATE 12877

AS FOUND RESULTS

Lab. Temperature 20.8 °C   Lab. Pressure 1004.2 mbar
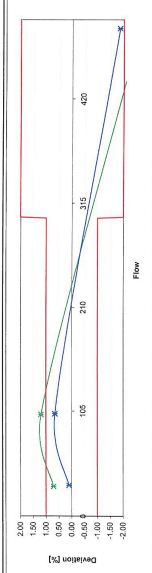
INSTRUMENT READING [ml/min]	LAB STANDARD READING Flow[ml/min]	Tool no.	DEVIATION (ERROR) Of Rate [%]	Flow[ml/min]	Limit [%]	UNCERTAINTY Flow [%]
29.45	29.25	B00101	0.70	0.20	1.00	0.32%
101.70	100.51	B00101	1.19	1.20	1.00	0.33%
485.45	498.24	B00101	-2.57	-12.79	2.00	0.33%

CALIBRATION RESULTS AFTER ADJUSTMENT

Lab. Temperature 20.8 °C   Lab. Pressure 1004.3 mbar

INSTRUMENT READING [ml/min]	LAB STANDARD READING Flow[ml/min]	Tool no.	DEVIATION (ERROR) Of Rate [%]	Flow[ml/min]	Limit [%]	UNCERTAINTY Flow [%]
30.76	30.72	B00101	0.10	0.03	1.00	0.33%
102.25	101.59	B00101	0.65	0.66	1.00	0.34%
491.15	500.40	B00102	-1.85	-9.25	2.00	0.32%

GRAPH DEVIATION vs FLOW

Remarks:

The deviation is determined by: Deviation = (Instrument reading - Lab standard reading) / Lab standard reading * 100 %

Form BM5 41.09 - Rev D dated 1-05-10   Page 2 of 2

TPF CONTROL

CALIBRATION CERTIFICATE 12878

AS FOUND RESULTS

Lab. Temperature 21.2 °C   Lab. Pressure 1004.5 mbar
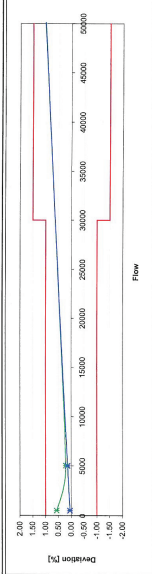
INSTRUMENT READING [ml/min]	LAB STANDARD READING Flow[ml/min]	Tool no.	DEVIATION (ERROR) Of Rate [%]	Flow[ml/min]	Limit [%]	UNCERTAINTY Flow [%]
501.20	498.41	B00101	0.56	2.79	1.00	0.32%
5034.00	5023.65	B00104	0.21	10.35	1.00	0.37%
50100.00	49602.00	B00104	1.00	498.00	1.50	0.38%

CALIBRATION RESULTS AFTER ADJUSTMENT

Lab. Temperature 20.7 °C   Lab. Pressure 1004.4 mbar

INSTRUMENT READING [ml/min]	LAB STANDARD READING Flow[ml/min]	Tool no.	DEVIATION (ERROR) Of Rate [%]	Flow[ml/min]	Limit [%]	UNCERTAINTY Flow [%]
491.25	491.05	B00101	0.04	0.21	1.00	0.32%
5012.00	5005.30	B00104	0.13	6.70	1.00	0.37%
50080.00	49573.50	B00104	1.02	506.50	1.50	0.37%

GRAPH DEVIATION vs FLOW

Remarks:

The deviation is determined by: Deviation = (Instrument reading - Lab standard reading) / Lab standard reading * 100 %

Form BM5 41.09 - Rev D dated 1-05-10   Page 2 of 2

Certificate 12878

CALIBRATION CERTIFICATE

12878

Applicant
Customer name: Westphal Mess- und Regeltechnik
Contact: E. Reuveni
Address: Laurinweg 20
85521 - Ottobrunn
Germany

Order reference applicant: R10-000379
Order reference TPF Control: 12875

Instrument information [DUT]
Instrument: Primary Flow Calibrator
Manufacturer: Bios International
Serial no.: 104034
Model: DC-HC-1
Revision: E

Calibration method
The device under test is connected in a parallel setup to the mentioned flow calibrator to compare flow readings. An appropriate warm up time is incorporated. Bios - Drycal products; a flow source is used to generate a flow. This flow is measured in on A-B method
(A=reading lab standard, B=reading device under test).

Period of calibration
8 juni 2010

Calibration result
The results of the calibration are presented on page 2 of 2. The reported uncertainty of measurement is based on the standard uncertainty multiplied by a coverage factor k=2 which provides a confidence level of approximately 95%.
The standard uncertainty of measurement has been determined in accordance with EA-4/02.

Calibration traceability
The measurements have been executed using standards for which the traceability to (inter)national standards has been demonstrated towards the RvA.

Remarks

Certificate issue date: Wijchen, 8 juni 2010

Calibration technician
Khalid Harkach

Technical Manager
Rik van de Bovenkamp

TPF Control b.v.
Nieuweweg 283a
6603 BN WIJCHEN (NL)
Tel. +31 24 379 2120
Fax. +31 24 379 1063
Web: www.tpf-control.nl

RvA is member of the European Cooperation for Accreditation (EA) and is one of the signatories to the EA Multilateral Agreement and to the ILAC Mutual Recognition Arrangements (MRA) for the mutual recognition of for the mutual recognition of calibration certificates.

Reproduction of the complete certificate is allowed Parts of the certificate may only be reproduced after written permission of the calibration laboratory. This certificate is issued under the provision that neither the RvaA nor Accreditatie, nor TPF CONTROL B.V. assumes any liability.

Form BMS 41.09 - Rev D dated 1-05-10

Page 1 of 2

Certificate 12877

CALIBRATION CERTIFICATE

12877

Applicant
Customer name: Westphal Mess- und Regeltechnik
Contact: E. Reuveni
Address: Laurinweg 20
85521 - Ottobrunn
Germany

Order reference applicant: R10-000379
Order reference TPF Control: 12875

Instrument information [DUT]
Instrument: Primary Flow Calibrator
Manufacturer: Bios International
Serial no.: 104061
Model: DC-L/C-1
Revision: F

Calibration method
The device under test is connected in a parallel setup to the mentioned flow calibrator to compare flow readings. An appropriate warm up time is incorporated. Bios - Drycal products; a flow source is used to generate a flow. This flow is measured in on A-B method
(A=reading lab standard, B=reading device under test).

Period of calibration
8 juni 2010

Calibration result
The results of the calibration are presented on page 2 of 2. The reported uncertainty of measurement is based on the standard uncertainty multiplied by a coverage factor k=2 which provides a confidence level of approximately 95%.
The standard uncertainty of measurement has been determined in accordance with EA-4/02.

Calibration traceability
The measurements have been executed using standards for which the traceability to (inter)national standards has been demonstrated towards the RvA.

Remarks

Certificate issue date: Wijchen, 8 juni 2010

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RvA is member of the European Cooperation for Accreditation (EA) and is one of the signatories to the EA Multilateral Agreement and to the ILAC Mutual Recognition Arrangements (MRA) for the mutual recognition of for the mutual recognition of calibration certificates.

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C.5. Optical Fiber – Thorlabs GmbH, Germany

TECS Coated Silica/Silica Fiber

TECS-Coated Silica/Silica Fiber Specifications

Core Diameter	μm	200 ± 8	365 ± 14	550 ± 19	910 ± 30
Clad Diameter	μm	240 ± 5	400 ± 8	600 ± 10	1000 ± 15
Coating Diameter	μm	260 ± 6	425 ± 10	630 ± 10	1035 ± 15
Buffer Diameter1	μm	400 ± 30	730 ± 30	1040 ± 30	1400 ± 50
Maximum Attenuation @ 820nm	dB/km	12	12	12	12
Maximum Core Offset	μm	5	7	9	10
Numerical Aperture2		0.22 ± 0.02	0.22 ± 0.02	0.22 ± 0.02	0.22 ± 0.02
Acceptance Angle (Full)		25˚	25˚	25˚	25˚
Maximum Power Capability					
– CW3	kW	0.2	0.7	1.5	5.0
– Pulsed4	MW	1.0	3.4	7.6	25.1
Operating Temperature @ 820nm		-60˚C to +125˚C	-60˚C to +125˚C	-60˚C to +125˚C	-60˚C to +125˚C
Proof Test Level	kpsi	100	100	100	100
Minimum Bend Diameter					
– Recommended Short Term5	mm	24	40	60	100
– Recommended Long Term6	mm	48	80	120	200
Standard Length	m	1100	500	300	50
Type					
Low-OH⁻	Part Number	FG-200-LCR	FG-365-LER	FG-550-LER	FG-910-LER
	Stock Number	98-0400-1367-8	98-0400-1361-1	98-0400-1362-9	98-0400-3373-4
High-OH⁻	Part Number	FG-200-UCR	FG-365-UER	FG-550-UER	FG-910-UER
	Stock Number	98-0400-1368-6	98-0400-1369-4	98-0400-1370-2	98-0400-3635-6

[1] Standard buffer coating is Tefzel® 210.
[2] 2 meters, 50% intensity; uncoated and mode stripped.
[3] Based on 1 MW/cm2 for 1064nm Nd:YAG laser and input spot size equal to 80 percent of the core diameter.
[4] Based on 5 GW/cm2 for 1064nm Nd:YAG laser with 10 nsec. pulse length and input spot size equal to 80 percent of the core diameter.
[5] Recommended geometric strain during installation is 100% of proof test level, based on statistical analysis of fiber failures.
[6] Recommended geometric strain is 50% of proof test level, based on statistical analysis of fiber failures.

Abbildung C.6.: Specifications of coated silica fiber used for transportation of the 308 nm UV light within HORUS. (Taken from manual, Thorlabs GmbH, Europe, Germany, www.thorlabs.com)
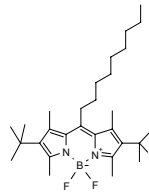
C.6. Laser Dye Pyrromethene-597 – Exciton, USA

PYRROMETHENE 597-8C9

Synonym: 2,6-di-tert-butyl-8-nonyl-1,3,5,7-tetramethylpyrromethene- BF_2 Complex
Catalog No.: 05971   **CAS Registry Number:** N/A
Chemical Formula: $C_{30}H_{49}N_2BF_2$ **MW:** 486.54
Appearance: Red-orange solid   **Melting Point:** 247°C

Suggested Use: lithography, fl hydrocarbon probe or tagant, electro-luminescence, DVD (digital video data)

Solubility Limits (g/l) (room temperature):

Ethanol	3.7	EPH	very soluble
Heptane	≥10.3	PPH	very soluble
Ethyl Acetate	very soluble	Toluene	very soluble
Acetonitrile	very soluble	THF	very soluble
p-Dioxane	very soluble	Dow Corning 200 Silcone Oil	0.47

Spectral Information:
$\lambda_{max,abs}$ = 524nm (ethanol), 525nm (methylene chloride), 527.8nm (diesel fuel)
$\lambda_{max,fl}$ = 588nm (ethanol), 585nm (methylene chloride), 590nm (diesel fuel)

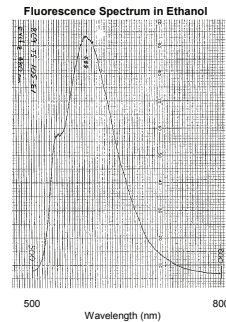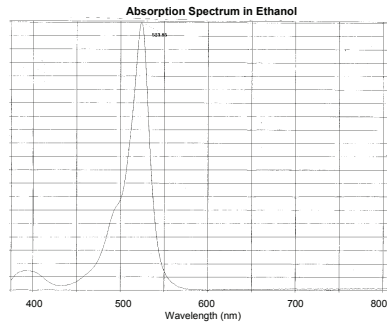Abbildung C.7.: Pyrromethene-597 laser dye, Exciton, USA, www.exciton.com

D. Abbreviations

BVOC	*B*iogenic *V*olatile *O*rganic *C*ompound
BEARPEX09	*B*iosphere *E*ffects on *AeR*osols and *P*hotochemistry *EX*periment 2009, USA
CAABA/MECCA	*C*hemistry *As A B*oxmodel *A*pplication / *M*odule *E*fficiently *C*alculating the *C*hemistry of the *A*tmosphere
CABINEX	*C*ommunity *A*tmosphere *B*iosphere *IN*teractions *EX*periments, USA
CIMS	*C*hemical *I*onisation *M*ass *S*pectroscopy
CRD	*C*avity *R*ing *D*own
DOAS	*D*ifferential *O*ptical *A*bsorption *S*pectroscopy
GABRIEL	*G*uyanas *A*tmosphere-*B*iosphere Exchange and *R*adicals *I*ntensive *E*xperiment with the *L*earjet, Oct. 2005, Suriname
GTHOS	*G*round-based *T*ropospheric *H*ydrogen *O*xides *S*ensor
HOPE12	*HO*henpeissenberg *P*hotochemistry *E*xperiment
HORUS	*H*ydr*O*xyl *R*adical Measurement *U*nit based on fluorescence *S*pectroscopy
HOxCOMP	HO_x Inter*comp*arison Campaign 2005, Jülich, Germany
HUMPPA-COPEC	*H*yytiälä *U*nited *M*easurements of *P*hotochemistry and *P*articles in *A*ir – *C*omprehensive *O*rganic *P*recursor *E*mission and *C*oncentration study, Finland
IPI	*I*nlet*P*re*I*njector
LIF	*L*aser *I*nduced *F*luorescence
LIF-FAGE	*L*aser *I*nduced *F*luorescence - *F*luorescence *A*ssay by *G*as *E*xpansion
NMHC	*N*on-*M*ethane *H*ydro*C*arbons
MCM	*M*aster *C*hemical *M*echanism
MCP	*M*icro *C*hannel *P*late
MIESR	*M*atrix *I*solation *E*lectron *S*pin *R*esonance
MIM	*M*ainz *I*soprene *M*echanism
MTM	*M*ainz *T*erpene *M*echanism

OP3	*O*xidant and *P*article Photochemical *P*rocesses above a Southeast Asian Tropical Rainforest
PARADE	*PA*rticles and *RA*dicals: *D*iel observations of the impact of urban and biogenic *E*missions
PROPHET	*P*rogram for *R*esearch on *O*xidants: *PH*otochemistry, *E*missions, and *T*ransport, USA
PTR-MS	*P*roton *T*ransfer *R*eaction *M*ass *S*pectroscopy
SMEAR II	*S*tation for *M*easuring Forest *E*cosystem-*A*tmosphere *R*elations
SOS99	*S*outhern *O*xidants *S*tudy 1999
TexAQS	*Tex*as *A*ir *Q*uality *S*tudy
Trace-P	*Tr*ansport and *C*hemical *E*volution over the *P*acific
UTC	*U*niversal *T*ime *C*oordinates
VOC	*V*olatile *O*rganic *C*ompound

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