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# Heterogeneous photochemistry of imidazole-2-carboxaldehyde: HO<sub>2</sub> radical formation and aerosol growth

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**Abstract.** The multiphase chemistry of glyoxal is a source of secondary organic aerosol (SOA), including its light-absorbing product imidazole-2-carboxaldehyde (IC). IC is a photosensitizer that can contribute to additional aerosol ageing and growth when its excited triplet state oxidizes hydrocarbons (reactive uptake) via H-transfer chemistry. We have conducted a series of photochemical coated-wall flow tube (CWFT) experiments using films of IC and citric acid (CA), an organic proxy and H donor in the condensed phase. The formation rate of gas-phase HO<sub>2</sub> radicals ( $P_{\text{HO}_2}$ ) was measured indirectly by converting gas-phase NO into NO<sub>2</sub>. We report on experiments that relied on measurements of NO<sub>2</sub> formation, NO loss and HONO formation.  $P_{\text{HO}_2}$  was found to be a linear function of (1) the  $[\text{IC}] \times [\text{CA}]$  concentration product and (2) the photon actinic flux. Additionally, (3) a more complex function of relative humidity (25 % < RH < 63 %) and of (4) the O<sub>2</sub> / N<sub>2</sub> ratio (15 % < O<sub>2</sub> / N<sub>2</sub> < 56 %) was observed, most likely indicating competing effects of dilution, HO<sub>2</sub> mobility and losses in the film. The maximum  $P_{\text{HO}_2}$  was observed at 25–55 % RH and at ambient O<sub>2</sub> / N<sub>2</sub>. The HO<sub>2</sub> radicals form in the condensed phase when excited IC triplet states are reduced by H transfer from a donor, CA in our system, and subsequently

react with O<sub>2</sub> to regenerate IC, leading to a catalytic cycle. OH does not appear to be formed as a primary product but is produced from the reaction of NO with HO<sub>2</sub> in the gas phase. Further, seed aerosols containing IC and ammonium sulfate were exposed to gas-phase limonene and NO<sub>x</sub> in aerosol flow tube experiments, confirming significant  $P_{\text{HO}_2}$  from aerosol surfaces. Our results indicate a potentially relevant contribution of triplet state photochemistry for gas-phase HO<sub>2</sub> production, aerosol growth and ageing in the atmosphere.

## 1 Introduction

The sources and sinks of radicals play an important role in the oxidative capacity of the atmosphere. Radicals and other oxidants initiate the chemical degradation of various trace gases, which is key in the troposphere (Jacob, 1999). The hydroxyl (OH) and peroxy (HO<sub>2</sub>) radicals belong to the HO<sub>x</sub> chemical family and are primarily generated by ultraviolet radiation photochemical reactions (Calvert and Pitts, 1966), like the reaction of O(<sup>1</sup>D) (from O<sub>3</sub>) with H<sub>2</sub>O or photolysis of HONO, HCHO, H<sub>2</sub>O<sub>2</sub> or acetone. Some secondary gas-phase sources are the ozonolysis of alkenes or O(<sup>1</sup>D) + CH<sub>4</sub>

(Monks, 2005). The oxidation of volatile organic compounds (VOCs) by OH and other oxidants in the presence of NO leads to perturbations in the HO<sub>x</sub>, NO<sub>x</sub> and RO<sub>x</sub> radical cycles that affect O<sub>3</sub> and aerosol formation (Monks, 2005; Sheehy et al., 2010). The kinetics and photochemical parameters of these reactions are relatively well-known in the gas phase (Atkinson et al., 2004; Sander et al., 2011). However, this does not apply to the sources and sinks for HO<sub>x</sub> in atmospheric droplets and on aerosol surfaces (Ervens et al., 2011). Uptake of OH from the gas phase and H<sub>2</sub>O<sub>2</sub> photolysis in the condensed phase are the primary known sources for HO<sub>x</sub> in the condensed phase. HO<sub>2</sub> is highly soluble and the concentrations of OH, the most effective oxidant in the condensed phase, depend on HO<sub>2</sub> radicals. Another source of HO<sub>x</sub> radicals is from the chemical reactions of reduced metal ions and H<sub>2</sub>O<sub>2</sub>, known as Fenton reactions (Fenton, 1894; Deguillaume et al., 2005). Direct photolysis of H<sub>2</sub>O<sub>2</sub>, nitrite, nitrate (Zellner et al., 1990), hydroperoxides (Zhao et al., 2013) and light-absorbing secondary organic aerosol (SOA) (Badali et al., 2015) are also sources of HO<sub>x</sub> in the condensed phase. Other studies have shown that the photochemistry of iron (III) oxalate and carboxylate complexes, present in aqueous environments (e.g., wastewater, clouds, fogs, particles), can initiate a radical chain reaction serving as an aqueous source of HO<sub>2</sub> and Fe<sup>2+</sup>. Fe<sup>2+</sup> can then regenerate OH starting a new cycle of Fenton reactions (Weller et al., 2013a, b). The temperature-dependent rate constants of OH in the aqueous phase have been studied for a limited subset of organics (Ervens et al., 2003). However, there is still a wide gap with respect to understanding the sources, sinks, kinetics and photochemical reaction pathways of HO<sub>x</sub> radicals in the condensed phase (George et al., 2015).

Our study investigates photosensitizers as an additional HO<sub>x</sub> source that may be relevant to further modify RO<sub>x</sub> and NO<sub>x</sub> reaction cycles in both the condensed and gas phases. It is motivated by the formation of superoxide in terrestrial aqueous photochemistry (Draper and Crosby, 1983; Faust, 1999; Schwarzenbach et al., 2002), by more recent observations that irradiated surfaces containing titanium dioxide generate HO<sub>x</sub> radicals in the gas phase (Yi et al., 2012) and by the generation of OH from metal oxides acting as photocatalysts in mineral dust (Dupart et al., 2012). Past studies have demonstrated the reactivity of glyoxal towards ammonium ions and amines as a source for light-absorbing brown carbon (Nozière et al., 2009; Galloway et al., 2009; Shapiro et al., 2009; Kampf et al., 2012). One of these products is imidazole-2-carboxaldehyde (IC; Galloway et al., 2009), which absorbs light at UV wavelengths ( $\lambda < 330$  nm) (Maxut et al., 2015). Other imidazole-type compounds and light-absorbing products are formed in minor amounts but can nonetheless impact optical and radiative properties of secondary organic aerosols (SOAs; Sareen et al., 2010; Trainic et al., 2011). Photochemical reactions by these species are not typically accounted for in models yet but have a possi-

ble role for SOA formation and aerosol aging mechanisms (Sumner et al., 2014).

Photosensitizers are light-absorbing compounds that absorb and convert the energy of photons into chemical energy that can facilitate reactions, e.g., at surfaces or within aerosols (George et al., 2015). For example, aerosol seeds containing humic acid or 4-(benzoyl)benzoic acid (4-BBA), two other known photosensitizers, can induce the reactive uptake of VOCs when exposed to light, leading to SOA formation (Monge et al., 2012). Aregahegn et al. (2013) and Rossignol et al. (2014) suggested a mechanism for autophotocatalytic aerosol growth, where radicals are produced from the reaction of an H-donor hydrocarbon species, in this case limonene, and the triplet state of IC. The condensed-phase citric acid and the gas-phase limonene are H-atom donors (in this article we refer to them as H donors) rather than proton donors as in the case of a Brønsted acid. In particular, the transfer of the H atom leads to the formation of an alkyl-radical species. The H-atoms transfer thus has the same effect as an H-atom abstraction reaction by Cl or OH radicals.

Field measurements on fog water samples confirmed that triplet excited states of organic compounds upon irradiation can oxidize model samples such as syringol (a biomass burning phenol) and methyl jasmonate (a green leaf volatile), accounting for 30–90% of their loss (Kaur et al., 2014). There are very few field measurements of imidazoles; a recent study by Teich et al. (2016) identified five imidazoles (1-butyylimidazole, 1-ethylimidazole, 2-ethylimidazole, IC and 4(5)-methylimidazole) in ambient aerosols in concentrations ranging from 0.2 to 14 ng m<sup>-3</sup>. IC, the molecule of interest in this study, was measured in its hydrated form in ambient aerosols in three urban areas with signs of air pollution and biomass burning (Leipzig, Germany; Wuqing and Xianghe, China). The observed quantities of hydrated IC ranged from 0.9 to 3.2 ng m<sup>-3</sup>. The authors claim that these values could be a lower limit due to high losses of IC during sample preparation indicated by low recovery from standard solutions. This suggests that IC and other imidazole derivatives are present in areas with high pollution and biomass burning. Field measurements in Cyprus during the CYPHEX campaign in 2014 detected IC and bis-imidazole in ambient aerosol samples (Jacob, 2015). The IC diurnal cycles showed the highest concentrations at night (0.02–0.115 ng m<sup>-3</sup>) and lower concentrations during the day, suggesting that ambient concentrations of IC in aerosols are a balance between photochemical sources and sinks. Imidazoles seem to be widespread in polluted and remote areas. However, the atmospheric implications of IC as a photosensitizer, a proxy species of brown carbon light absorption, and as a radical source in ambient aerosols remains unclear.

The existence of such photocatalytic cycles could be of atmospheric significance. Indeed, Canonica et al. (1995) suggested that the initial carbonyl, triggering the photochemical properties, is regenerated via a reaction with oxygen-producing HO<sub>2</sub>. To our knowledge, the production of such

radical side products has not been investigated under atmospheric conditions previously. We therefore report here on the HO<sub>2</sub> radical production from IC in the condensed phase.

## 2 Experimental section

A series of flow tube experiments were conducted to investigate the formation of gas-phase HO<sub>2</sub> radicals from IC photochemistry using two different coated-wall flow tube (CWFT) reactors (Sect. 2.1). Section 2.2 describes aerosol flow tube experiments that confirm the photochemical production of HO<sub>2</sub> radicals in the absence of other known gas-phase radical sources in aerosols. All experiments were performed at atmospheric pressure.

### 2.1 Coated-wall flow tube experiments

The CWFT experiments were designed to investigate the gas-phase production of HO<sub>2</sub> radicals from a film containing IC and citric acid (CA) matrix as a function of UV light intensity, IC concentration in the film, relative humidity (RH) and O<sub>2</sub> mixing ratio. Two similar experimental setups were used as shown in Fig. 1. Some of the differences, not major, consist in the flow-reactor volume, surface area, flow rates, IC mass loading, NO mixing ratio, temperature inside the reactor and the connected instrumentation.

Setup 1. Experiments were conducted in a photochemical flow system equipped with a Duran glass CWFT (0.40 cm inner radius, 45.2 and 40.0 cm length, 113.6 and 100.4 cm<sup>2</sup> inner surface, surface-to-volume ratio ( $S/V$ ) = 5.00 cm<sup>-1</sup>), which was housed in a double-jacketed cell coupled to a recirculating water bath to control the temperature at 298 K; the setup is shown in Fig. 1a. A thin film of IC + CA was deposited inside the tubular glass flow tube. The experimental procedure for the preparation of the films is described in Sect. 2.1.2. The system consisted of seven ultraviolet lamps (UV-A range, Philips Cleo Effect 22 W: 300–420 nm, 41 cm, 2.6 cm o.d.) surrounding the flow tube in a circular arrangement of 10 cm in diameter.

Setup 2. The second CWFT (CWFT 0.60 cm inner radius, 50 cm length, inner surface 188.5 cm<sup>2</sup>,  $S/V$  = 3.33 cm<sup>-1</sup>) reactor had a glass jacket to allow water to circulate and maintain temperature control inside the tube at 292 K. The coated-wall tubes were snugly fit into the CWFT as inserts. The CWFT was surrounded by the same seven fluorescent lamps as in Setup 1. The light passed through different circulating water cooling jackets for both setups, thus providing a different light path for each setup.

Setup 1 and 2. The actinic flux in the flow tube reactor,  $F_{FT}(\lambda)$ , was measured by actinometry of NO<sub>2</sub> (see Supplement for description of  $J_{NO_2}$  measurements), independently for both setups. The flows of N<sub>2</sub>, O<sub>2</sub>, air and NO were set by mass flow controllers. The RH was set by a humidifier placed after the admission of N<sub>2</sub> and O<sub>2</sub> gases but before the

admission of NO or NO<sub>2</sub> (see Fig. 1), in which the carrier gas bubbles through liquid water at a given temperature. The humidifier could also be bypassed to set a RH of near zero. A typical measurement sequence is described in Sect. 2.1.2.

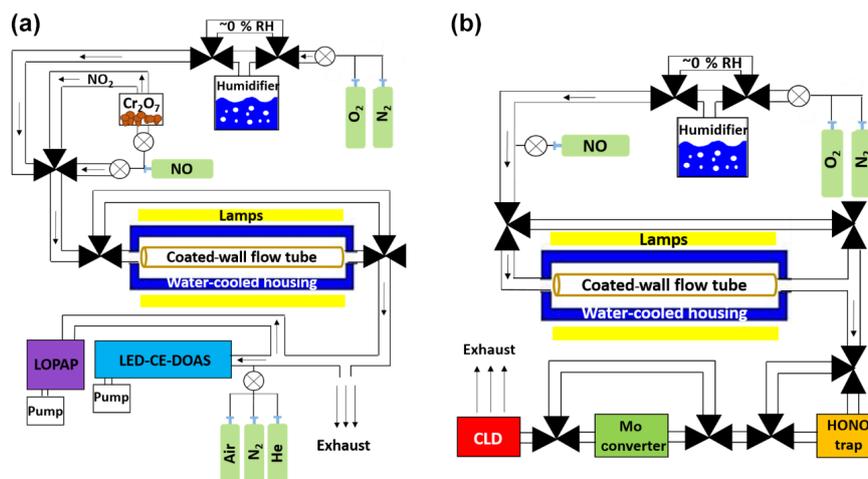
The  $J_{NO_2}$  was measured for both Setup 1 and 2 using NO<sub>2</sub> actinometry. The  $J_{NO_2}$  with seven lamps was found to be  $2 \times 10^{-2} \text{ s}^{-1}$  for Setup 1 and  $1 \times 10^{-2} \text{ s}^{-1}$  for Setup 2 (see Fig. S1 for Setup 1 and Supplement text for both Setups). These values were compared to direct actinic flux measurements in the flow tube and thus normalized (see Sect. 3.1.1).

#### 2.1.1 Flow tube instrumentation

The following gas-phase products exiting the flow tube were measured by three different instruments: NO<sub>2</sub> by the University of Colorado Light Emitting Diode Cavity-Enhanced Differential Optical Absorption Spectroscopy (LED-CE-DOAS) instrument (Thalman and Volkamer, 2010), HONO by a Long Path Absorption Photometer (LOPAP, QuMA GmbH, Heland et al., 2001; Kleffmann et al., 2002) and NO by a chemiluminescence analyzer (Ecophysics CLD 77 AM, also used for NO<sub>2</sub> in Setup 2). HO<sub>2</sub> radicals were indirectly measured by detecting NO<sub>2</sub> with the LED-CE-DOAS (Setup 1) and by the loss of NO with the chemiluminescence detector (Setup 2). The latter was preceded by a molybdenum converter to transform HONO and NO<sub>2</sub> to NO and by an alkaline trap for HONO. Both trap and converter had a bypass to allow sequential measurements, thereby obtaining the concentration of NO<sub>2</sub> and HONO separately. HONO was measured by the LOPAP during some selected experiments (Kleffmann et al., 2002, 2006).

#### LED-CE-DOAS

The LED-CE-DOAS instrument (Thalman and Volkamer, 2010) detects NO<sub>2</sub> absorption at blue wavelengths. A high-power blue LED light source (420–490 nm) is coupled to a confocal high-finesse optical cavity consisting of two highly reflective mirrors ( $R = 0.999956$ ) peaking at 460 nm that are placed about 87.5 cm apart (sample path length of 74 cm). The absorption path length depends on wavelength, and was about  $\sim 11$  km near peak reflectivity here. A purge flow of dry nitrogen gas is added to keep the mirrors clean. The light exiting the cavity is projected onto a quartz optical fiber coupled to a Princeton Instruments Acton SP2156 Czerny-Turner imaging spectrometer with a PIXIS 400B CCD detector. The mirror reflectivity was calculated by flowing helium and nitrogen gas, exploiting the difference in the Rayleigh scattering cross sections of both gases as described in Thalman et al. (2014). The gas exiting the flow tube was directly injected into the CE-DOAS cavity, and spectra were recorded every 60 s and stored on a computer. For analysis we use broadband cavity enhanced absorption spectroscopy (BBCEAS) fitting at NO<sub>2</sub> concentrations exceeding a few parts per billion by volume (Washenfelder et al., 2008) and



**Figure 1.** Sketch of the photochemical flow tube reactor setups at PSI for (a) Setup 1 in 2013 measuring  $\text{NO}_2$  generation and (b) for Setup 2 in 2014 measuring NO loss.

DOAS least-squares fitting methods at lower concentrations (Thalman et al., 2015). The mirror alignment was monitored online as part of every spectrum by observing the slant-column density of oxygen collision complexes,  $\text{O}_2\text{--O}_2$  ( $\text{O}_4$ ) (Thalman and Volkamer, 2010, 2013). The following reference spectra were taken from the literature:  $\text{NO}_2$  (Vandaele et al., 2002) and  $\text{O}_2\text{--O}_2$  collision complexes (Thalman and Volkamer, 2013). The detection limit for  $\text{NO}_2$  was 50–100 pptv.

### 2.1.2 Experimental conditions

The IC + CA solutions were prepared by adding IC into a 1 M CA solution in 18 M $\Omega$  cm ultrapure water to achieve IC to CA molecular ratios of between 0.026 and 0.127 in the film. The bulk solutions for both setups were prepared by weighing out 384–400 mg of CA in 2 mL of water and adding 4–20 mg of IC to the solution. The solutions for both setups were freshly prepared for each experiment, and the masses in the film were calculated at 50 % RH from the CA hygroscopic growth factors reported by Zardini et al. (2008) for both setups (for Setup 1: 5–18 mg of IC and 44 mg of CA; for Setup 2: 1–5 mg of IC and 77 mg of CA). The range of concentrations in the films was between 0.148 and 0.671 M of IC and 5.29 and 6.68 M of CA.

The IC + CA solution coatings were produced by depositing 220–250 (Setup 1) and 400  $\mu\text{L}$  (Setup 2) of the desired solution in a Duran glass tube, which was then dispersed into a thin and viscous film of 3–4  $\mu\text{m}$ . The film was dried with a gentle  $\text{N}_2$  stream humidified to a RH similar to the experimental RH and room temperature. The film was rolled and turned upside down to deposit a homogenous film throughout the entire inner surface of the flow tube. The homogeneity of the film was confirmed by visual inspection. If a bright clear homogenous amorphous film from the supercooled solution

was not observed, the film was discarded (e.g., observation of a turbid and cracked crystallized appearance). The carrier gas flows consisted of premixed dry  $\text{N}_2$  and  $\text{O}_2$  (a ratio of 4.5 / 1 in Setup 1 and a ratio of 2 in Setup 2), and NO was controlled by mass flow controllers. The total flow rates were  $500 \text{ mL min}^{-1}$  for Setup 1 and  $1500 \text{ mL min}^{-1}$  for Setup 2. In Setup 1, a dilution flow of  $1000 \text{ mL min}^{-1}$  was added at the end of the flow tube for a total of  $1500 \text{ mL min}^{-1}$  during experiments when HONO was measured along with  $\text{NO}_2$ . All experiments were conducted at ambient pressure, leading to gas residence times of 2.1–2.4 s (depending on flow tube volume, for both setups) under laminar flow conditions. The  $\text{O}_2$  flow rate was varied between 0 and  $110 \text{ mL min}^{-1}$  to observe the dependence of  $\text{O}_2$  while keeping the total flow rate constant. A ratio of 4.5 : 1 of  $\text{N}_2$  :  $\text{O}_2$  was maintained if any of the other gas flows were changed (e.g., NO and/or  $\text{NO}_2$ ) for Setup 1. For Setup 2, a ratio of 2 : 1 of  $\text{N}_2$  :  $\text{O}_2$  was also maintained, except for the  $\text{O}_2$  concentration dependence studies. The RH was kept constant at 50 % RH during most experiments and varied between 10 and 60 % RH to study humidity effects of the  $\text{HO}_2$  radical production. The concentration of NO was  $\sim 1$  ppmv (Setup 1) and varied between 100 and 500 ppbv (Setup 2). Scavenging of  $\text{HO}_2$  was achieved by the following reaction:



The lifetime of  $\text{HO}_2$  is about 5 ms when  $2.5 \times 10^{13} \text{ molecules cm}^{-3}$  of NO are present (Setup 1), which ensures efficient conversion of  $\text{HO}_2$  molecules into  $\text{NO}_2$  ( $k = 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K; Sander et al., 2011). As shown in Fig. S2, 500 ppbv NO, the concentration used in Setup 2, was sufficient to efficiently convert  $\text{HO}_2$  into  $\text{NO}_2$ ; see Sect. 3.1.1. The lifetime of gas-phase  $\text{HO}_2$  with respect to loss to the organic film is about 0.1 s, based on a similar formula shown in Eq. (S3),

where  $\gamma = 10^{-3}$  (upper limit by Lakey et al., 2015). Note that in view of the essentially diffusion-controlled loss of  $\text{HO}_2$  to the CWFT and tubing walls, the chosen scheme for determining the production of  $\text{HO}_2$  radicals from the films by fast scavenging with  $\text{NO}$  is superior to a more selective detection method, e.g., laser-induced fluorescence (LIF), which would require passing the  $\text{HO}_2$  radicals into a separate setup with substantial losses. For selected experiments, the films were exposed to UV irradiation for over 6 h which showed only a minor change in the decrease in  $\text{NO}_2$ , leading to the conclusion that the reactivity of the films was stable.

### 2.1.3 $J_{\text{IC}}$ calculations

The absorption cross section of IC and the calculated photolysis rate are shown in Fig. S3. The photolysis frequencies of IC were calculated using a similar procedure as described in Schwarzenbach et al. (2002). The spectral actinic flux in the flow tube,  $F_{\text{FT}}(\lambda)$ , was converted to the spectral photon flux density that reaches the film in the flow tube,  $F_{\text{film}}(\lambda)$ , and the photon flux absorbed by IC,  $F_{\text{a}}^{\text{IC}}$ , as follows:

$$F_{\text{a}}^{\text{IC}} = \int_{300}^{420} F_{\text{film}}(\lambda) \times [1 - 10^{-\sigma_{\text{IC}}(\lambda) \times b \times C_{\text{IC}}}] d\lambda, \quad (1)$$

$$\text{where } F_{\text{film}}(\lambda) = \frac{F_{\text{FT}}(\lambda) \times \text{SA}}{N_{\text{a}} \times V_{\text{film}}},$$

where  $F_{\text{a}}^{\text{IC}}$  has units of  $\text{Ein L}^{-1} \text{s}^{-1}$  (1 Ein = 1 mole ( $6.022 \times 10^{23}$ ) of photons),  $F_{\text{film}}(\lambda)$  has units of  $\text{Ein L}^{-1} \text{s}^{-1} \text{nm}^{-1}$ ,  $b$  is the optical path length taken as the thickness of the film in cm,  $C_{\text{IC}}$  is the concentration of IC in the film in units of M, and  $\sigma_{\text{IC}}$  is the IC absorption cross section. The absorption spectrum of IC in water was based on the measurements by Kampf et al. (2012) and renormalized to the peak value of  $10\,205 \pm 2400 \text{ M}^{-1} \text{cm}^{-1}$  at 284 nm (Maxut et al., 2015).  $V_{\text{film}}$  is the volume of the film in  $\text{cm}^3$ , calculated from the deposited mass of CA and the hygroscopic growth factors of CA (Zardini et al., 2008); SA is the surface area of the film, taken as the geometric area of the inner surface area of the flow tube in  $\text{cm}^2$ ;  $N_{\text{a}}$  is Avogadro's number in molecules  $\text{mole}^{-1}$ . The IC photoexcitation rate  $J_{\text{IC}}$  was about  $1.0 \times 10^{-3} \text{ s}^{-1}$  (upper limit).

We have also attempted to calculate an effective quantum yield for the formation of gas-phase  $\text{HO}_2$  radicals ( $\phi_{\text{HO}_2}$ ):

$$P_{\text{HO}_2} = \frac{[\text{NO}_2] \times \text{flow}}{N_{\text{a}} \times V_{\text{film}}} \phi_{\text{HO}_2} = \frac{P_{\text{HO}_2}}{F_{\text{a}}^{\text{IC}}}, \quad (2)$$

where  $P_{\text{HO}_2}$  is the  $\text{HO}_2$  production rate in  $\text{mol L}^{-1} \text{s}^{-1}$ ,  $F_{\text{a}}^{\text{IC}}$  is the calculated mean absorbed photon flux by IC (Eq. 1),  $[\text{NO}_2]$  is the gas-phase concentration of  $\text{NO}_2$  in molecules  $\text{cm}^{-3}$  assuming a 1 : 1 ratio to  $\text{HO}_2$  conversion, flow is the volumetric gas flow at the temperature in the CWFT and atmospheric pressure in  $\text{cm}^3 \text{s}^{-1}$  and  $V_{\text{film}}$  is in L.

### 2.1.4 Aerosol flow-reactor experiments

A detailed description of the aerosol flow tube (AFT) is reported elsewhere (Monge et al., 2012; Aregahegn et al., 2013); therefore, only some principles are given below. The SOA experiments were conducted in a horizontal, cylindrical Pyrex aerosol flow reactor (13 cm i.d., 152 cm length) surrounded by seven UV lamps (Philips CLEO, 80W) with a continuous emission spectrum ranging from 300 to 420 nm (total irradiance of  $3.31 \times 10^{16}$  photons  $\text{cm}^{-2} \text{s}^{-1}$ ). The flow reactor consisted of Teflon stoppers and different flow controllers that maintained the gas–aerosol–UV irradiation contact time between 20 and 50 min. This flow reactor also consisted of an outer jacket that controlled the temperature at  $293 \pm 2 \text{ K}$  by water circulation using a thermostat (Model Huber CC 405).

Seed aerosols (50 nm) were produced by nebulizing a solution (at pH 6) containing ammonium sulfate (AS, 0.95 mM) and IC (1.3 mM), size selected by a DMA and exposed to gas-phase limonene (500 ppbv) in the aerosol flow reactor. The typical aerosol mass loading in the reactor was  $2\text{--}3 \mu\text{g cm}^{-3}$ , corresponding to  $\sim 15\,000$  particles  $\text{cm}^{-3}$  with a starting diameter of 50 nm. As shown by Aregahegn et al. (2013), limonene is an efficient H-donor VOC that forms SOA via reactive uptake to IC-containing seed aerosol. Due to the excess of limonene and low seed aerosol surface area, the consumption of limonene was below the detection limit. The aerosol growth was measured by means of an ultrafine condensation particle counter (UCPC) and a scanning mobility particle sizer spectrometer (SMPS; both TSI), and similarly to the CWFT experiment, a flow of gaseous  $\text{NO}$  (from a 1 ppmv cylinder, Linde) was added to the carrier gas, and its conversion to  $\text{NO}_2$  was monitored by a chemiluminescence detector with a detection limit of 0.05 ppbv (ECO PHYSICS CLD 88). Due to the long residence time, the  $\text{NO}_2$  concentration is affected by its photolysis in the AFT. As discussed below,  $P_{\text{HO}_2}$  was calculated, in this case, from the growth of the particle diameter measured at the exit of the flow tube; the assumption is that growth was due to reactive uptake of limonene only and that each limonene forms one  $\text{HO}_2$  radical. At 30 ppbv  $\text{NO}$ , the  $\text{HO}_2$  radical lifetime is around 2 s.

### 2.1.5 Experimental conditions

The total flow rate in the aerosol flow reactor was between  $400\text{--}1000 \text{ mL min}^{-1}$ , ensuring laminar flow conditions. The RH was varied between 0 and 50 %. The RH of particles in the flow reactor was controlled by saturating the carrier gas via a bubbler containing ultrapure water (Milli Q, 18 M $\Omega$  cm). The RH in the flow-reactor system was varied by changing the gas flow rates to the bubbler and the temperature of the circulating water jacket of the bubbler. The RH was measured with a humidity sensor (Meltec UFT 75-AT, Germany) at the exit of the flow reactor. The concentrations

for the flow tube experiments were the following: 30 ppbv of NO and 500 ppbv of limonene.

## 2.2 Chemicals

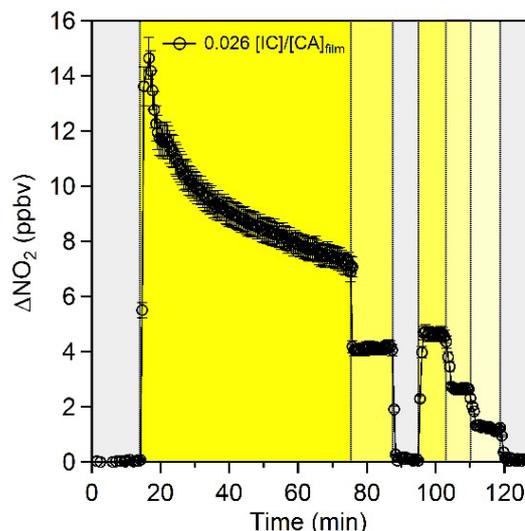
The following chemicals were used without further purification for CWFT studies: IC (97 %, Sigma Aldrich) and CA (Sigma Aldrich). For Setup 1, the Duran glass tubes were soaked in a deconex<sup>®</sup> cleaning solution overnight; the next day they were rinsed with 18 MΩ cm water (Milli Q Element system). These flow tubes were etched with a 5 % hydrofluoric acid solution after the washing procedure and again rinsed with water before any experimental use. The Duran flow tubes for Setup 2 were not initially etched with any acid but stored in a NaOH solution after washing and lastly rinsed with water; Setup 2 later confirmed that the treatment of flow tube with acids affects  $P_{\text{HO}_2}$  by rinsing with HCl and etching with HF solutions.

For the aerosol flow-reactor experiments, gas-phase limonene was generated from commercially available limonene (Aldrich, 97 %) by means of a permeation tube. The following chemicals were used without further purification: IC (97 %, Sigma Aldrich) and succinic acid (Sigma Aldrich,  $\geq 99.5\%$ ); 4-benzoylbenzoic acid (4-BBA, Aldrich 99 %) and adipic acid (AA, Aldrich,  $\geq 99.5\%$ ) were used to expand the CWFT studies to other photosensitizers.

## 3 Results and discussion

### 3.1 Coated-wall flow tube

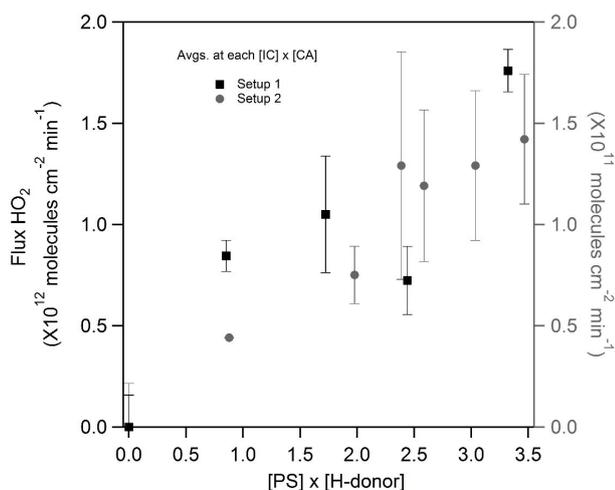
The following results represent the light-dependent formation of HO<sub>2</sub> indirectly from measurements of NO<sub>2</sub> production and NO loss, measured with Setup 1 and 2, respectively. Figure 2 shows a time series of NO<sub>2</sub> measured with Setup 1 as a function of UV-A light, which confirms the light-dependent radical production. This particular film had an IC / CA ratio of 0.026 (0.148 M IC and 5.77 M CA in the film). An evident increase in NO<sub>2</sub> is observed upon UV irradiation, directly reflecting the light-mediated release of HO<sub>2</sub>, as shown in Reaction (R1). The NO<sub>2</sub> signal decreases over time with all seven lamps; this was a common feature observed in all films and could be due to HO<sub>2</sub> sinks in the film increasing with time. Thus, the system only slowly evolves into a steady state. A small amount of NO<sub>2</sub> (0.5–1.5 ppbv) was observed during experiments that used only CA in the absence of IC; therefore, the data in Fig. 2 and all data reported below have been corrected for this NO<sub>2</sub> background, measured routinely in between experiments. Figure 2 also indicates a strong correlation with light intensity, which is further discussed in the context of Fig. 4. For irradiation, humidity and oxygen dependence experiments, each data point represents a separate experiment using a freshly prepared coated film in the flow tube. The uncertainty for experiments was based on the standard deviation of  $n$ , the number of exper-



**Figure 2.** NO<sub>2</sub> profile for a 0.025 MIC bulk solution, whose concentration increases to  $\sim 0.2$  M of IC in the film due to the citric acid hygroscopic properties. The gray shaded areas indicate periods where NO was exposed in the dark. The yellow shaded areas indicate the period of irradiation; the decrease in the intensity of yellow represents  $2.26 \times 10^{16}$ ,  $1.47 \times 10^{16}$ ,  $1.14 \times 10^{16}$  and  $3.94 \times 10^{15}$  photons  $\text{cm}^{-2} \text{s}^{-1}$  for seven, five, three and one lamp, respectively. This time series clearly indicates the light dependence production of HO<sub>2</sub> radicals from the photosensitization of IC in a CA film.

iments. The total uncertainty was  $\pm 6\text{--}27\%$  (propagated error for normalization was  $\pm 7\text{--}29\%$ ) for the IC mass loading experiments in Setup 1 and up to a factor of 2 for the light dependence experiments. The uncertainty in Setup 2 was 10–50 %. As discussed earlier, the lifetime of HO<sub>2</sub> in the system was about 3 orders of magnitude less than the residence time in the flow tube, therefore suggesting that most, if not all, HO<sub>2</sub> reacted with NO to produce the observed NO<sub>2</sub> (Reaction R1). Theoretically, the system was clean of other oxidants such as O<sub>3</sub> (and thus NO<sub>3</sub>). The uptake of NO<sub>2</sub> in the film was too small to further produce any nitrate radicals, and the photolysis of NO<sub>2</sub> in the experiments to produce O<sub>3</sub> was insignificant ( $< 1\%$ ). The recombination of NO and O<sub>3</sub> contributes a negligible ( $< 0.1\%$ ) NO<sub>2</sub> source under our experimental conditions. RO<sub>2</sub> generation from the reaction between CA and OH from HONO photolysis was also ruled out since it is approximated to account for only 1 % of the NO<sub>2</sub> production if we assume every OH from the photolysis reacts with CA. To our knowledge, the direct photolysis of CA to produce any RO<sub>2</sub> radicals has not been observed. Therefore, we believe that HO<sub>2</sub> is the essential oxidant for NO and refer to the measured NO<sub>2</sub> as HO<sub>2</sub> formation.

Figure 3 shows that the HO<sub>2</sub> production fluxes, in molecules  $\text{cm}^{-2} \text{min}^{-1}$ , increased with IC mass loading. The CA concentration was kept constant, and results are shown as the product between  $[\text{IC}] \times [\text{CA}]$ , since we expect that the



**Figure 3.** A linear correlation of HO<sub>2</sub> as a function of IC concentration. The left y axis represents the values for Setup 1, while the right y axis represents the values for Setup 2 (an order of magnitude difference for both scales). The Setup 2 data fall between a factor of 2 and 3 from Setup 1 after accounting for differences between Setup 1 and 2; see Sect. 3.1.1.

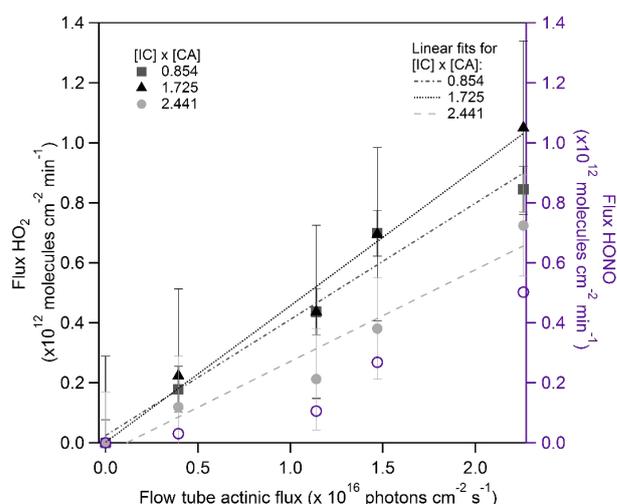
production rate of HO<sub>2</sub> is proportional to the concentration of IC, at constant illumination, and to that of the potential H donor, CA. For Setup 1, the HO<sub>2</sub> fluxes were measured as NO<sub>2</sub> mixing ratios and calculated using the following equation:

$$\text{Fluxes}_{\text{HO}_2} = \frac{[\text{NO}_2] \times \text{flow}}{\text{SA}} \quad (3)$$

The description of these parameters has been previously explained (see Sect. 2.1.3). For Setup 2, the HO<sub>2</sub> flux was calculated similarly, but only about half of the observed NO loss was considered to account for the loss of NO via the reaction with OH (see Reaction R1 in Supplement), meaning that for each HO<sub>2</sub> scavenged, two NO molecules were lost. In Fig. 3, the data from Setup 1 are represented by the black squares and the data from Setup 2 are represented by the gray circles. Setup 1 measurements were taken at about ~50% RH and at room temperature. Setup 2 measurements were taken at 45% RH and at 292 K. Temperature has an effect on the observed gas-phase HO<sub>2</sub> release from the film and thus needs to be accounted for, which is not done in Fig. 3, but it is described in detail in Sect. 3.1.1.

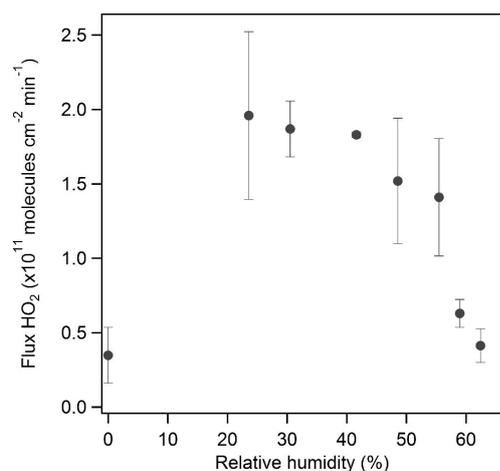
Figure 4 shows that the HO<sub>2</sub> production exhibited a linear dependence on the actinic flux for various [IC] × [CA] molar products. From Sect. 2.1.3, we estimated an experimental  $\phi_{\text{HO}_2}$  of about  $6 \times 10^{-5}$ , reflecting other probable, unknown quenching processes in our system. Figure 4 also shows the formation of HONO from three different IC mass loadings. In all three cases, the HONO : NO<sub>2</sub> ratio is < 1, confirming HO<sub>2</sub> as a primary product and OH as a secondary product.

Figure 5 shows the dependence of HO<sub>2</sub> production observed via the loss of NO (Setup 2) on relative humidity



**Figure 4.** HO<sub>2</sub> fluxes in molecules cm<sup>-2</sup> min<sup>-1</sup> as a function of actinic flux for a 300–420 nm range (solid symbols). The data are plotted as a concentration product of [IC] × [CA] (shown in the legend), which shows the photochemical reaction between IC and CA in H<sub>2</sub>O matrix and gaseous NO. HONO for 2.441 ([IC] × [CA]) is plotted on the right axis (open circles), showing a ratio of HONO : NO<sub>2</sub> < 1, which suggests OH as a secondary product.

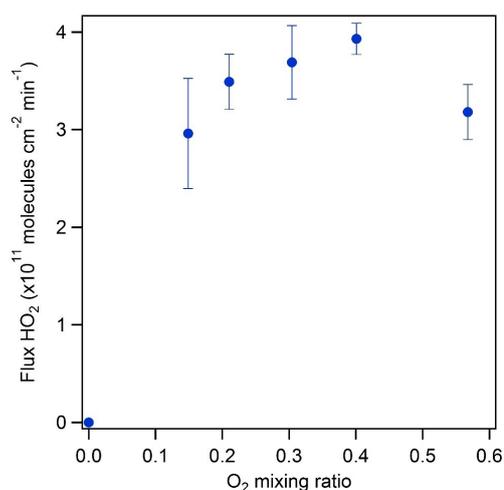
(0–65%). Water partial pressure is an important parameter in the atmosphere, and it also seems to have an important effect on the photochemical reactions studied here. At RH below ~10%, and at high RH above ~55%, the yield of HO<sub>2</sub> radicals decreases. The maximum HO<sub>2</sub> radical production is observed at moderate RH (20–55%). This is probably due to a combination of factors. In particular, at low RH the film may become more viscous, reducing mobility and thus the energy transfer within the film. This may decrease the HO<sub>2</sub> yield as shown in Fig. 5. Hinks et al. (2016) observed that the movement of molecules in a viscous film at a low RH is hindered and thus decreases the photochemical reaction rate of secondary organic material. The reduced diffusivity of HO<sub>2</sub> may also increase the residence time in the film and facilitate the self-reaction in the bulk phase: the diffusivity of H<sub>2</sub>O in citric acid is in the range of 10<sup>-7</sup>–10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup> at 50% RH. If the HO<sub>2</sub> diffusivity is between a factor of 10 and 100 lower than that of H<sub>2</sub>O due to its larger size (10<sup>-9</sup> cm<sup>2</sup> s<sup>-1</sup>), the first-order loss rate coefficient for diffusion out of the film ( $D/\delta^2$ ,  $\delta$  denoting the film thickness ( $4 \times 10^{-4}$  cm)) becomes about  $k_D = 10^{-2}$  s<sup>-1</sup>. From the observed  $F_{\text{HO}_2}$ , the steady-state concentration is then about  $F_{\text{HO}_2}/k_D/\delta = 4 \times 10^{16}$  cm<sup>-3</sup> = 10<sup>-7</sup> M. The loss rate coefficient due to HO<sub>2</sub> self-reaction in the condensed phase ( $7.8 \times 10^5$  M<sup>-1</sup> s<sup>-1</sup>) at this concentration would become nearly 0.1 s<sup>-1</sup>, somewhat higher than that for diffusional loss. Of course these estimates carry a high uncertainty but indicate that at lower humidity, diffusivity gets low enough to effectively reduce the diffusional loss of HO<sub>2</sub> to the gas phase and favor its loss by self-reaction in the con-



**Figure 5.** The indirect flux of HO<sub>2</sub> in molecules cm<sup>-2</sup> min<sup>-1</sup>, measured by NO loss and normalized to the film surface area as a function of relative humidity.

densed phase. The potential presence of condensed phase sinks, such as RO<sub>2</sub>, formed from secondary chemistry of oxidized citric acid, may add to this uncertainty. Figure S4 shows that bulk diffusion can be neglected since any HO<sub>2</sub> produced below the first couple of micrometers at the top of the film is likely lost to self-reaction in the condensed phase. This supplementary experiment studied the thickness dependence of the films keeping the IC:CA ratio constant. The results show that  $P_{\text{HO}_2}$  increases linearly with thickness up to  $\sim 2.5$   $\mu\text{m}$ ; however, after this thickness the film saturates, showing that this must happen in our films that are between 3 and 4  $\mu\text{m}$  thick. At high RH ( $> 55\%$ ), the amount of water associated with CA dilutes the reactants, and the quenching of the excited IC triplet states gains in relative importance, consistent with findings in other studies (Stemmler et al., 2006, 2007; Jammoul et al., 2008). The RH effect can decrease the HO<sub>2</sub> production by a factor of 3, compared to the plateau of maximum HO<sub>2</sub> production between 20 and 55 % RH.

Figure 6 shows the dependence of the HO<sub>2</sub> production based on the observed NO loss on the O<sub>2</sub> mixing ratio (Setup 2). The HO<sub>2</sub> production varied by about 20 % over the range of conditions investigated. A decrease below 15 % O<sub>2</sub> appears to be significant compared to the maximum HO<sub>2</sub> production at  $\sim 40\%$  O<sub>2</sub>, indicating that O<sub>2</sub> is needed for HO<sub>2</sub> formation. Sufficient O<sub>2</sub> dissolves in the aqueous phase to produce HO<sub>2</sub> radicals efficiently at atmospheric O<sub>2</sub> mixing ratios. We assume that at 55 % O<sub>2</sub>, the quenching of excited IC triplet states by O<sub>2</sub> has an effect on HO<sub>2</sub> production. This effect may decrease  $P_{\text{HO}_2}$  based on our results being qualitatively consistent with the observations of decreasing aerosol growth at high O<sub>2</sub> in the autophotocatalytic aerosol growth described in Aregahegn et al. (2013). However, the experimental focus of this study was based on atmospheric O<sub>2</sub> mix-



**Figure 6.** The flux of HO<sub>2</sub> in molecules cm<sup>-2</sup> min<sup>-1</sup>, measured by NO loss, above a film composed of IC and CA normalized to the film surface area as a function of the O<sub>2</sub> mixing ratio.

ing ratios, and thus we cannot draw conclusions about the HO<sub>2</sub> production at high O<sub>2</sub> mixing ratios.

In order to test the possibility for excited IC triplet states to react with NO<sub>2</sub> at the surface of the film, experiments were conducted with NO<sub>2</sub>. While we did observe that the uptake of NO<sub>2</sub> on irradiated surfaces scaled with light intensity (see Fig. S5), the reactive uptake coefficient of NO<sub>2</sub> to produce HONO at the surface is rather small ( $< 2.5 \times 10^{-7}$ ), corresponding to a  $k_w$  of  $10^{-3}$  s<sup>-1</sup>, and is thus neither a significant loss of NO<sub>2</sub> nor a significant source of HONO. The primary fate of the nitrogen-containing aromatic alkoxy IC radical under atmospheric conditions is reaction with O<sub>2</sub>. However, we have not tested alternative quenching reactions of the triplet state or other pathways of the reduced ketyl radical that do not result in the formation of HONO.

### 3.1.1 Comparison of data sets

The experimental conditions probed differ in the actinic flux, NO concentration, temperature and acidity. Here, we use the dependencies established in Sect. 3.1 to compare results from both setups. The data from Setup 2 were normalized to conditions of Setup 1. The difference in  $J_{\text{NO}_2}$  corresponds to multiplying results from Setup 2 with a factor of  $2.0 \pm 0.1$ . HO<sub>2</sub> was measured indirectly by reacting it with NO, and Fig. S2 indicates that the minimum NO concentration needed to efficiently scavenge all gas-phase HO<sub>2</sub> is  $\sim 460$  ppbv of NO, indicating efficient conversion for Setup 1 and a conversion efficiency of  $\sim 0.6$  for Setup 2. The data from Setup 2 were multiplied by  $1.66 \pm 0.10$  to normalize for the NO conversion efficiency (Fig. S2) and by an additional factor of  $1.25 \pm 0.10$  to match temperatures. We observed some limited variability depending on whether HF or HCl were used to clean the flow tube prior to experiments. A higher  $P_{\text{HO}_2}$

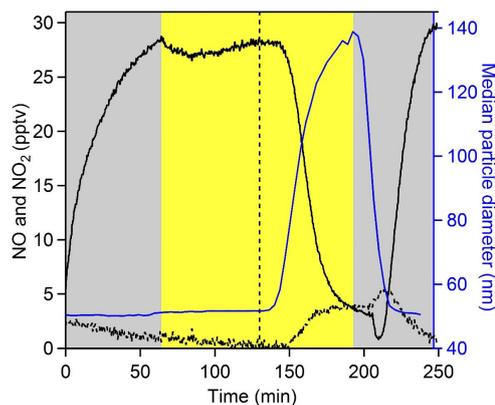
was observed when cleaning with HF (Setup 1) compared to storing in NaOH and either rinsing with water or HCl (Setup 2); this is accounted for by multiplying data from Setup 2 with a factor of  $1.25 \pm 0.30$ . Notably, the error of the correction for the cleaning procedure that is propagated here is larger than the correction factor. The effect of the pre-treatment of the flow tubes was not systematically studied and thus remains a primary uncertainty in the comparison. No further correction was applied for slight differences in RH. The overall correction factor amounts to  $5.2 \pm 1.4$ , with the error reflecting the propagated uncertainty. This explains most of the difference in  $P_{\text{HO}_2}$  between both setups. The normalized results agree within a factor of 2, which is a reasonably good agreement.

### 3.1.2 Extension to other photosensitizers

A limited number of experiments were performed using the CWFT approach, using 4-BBA as a photosensitizer, in the presence of 790 ppbv of gaseous limonene (a possible H donor) and NO. The organic thin film contained an organic acid matrix made of 4-BBA with and without adipic acid (AA). A substantial conversion of NO into NO<sub>2</sub> was also observed in this system (see Fig. S6). That 4-BBA behaves similar to the IC system demonstrates that the chemistry discussed above can occur on different excited carbonyls. It is interesting to note that this photoinduced conversion, and HO<sub>2</sub> production, was observed to be sustained over long times, i.e., more than 15 h, probably due to the catalytic nature of the underlying chemical cycles. However, a fraction of the IC did get consumed by photolysis reactions that do not form the excited triplet state (observed during overnight experiments). The HO<sub>2</sub> flux for the 4-BBA system was estimated to be  $2.77 \times 10^{10}$  molecules cm<sup>-2</sup> min<sup>-1</sup> making the same assumption that each HO<sub>2</sub> molecule reacts with NO to generate an NO<sub>2</sub> molecule. The calculation is based on Eq. (3), where it depends on the concentration of NO<sub>2</sub> as well as the surface area and residence time.

### 3.2 Aerosol flow tube

The aerosol flow tube experiments were conducted similarly to the study by Aregahegn et al. (2013), i.e., who demonstrated that in the absence of NO and known gas-phase oxidants, seed particles containing IC can initiate SOA growth in the presence of a gaseous H donor (limonene). Figure 7 shows the results from similar experiments when NO was added to the system. No conversion of NO to NO<sub>2</sub> was observed prior to the injection of limonene into the flow tube. The presence of a gaseous H donor and light clearly initiated a series of photochemical processes, leading to SOA growth and gaseous NO<sub>2</sub> production. However, the quantitative interpretation of these experiments is not straightforward due to efficient radical cycling in the VOC–NO<sub>x</sub>–light photochemical system and the lack of a blank experiment



**Figure 7.** Aerosol flow tube experiments show rapid conversion of NO (solid black line) into NO<sub>2</sub> (dashed black line) only after the time when limonene (gaseous H donor) is added into the flow tube (vertical dashed line). The gray shaded areas represent the experiment in the dark, and the yellow shaded area represents the experiment under light exposure. The blue line represents the growth of aerosols (right axis).

that did not contain IC as part of the seed particles. Limitations arise from the much longer residence time, which allows NO<sub>2</sub> to be significantly photolyzed. The  $J_{\text{NO}_2}$  was estimated as  $\sim 6.75 \times 10^{-3}$  s<sup>-1</sup> and corresponds to a photolysis lifetime of 2.5 min, which is smaller than the actual residence time in the flow tube ( $\sim 40$  min). Secondary chemistry can lead, among others, to ozone production (O<sub>3</sub> lifetime at 500 ppbv limonene is  $\sim 7$  min) and secondary OH radical formation from the ozonolysis of limonene. Notably, NO<sub>x</sub> is not consumed in Fig. 7. The overall effect of this secondary chemistry is an increased SOA growth compared to an experiment without added NO (Areagahegn et al., 2013). As a consequence, the NO<sub>2</sub> yield cannot be used directly to assess  $P_{\text{HO}_2}$  in the presence of NO.

However, in the absence of NO these secondary processes can largely be avoided and are reduced to a level at which they cannot be identified (Areagahegn et al., 2013). Under such conditions, the particle growth rates presumably carry information about the photosensitizer cycling and subsequent HO<sub>2</sub> production. If we assume one molecule of limonene reacts to produce one HO<sub>2</sub>, the volume change of aerosols is proportional to the overall number of HO<sub>2</sub> produced. For example, a growth of 15 000 particles cm<sup>-3</sup> from diameter 51.4 to 68.5 nm in 40 min (residence time) is equal to a  $P_{\text{HO}_2}$  of  $1.67 \times 10^{14}$  molecules cm<sup>-2</sup> min<sup>-1</sup>. This should be interpreted as an upper limit for the actual  $P_{\text{HO}_2}$  because water uptake may also be contributing to the volume growth. However, compared to the CWFT experiments the much higher surface-to-volume ratio of nanoparticles is expected to enhance the chemical coupling of a gas-phase H donor and the excited IC triplet state at the aerosol surface. This is at least in part deemed responsible for the 2 orders of magnitude higher  $P_{\text{HO}_2}$  in the aerosol flow tube compared to the CWFT exper-

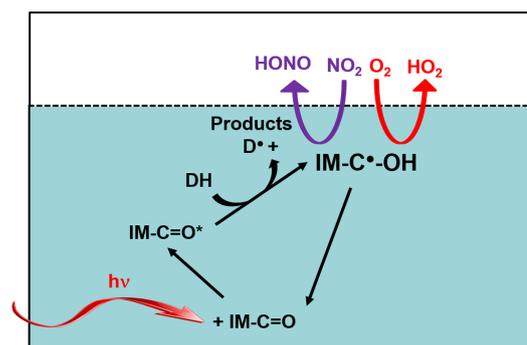
iments. Notably, even if  $\phi_{\text{HO}_2}$  in the aerosol flow tube was 2 orders of magnitude higher than in the CWFT, it is still significantly smaller than unity.

### Primary HO<sub>2</sub> formation from IC

One of the main advantages of the CWFT is that it operates at a much shorter residence time. From Setup 1, we derive a  $P_{\text{HO}_2}$  of  $1.76 \times 10^{12}$  molecules  $\text{cm}^{-2} \text{min}^{-1}$  for IC/CA = 0.1 and  $J_{\text{NO}_2} = 8 \times 10^{-3} \text{ s}^{-1}$ . This corresponds to  $2.9 \times 10^4$  molecules  $\text{cm}^{-3} \text{ s}^{-1}$  once normalized by aerosol surface area ( $1.18 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ ) and  $J_{\text{NO}_2}$  in the aerosol flow tube. Such a primary radical flux is equivalent to the OH radical production rate resulting from photolysis of  $\sim 1$  pptv of HONO in the aerosol flow tube. Conversely, a  $P_{\text{HO}_2}$  of  $1.67 \times 10^{14}$  molecules  $\text{cm}^{-2} \text{min}^{-1}$  is equivalent to the OH radical production rate from  $\sim 100$  pptv HONO in the aerosol flow tube. We conclude that seed particles containing IC contribute significantly (equivalent to 1–100 pptv HONO) to the primary HO<sub>x</sub> radical production rate in the aerosol flow tube experiments in the presence of NO (Fig. 7). Primary HO<sub>2</sub> radicals formed from IC-containing seed particles react rapidly with NO to form OH radicals under the conditions shown in Fig. 7. The H-donor species is further expected to form primary RO<sub>2</sub> radicals. These primary HO<sub>2</sub> and RO<sub>2</sub> radicals add directly to the conversion of NO into NO<sub>2</sub> and indirectly by driving secondary NO-to-NO<sub>2</sub> conversion from the RO<sub>2</sub>/HO<sub>2</sub> radical chain. The aerosol flow tube experiments thus qualitatively confirm the results obtained from macroscopic surfaces and highlight the potentially important role of surface-to-volume ratio and gaseous H donors to enhance the relevance of H-donor photochemistry as sources for HO<sub>x</sub>-RO<sub>x</sub> radicals and SOA.

### 3.3 Proposed mechanism

A mechanism that can describe the results from the CWFT experiments is shown in Fig. 8. It follows the mechanism first proposed by Canonica et al. (1995). The primary product in our system is the HO<sub>2</sub> radical, which forms from the reaction between a nitrogen-containing aromatic alkoxy IC radical and a ground-state oxygen molecule, recycling the IC molecule. The aromatic alkoxy radicals form from the excited triplet state of IC via transfer of an H atom from an H donor (in our case likely to be CA or the CA/H<sub>2</sub>O matrix). While a fraction of the IC will get consumed by photolysis reactions that do not form the excited triplet state (see Sect. 3.1.2.), IC is also continuously produced from multiphase reactions, e.g., of glyoxal (Yu et al., 2011; Kampf et al., 2012; Maxut et al., 2015). Another conclusion is that OH is a secondary product. If OH was a first-generation product, we would have expected HONO:NO<sub>2</sub> ratios larger than 1:1. A smaller ratio was observed, as shown in Fig. 4, indicating that there was no direct evidence for primary formation of OH radicals. Interestingly, the H-donor species becomes ac-



**Figure 8.** Proposed mechanism, modified and expanded to photosensitization of IC based on Canonica et al. (1995), George et al. (2005) and Aregahegn et al. (2013). The reaction in the white square represents the gas-phase, and the blue square represents the aqueous phase. DH is an H donor (e.g., CA, another IC, H<sub>2</sub>O + CA matrix to be determined from flash photolysis).

tivated as a result of H abstraction and can react further to produce organic peroxy radicals, as evidenced by the aerosol flow tube results.

## 4 Atmospheric relevance

The atmospheric relevance of our findings consists of the possible effect of heterogeneous radical sources to modify atmospheric HO<sub>2</sub> radical concentrations and facilitate aerosol growth and ageing by adding a radical source within aerosol particles. The production of HO<sub>2</sub> from IC photosensitized heterogeneous chemistry is a possible source of gas-phase HO<sub>2</sub> radicals in ambient air. In order to estimate the possible relevance for HO<sub>2</sub> radical concentrations in urban air, we assume  $P_{\text{HO}_2}$  of  $2 \times 10^{12}$  molecules  $\text{cm}^{-2} \text{min}^{-1}$  (IC/CA = 0.1, Setup 1) as a lower limit and  $2 \times 10^{14}$  molecules  $\text{cm}^{-2} \text{min}^{-1}$  (IC/AS = 0.1, aerosol flow tube) as an upper limit and typical conditions in Mexico City (i.e.,  $J_{\text{NO}_2} = 8 \times 10^{-3} \text{ s}^{-1}$  at noontime in Mexico City, aerosol surface area =  $15 \text{ cm}^2 \text{ m}^{-3}$ ; Volkamer et al., 2007). The normalized  $P_{\text{HO}_2}$  during noontime in Mexico City ranges from  $2 \times 10^5$  to  $2 \times 10^7$  molecules  $\text{cm}^{-3} \text{ s}^{-1}$ . This corresponds to a rate of new HO<sub>x</sub> radical production of 4 to 400 pptv h<sup>-1</sup> HONO around solar noon in Mexico City (Li et al., 2010), where other radical sources produce about  $5.9 \times 10^7$  molecules  $\text{cm}^{-3} \text{ s}^{-1}$  at solar noon (Volkamer et al., 2010). The upper range value suggests that aerosol surfaces can be a significant source of gas-phase HO<sub>x</sub> in places like Mexico City. However, the IC molar ratios used here are likely an upper limit compared to ambient aerosols, yet, in principle other brown carbon molecules (i.e., HULIS and/or other imidazole derivatives) may form additional gas-phase HO<sub>2</sub>. The heterogeneous HO<sub>2</sub> radical source could further be relatively more important in unpolluted regions under biogenic influences, where gas-phase radical production rates

are lower. Hence a more comprehensive characterization of the heterogeneous HO<sub>2</sub> source effect on gas-phase HO<sub>2</sub> radical concentrations deserves further investigation.

OH radical uptake from the gas phase is a primary OH source in aerosols (Ervens and Volkamer, 2010). Assuming a gas-phase OH concentration of 10<sup>6</sup> molecules cm<sup>-3</sup>, 15 cm<sup>2</sup> m<sup>-3</sup> aerosol surface area and γ<sub>OH</sub> of unity, the rate of OH uptake is approximately 2.3 × 10<sup>5</sup> molecules cm<sup>-3</sup> s<sup>-1</sup>. The above estimated P<sub>HO<sub>2</sub></sub> is a result from H transfer to form organic peroxy radicals, which is comparable to the rate of OH uptake. The two similar estimates of HO<sub>x</sub> suggest that IC is a significant source of radicals in the condensed phase of particles. This is a lower limit due to the unknown radical losses of HO<sub>x</sub> to the condensed phase, which have the potential to raise the HO<sub>x</sub> source by up to a factor of 10 000 if limited by the IC excitation rate. The unknown amount of HO<sub>2</sub> that remains in the condensed phase is a further source of OH in the same phase; this OH, in the presence of reduced metals, can trigger a cycle of Fenton reactions or other oxidizing pathways that can further age the aerosol.

These results show that IC, and other aromatic carbonyl photosensitizers, are likely a relevant radical source in aerosol particles. Photoinduced radical generation in condensed phases is currently not represented in atmospheric models that describe aerosol ageing and warrants further study.

## 5 Conclusion

Three different experimental setups consistently show that HO<sub>2</sub> radicals are produced from the photochemistry of IC in a CA + H<sub>2</sub>O matrix and in seed aerosols containing ammonium sulfate (in the presence of a gas-phase H donor, limonene). The linear correlations of P<sub>HO<sub>2</sub></sub> (with [IC] / [CA] and irradiation) yielded maximum P<sub>HO<sub>2</sub></sub> under atmospherically relevant irradiation, O<sub>2</sub> and RH but also revealed a complex role of film viscosity and possibly acidity effects (a systematic study of the effect of pH on the IC and CA absorption cross sections and the product yields from the IC photochemistry is desirable). If the H-donor species is in the condensed phase, significant amounts of HO<sub>2</sub> reach the gas phase only for moderately high RH (~ 25–55 % RH) that facilitates H transfer and allows molecules (IC, HO<sub>2</sub>) to move freely towards the surface of the film. When the film is too dry, this mobility is inhibited due to enhanced viscosity and significantly decreases the P<sub>HO<sub>2</sub></sub>. At RH and O<sub>2</sub> higher than 55 %, we observe a decrease in P<sub>HO<sub>2</sub></sub> probably due to dilution by water and competing quenching reactions in the film. We know from Zardini et al. (2008) that pure citric acid does not efflorescence, and thus the film remains homogenous in its aqueous phase under all RH conditions. This supports our conclusion that the P<sub>HO<sub>2</sub></sub> is RH dependent since it is partially controlled by the diffusivity in the film. On the contrary, if the H-donor species is in the gas phase, significant HO<sub>2</sub> pro-

duction is also observed under dry conditions. The primary fate of the IC•OH radical at the surface is reaction with O<sub>2</sub> to form HO<sub>2</sub>. NO<sub>2</sub> reactions do not appear to form HONO at the surface. Our results suggest that the radical source from photosensitizers such as IC can help jump-start the photochemistry of VOCs. The effect on the gas-phase HO<sub>2</sub> radical concentration increases for higher surface-to-volume ratio of aerosols and in the presence of gas-phase H donors. The autophotocatalytic growth of aerosols containing photosensitizers via H-donor chemistry is an SOA source also in the presence of NO and adds oxidative capacity inside aerosol particles. Further research on other types of H donors and photosensitizers is necessary to compare different P<sub>HO<sub>2</sub></sub> and rates of aerosol growth from the reactive uptake of VOC that could potentially have a significant atmospheric relevance for SOA formation and heterogeneous aerosol ageing.

## 6 Data availability

The data shown in the graphs are available in digital format (xlsx file) as part of the Supplement related to this article.

**The Supplement related to this article is available online at doi:10.5194/acp-16-11823-2016-supplement.**

*Author contributions.* Markus Ammann and Rainer Volkamer designed the experiments at PSI and Christian George and Barbara Nozière those at IRCELYON. Laura González Palacios, Pablo Corral Arroyo and Kifle Z. Aregahegn conducted the measurements, analyzed data and contributed equally to this work. Sarah S. Steimer and Thorsten Bartels-Rausch helped during the experiments, and all coauthors contributed to the data interpretation. Laura González Palacios and Rainer Volkamer prepared the manuscript with contributions from all coauthors.

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