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**Explicit modeling of
volatile organic
compounds**

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Explicit modeling of volatile organic compounds partitioning in the atmospheric aqueous phase

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Abstract

The gas phase oxidation of organic species is a multigenerational process involving a large number of secondary compounds. Most secondary organic species are water-soluble multifunctional oxygenated molecules. The fully explicit chemical mechanism GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) is used to describe the oxidation of organics in the gas phase and their mass transfer to the aqueous phase. The oxidation of three hydrocarbons of atmospheric interest (isoprene, octane and α -pinene) is investigated for various NO_x conditions. The simulated oxidative trajectories are examined in a new two dimensional space defined by the mean oxidation state and the solubility. The amount of dissolved organic matter was found to be very low ($< 2\%$) under a water content typical of deliquescent aerosols. For cloud water content, 50 % (isoprene oxidation) to 70 % (octane oxidation) of the carbon atoms are found in the aqueous phase after the removal of the parent hydrocarbons for low NO_x conditions. For high NO_x conditions, this ratio is only 5 % in the isoprene oxidation case, but remains large for α -pinene and octane oxidation cases (40 % and 60 %, respectively). Although the model does not yet include chemical reactions in the aqueous phase, much of this dissolved organic matter should be processed in cloud drops and modify both oxidation rates and the speciation of organic species.

1 Introduction

The atmospheric aqueous phase includes water in clouds and fogs droplets and deliquescent particles. There is a lack of knowledge concerning the aqueous phase contribution to the atmospheric chemistry (Ravishankara, 1997). Inorganic compounds reactivity in atmospheric water and their contribution to particulate matter formation has been extensively studied (e.g. Finlayson-Pitts and Pitts, 2000; Kreidenweis et al., 2003; Monod and Carlier, 1999). However large uncertainties still remain about the fate of dissolved organics. Most secondary organic species are water-soluble multifunctional

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oxygenated species. Because gas phase oxidation mechanisms are unable to reproduce experimental secondary organic aerosol (SOA) yields (Carlton et al., 2009; Ervens et al., 2011; Hallquist et al., 2009), aqueous phase mediated SOA formation is currently studied as a way to enhance aerosol yields (Carlton et al., 2009; El Haddad et al., 2009; Ervens and Volkamer, 2010; Ervens et al., 2008, 2011; Fu et al., 2009; Hallquist et al., 2009).

The study of aqueous phase chemistry as a potential source of SOA has shown that oxidation in water of secondary species could contribute to SOA mass. For example, Lim et al. (2005) have shown in a modeling study that the cloud oxidation of aldehydes originating from isoprene oxidation could be responsible for 4–20% of the total isoprene SOA yield. Similarly, Myriokefalitakis et al. (2011) have shown that cloud chemistry could enhance oxalate production by 2 Tg yr^{-1} , a contributor to SOA mass. Ervens and Volkamer (2010) modeled the SOA formation through aqueous phase processing of glyoxal, one of the oxidation products of isoprene, and have confirmed that there is a correlation between SOA mass increase and the liquid water content (L). Biogenic terpenes SOA yields from gas phase photo-oxidation have been explored in detail (e.g. Hallquist et al., 2009). Several recent experimental works have studied the influence of aqueous phase photooxidation on the composition of SOA formed after oxidation of biogenic compounds (Lee et al., 2011, 2012; Bateman et al., 2011). As for anthropogenic hydrocarbons, several recent studies have measured (Lim and Ziemann, 2005; Russell et al., 2011) or modeled (Jordan et al., 2008; Aumont et al., 2012) the gas phase SOA yields of alkanes. Recent experimental results from Zhou et al. (2011) suggest that SOA yields of four aromatic hydrocarbons (toluene and xylenes) are correlated to the ambient liquid water.

The mechanism of volatile organic compound (VOC) processing by the aqueous phase can be split in two steps:

- i. Phase partitioning. Specifically, many secondary organic species formed during the gas phase oxidation of hydrocarbons are highly soluble and are thus expected

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to be found in atmospheric water (e.g. Aumont et al., 2000; van Pinxteren et al., 2005).

- 5 ii. Aqueous phase reactivity. Like in the gas phase, dissolved compounds are oxidized by radicals in water, mainly by OH and NO₃ (Herrmann, 2003; Warneck, 2005). Resulting products are similar to those observed in the gas phase, but rate constant are generally faster and the yields of the various products are substantially modified (Herrmann, 2003). Moreover in the aqueous phase, hydration and acid dissociation can occur, which lead to the formation of some organic products (hydrates and carboxylate ions) not formed in the gas phase. Additional processes forming heavier species can occur in the aqueous phase, like esterification and aldol condensation (e.g. Nguyen et al., 2011; Altieri et al., 2008).

15 As experimental studies inside clouds are scarce and very difficult to set up (Crahan et al., 2004; Herrmann et al., 2005; Sorooshian et al., 2007), most of the organics clouds chemistry studies have been performed based on modeling approaches. These models usually represent the condensed phase as a single well mixed aqueous phase in which organic species undergo oxidation. This aqueous oxidation scheme is coupled with specifically tailored gas phase mechanisms taking into account mass transfer between the two phases (e.g. Jacob, 1986; Barth et al., 2003; Lelieveld and Crutzen, 1991; Leriche et al., 2000; Ervens et al., 2008; Tilgner and Herrmann, 2010). Current detailed models are limited to certain kinds of species. For example, the model from Ervens and Volkamer (2010) has been developed to study isoprene and its oxidation products like glyoxal. The CAPRAM 3.0i mechanism used by Tilgner and Herrmann (2010) is currently the most detailed aqueous phase organic chemistry model, taking into account the dissolution and aqueous chemistry of inorganic species and organic species up to four carbon atoms. However, atmospheric processing of long chain hydrocarbons is also expected to lead to the production of highly water soluble multifunctional organics in a few oxidation steps (e.g. van Pinxteren et al., 2005; Mazzoleni et al., 2010).

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This study aims at exploring the production of water soluble compounds from the gaseous oxidation of long chain hydrocarbons of atmospheric interest and the sensitivity of this dissolution to NO_x levels. To our knowledge, no modeling tool is currently available to describe in details the multiphase oxidation of long chain hydrocarbons.

This study describes the first stage in the development of such a modeling tool and examines the phase partitioning of organic species produced during the gas phase oxidation of hydrocarbons. A fully explicit chemical mechanism is used to describe the oxidation of organics in the gas phase and their mass transfer to the aqueous phase. The oxidation of three hydrocarbons of atmospheric interest (isoprene, octane and α -pinene) is investigated for various NO_x conditions. Two scenarios are considered with a liquid water content corresponding either to a cloud or to deliquescent particles. The simulated carbon budget and the composition of the gas and aqueous phase are explored in detail.

2 Modeling tools

2.1 Gas phase chemistry

Formation of SOA through aqueous phase oxidation involves water soluble species produced during the gaseous phase oxidation of volatile organic compounds (VOC) (Aumont et al., 2000). Candidate species are typically highly functionalized molecules produced during the multigenerational oxidation of the hydrocarbons emitted in the atmosphere. The number of species needed to describe explicitly this multigenerational oxidation increases exponentially with the size of the carbon skeleton of the parent compound (Aumont et al., 2005). For long chain species ($\text{C}_{>5}$), explicit oxidation schemes involve a number of intermediates that far exceeds the size of chemical schemes that can be written manually. The Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) is a computer tool that was developed to overcome this difficulty (Aumont et al., 2005). GECKO-A generates gas phase chemical

schemes according to a prescribed protocol, assigning reaction pathways and kinetics data, on the basis of experimental data and structure activity relationships.

The GECKO-A protocol is described by Aumont et al. (2005). This protocol was updated to take into account recent experimental results. The branching ratios for the isoprene + OH reaction have been prescribed following recommendations from Paulot et al. (2009a). As proposed by Paulot et al. (2009b), a new oxidative pathway for hydroperoxides has been added in the protocol, allowing the formation of tetrol species through the formation of epoxides that were detected as isoprene oxidation products. The first oxidation steps of α -pinene and alkane chemistry were also updated, as described by Valorso et al. (2011) and Aumont et al. (2012).

Explicit schemes generated with GECKO-A reach 1 million species for C_8 compounds, close to current computational limits (Camredon et al., 2007). A reduction protocol was therefore implemented in GECKO-A to allow the generation of oxidation schemes for $C_{>8}$ hydrocarbons (Valorso et al., 2011). The reduction protocol was designed to keep the oxidation schemes as detailed as possible, without losing the chemical information that determines molecular properties such as reactivity or volatility. The reduction approaches currently implemented in GECKO-A are based on the lumping of position isomers. For the purpose of this study, we also reduced the size of the chemical schemes by omitting the gas phase oxidation reactions for the highly soluble species, as it was done by Valorso et al. (2011) for non-volatile organic species. Under atmospheric conditions, a species having a Henry's law constant above $10^{12} \text{ M atm}^{-1}$ is expected to be predominantly in the aqueous phase, even for small tropospheric liquid water content (ca. $L = 10^{-12} \text{ cm}^3$ liquid water per cm^3 air). For such species, gas phase concentration is negligible and their gas phase chemistry was thus omitted.

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2.2 Phase transfer

For each water soluble species A, the mass transfer between the gas and the aqueous phase is treated in a time dependent sense:



where k_1 (s^{-1}) is the pseudo first order rate constant of the gas-particle mass transfer and H_A ($M \text{ atm}^{-1}$) is the Henry's law coefficient for the species A. The rate constant k_1 can be expressed as (Schwartz, 1986):

$$10 \quad k_1 = Lk_T = L \left(\frac{r^2}{3D_g} + \frac{4r}{3v\alpha} \right)^{-1} \quad (3)$$

where r (cm) is the radius of the particles or the droplets, D_g ($\text{cm}^2 \text{ s}^{-1}$) is the gas diffusion coefficient, v (cm s^{-1}) is the mean molecular speed and α (dimensionless) is the mass accommodation coefficient. The diffusion coefficient D_g can be estimated by scaling from a known reference compound:

$$15 \quad \frac{D_g}{D_{g,\text{ref}}} = \sqrt{\frac{M_{\text{ref}}}{M}} \quad (4)$$

where M (g mol^{-1}) is the molar mass and ref subscripts denote values for a reference species. We used water as reference compound, $D_{g,\text{H}_2\text{O}} = 0.214/P \text{ cm}^2 \text{ s}^{-1}$ in air at 298 K (Ivanov et al., 2007), P (atm) being the atmospheric pressure. H is taken from the literature when available, using the database compiled by Raventos-Duran et al. (2010) for ca. 600 species. The empirical group contribution method GROMHE was used to estimate unknown constants (Raventos-Duran et al., 2010). GROMHE is able

to estimate Henry's law constants at temperature $T = 298$ K for every atmospherically relevant organic species. The temperature dependence of H is represented with the Van't Hoff equation:

$$H(T) = H(298) \times \exp\left(\frac{\Delta H_{\text{soln}}}{R} \left(\frac{1}{298} - \frac{1}{T}\right)\right) \quad (5)$$

The enthalpy of dissolution ΔH_{soln} (J mol^{-1}) is also taken from the literature when available. ΔH_{soln} typically ranges from 10 to 100 kJ mol^{-1} (Kuhne et al., 2005) and a value of 50 kJ mol^{-1} was used as a default value in the model. The mass accommodation coefficient α is very poorly documented (ca. 40 constants in the literature, Davidovits et al., 2011; Sander et al., 2011). To our knowledge, the only SAR available to estimate α was proposed by Davidovits et al. (1995) and Nathanson et al. (1996). However the performances of that method cannot be rigorously evaluated due to the lack of experimental data. This method has therefore not been implemented and when no data are available, α is set to a default value of $\alpha = 0.05$ (Davidovits et al., 2011).

In this version of the model devoted to examine the phase partitioning of organics produced during gas phase processing, the only reactions taken into account in water are:

- i. Hydration of carbonyls. Species bearing ketone or aldehyde moieties undergo hydration equilibrium once they are dissolved. Equilibrium constants are estimated using the SAR from Raventos-Duran et al. (2010).
- ii. Dissociation of acids. Carboxylic acids undergo acid/base equilibrium in water. Acidity constant are estimated following recommendations from Perrin et al. (1981).

Species are therefore not further oxidized in water. In the model, the only sink for the dissolved organic matter is caused by the gas phase chemical pump that shifts the water/gas equilibrium. For very soluble species, gas phase oxidation becomes slow

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and the species remain in the aqueous phase in a form that can be considered as “permanent” in this version of the model.

2.3 Initial conditions

The modeling framework described above has been applied to the generation of the detailed mechanisms for three species of atmospheric interest: isoprene, octane and α -pinene. Table 1 gives the total number of species after the complete generation of these chemical schemes. The number of species in the aqueous phase is in the same order of magnitude as the number of species in the gas phase. The phase partitioning is considered for non radical species only, but gem-diols (carbonyl hydration) and carboxylates (acid dissociation) are newly formed in water. Some of these newly formed species are highly soluble and therefore are not transferred to the gas phase.

As initial condition, the initial concentration of the precursor and O_3 were set to 10 ppb and 40 ppb, respectively. The simulations were run with constant environmental conditions. Temperature was fixed to 278 K. Photolysis frequencies were calculated for mid-latitude and for a solar zenith angle of 45° using TUV (Madronich and Flocke, 1997). NO_x concentrations were held constant and three scenarios were considered corresponding to low NO_x (0.1 ppb), intermediate NO_x (1 ppb) and high NO_x (10 ppb) conditions. Oxidation of the organic species was initiated by adding a constant OH source of 10^7 radicals $cm^{-3} s^{-1}$. In these conditions, depending on the parent hydrocarbon, organic oxidation can be driven by OH, O_3 or both. In this model configuration, the contribution of OH (97 % of the total oxidation of the precursor) is one order of magnitude higher than the contribution of O_3 (3 %) to the oxidation of isoprene; OH and O_3 contribute comparably (61 % and 39 %, respectively) to the oxidation of α -pinene; octane is only oxidized by OH.

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3 Results

3.1 Carbon budget and liquid water content

Figure 1 shows the time evolution of the carbon atom ratio during the oxidation of isoprene, octane and α -pinene. Simulations were performed for three liquid water conditions: without aqueous phase ($L = 0$), with a water content representative of deliquescent aerosols ($L = 10^{-12}$, e.g. Engelhart et al., 2011) and for typical cloud conditions ($L = 3 \times 10^{-7}$, e.g. Seinfeld and Pandis, 2006). We assume that the particle and cloud droplet sizes are monodisperse, with particle radii of 0.1 μm and 5 μm , respectively. Simulations are shown for a NO_x concentration set to 1 ppb.

Physical time is not fully appropriate to describe the temporal evolution for simulations conducted under constant environmental conditions. The temporal evolution is examined below as a function of the number of lifetime N_τ of the parent hydrocarbon defined as:

$$N_\tau = \frac{t}{\tau} = \ln \frac{C_0}{C(t)} \quad (6)$$

where t is the simulated (physical) time, τ is the lifetime of the parent hydrocarbon, C_0 and $C(t)$ its concentration at t_0 and t , respectively. For these simulations, lifetimes of isoprene, α -pinene and octane were approximately 1 h, 1.5 h and 1 day, respectively.

Under dry conditions ($L = 0$), isoprene is slowly oxidized into CO and CO₂ through a multigenerational process involving the formation of successive gaseous secondary intermediates of higher oxidation state (see Fig. 1a). The carbon budget is not affected by the presence of an aqueous phase representative of deliquescent aerosols (not shown). Dissolved organic carbon accounts for less than 1 % of the carbon atom ratio. With such low water content, only the more soluble species contribute to the organic content of the aqueous phase, i.e. the more functionalized ones. The top 10 contributors to the aqueous phase composition are C₅ species bearing 4 functional groups each. For L set to a cloud value (Fig. 1b), moderately soluble species contribute

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substantially to aqueous phase organic mass. At the end of the simulation, 25 % of the total carbon initially in the isoprene backbone is found in water.

The carbon budget during octane oxidation is depicted in Fig. 1c for dry conditions. Gas phase secondary organic carbon reaches a peak for $N_\tau = 2.5$. This secondary organic fraction is progressively oxidized, ultimately leading to CO + CO₂ with a yield of 66 % for $N_\tau = 20$. Note that the production of CO and CO₂ at a given N_τ is comparatively higher for octane, owing to its greater lifetime ($\tau_{\text{octane}} \approx 1$ day) compared to isoprene ($\tau_{\text{isoprene}} \approx 1.5$ h). Adding deliquescent aerosols in the model has no impact on the carbon budget (not shown). However the addition of a water content representative of cloud conditions leads to a large organic content in the aqueous phase (see Fig. 1d). For these conditions, the secondary organic species first split equally in the gas and aqueous phases (for $N_\tau < 2.5$). The functionalization of the carbon backbone by atmospheric processing leads progressively to species of increasing solubility and dissolved carbon prevails for $N_\tau > 2.5$. The carbon atom ratio in the aqueous phase reaches a maximum of 55 % at $N_\tau = 13$ and next slowly declines with aging due to fragmentation of the carbon backbone by gas phase oxidation. At the end of the simulation ($N_\tau = 20$), 54 % of initial carbon atoms are still in the aqueous phase. The production rate of CO + CO₂ is much slower in this case, most organic species being temporally trapped in condensed phase and therefore not subjected to oxidation in this version of the model. The simulation results clearly show that most secondary organic species produced during the oxidation of aliphatic hydrocarbons are soluble enough to be dissolved in the aqueous phase during cloud events. This dissolved organic matter is then likely subject to a fast processing and may significantly shape the ultimate oxidation budget. This process is so far ignored in current atmospheric chemical models.

The time evolution of the carbon atoms distribution during α -pinene oxidation is given in Fig. 1e for dry conditions. Carbon distributions exhibit a behavior similar to the isoprene oxidation case. The simulated organic content in the deliquescent particle remains below 2 % (not shown). Figure 1f shows that for L set to a cloud value, a significant fraction of the carbon atoms is transferred into the aqueous phase. The majority

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of the initial carbon atoms are found in water (52 % on a carbon basis) at the end of the simulation. Similar to the octane oxidation simulation, cloud water acts in this version of the model as an inert reservoir and slows down the CO + CO₂ formation. The CO + CO₂ fraction at $N_T = 20$ decreases from 18 % for the dry scenario to 11 % for the cloud scenario.

3.2 Carbon budget and NO_x conditions

The Henry's law constant of an organic compound is linked to the functional groups on the carbon backbone as well as the length of the carbon skeleton (e.g. Raventos-Duran et al., 2010; Schwarzenbach et al., 2005). The nature and the number of organic moieties added to the carbon skeleton during atmospheric processing depend in particular on NO_x concentration (e.g. Finlayson-Pitts and Pitts, 2000; Atkinson and Arey, 2003). Simulations were therefore conducted for various scenarios: low NO_x conditions (0.1 ppb), intermediate NO_x conditions (1 ppb) and high NO_x conditions (10 ppb). Figure 2 shows the results of these simulations for isoprene, octane and α -pinene with a water content corresponding to cloud conditions. Note that modifications of the NO_x conditions also impact on the concentrations of OH, O₃ and NO₃. The relative contribution of these oxidants to oxidation of the precursors depends generally on NO_x levels, especially for isoprene and α -pinene. However, for all NO_x conditions explored here, OH drives the oxidation of isoprene and both OH and O₃ drive the oxidation α -pinene during the first oxidation steps. Therefore, NO_x concentrations have an impact on secondary organics speciation mostly through the fate of peroxy radicals, rather than the initiation reactions.

Figure 2 shows that the dissolved organic content tends to increase with decreasing NO_x concentration. The carbon atom ratio in the various phases appears to be especially sensitive to NO_x for isoprene simulation. For the 3 hydrocarbons examined in this study, the largest effects on carbon partitioning are seen at the lower NO_x concentrations. At the end of the simulations, the fraction of dissolved aqueous carbon is increased by 39 % for isoprene, 23 % for octane and 23 % for α -pinene, from the

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intermediate to the low NO_x scenario (Fig. 2a, d, g). The amount of dissolved organic carbon is reduced by 20 % when NO_x concentration is switched from intermediate to high NO_x conditions in the isoprene case (see Fig. 2b, c).

3.3 Functional groups in the gas and aqueous phase

Figure 3a shows the distribution of the organic moieties of the simulated secondary organics at $N_\tau = 2$ for the isoprene oxidation. The distribution is given for gas and aqueous phases, for the three NO_x scenarios and for L set to cloud conditions. Results are provided as the number of functional groups per carbon atom ratio $R_{OF/C}$, defined as:

$$R_{OF/C} = \frac{\sum_i n_i^{OF} C_i}{\sum_i n_i^C C_i} \quad (7)$$

where OF is a given organic function. C_i is the concentration of species i in the considered phase and n_i^{OF} or n_i^C are the number of organic function OF or carbon atoms in the species i , respectively. In the gas phase, the degree of substitution of the organics ranges from 28 % (low NO_x scenario) to 38 % (high NO_x scenario). The distribution is dominated by carbonyls for all NO_x scenarios. The substitution degree is comparatively larger in the aqueous phase than in the gas phase and ranges from 45 % (low NO_x scenario) to 64 % (high NO_x scenario). The hydroxyl group is a major moiety in the aqueous phase (substitution degree in the 22–30 % range). Under low NO_x conditions, the organic peroxy radical chemistry is dominated by RO₂ + HO₂ reactions, leading to the formation of hydroperoxides ROOH. These hydroperoxides are major contributors to the aqueous phase organic content. Under high NO_x conditions, the reaction RO₂ + NO dominates the evolution of peroxy radicals, leading among other things to the formation of the nitrate moiety. As expected, switching from low NO_x to high NO_x

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conditions make the nitrate moiety grow at the expense of the hydroperoxide moiety (see Fig. 3a).

Figure 3b gives the distribution of organic species as a function chain length and the number of functional groups born by the molecules for the isoprene simulations at $N_{\tau} = 2$. The distribution is dominated by C_4 species in the gas phase, mainly methyl vinyl ketone and methacrolein. In the aqueous phase, the distribution is dominated by C_5 species bearing two functional groups, i.e. hydroxy-hydroperoxides species under low NO_x conditions and hydroxy-nitrate or hydroxy-nitrate or hydroxyl-carbonyl species under high NO_x conditions. Under high NO_x conditions, quadrifunctional C_5 and C_4 species contribute also substantially (11 %) to the organic content of the aqueous phase.

Figure 4 shows the distribution of organic moieties (panel a) and the distribution as a function of chain length and number of functional group (panel b) for the octane simulations at $N_{\tau} = 2$. The substitution degree ranges from 16–20 % in the gas phase to 31–33 % in the aqueous phase. The distribution is dominated by C_8 species bearing one or two functional groups in the gas phase and two or three functional groups in the aqueous phase. The gas phase distribution is dominated by the carbonyl moieties, with a substantial contribution of nitrate moieties under high NO_x conditions. In the aqueous phase, about 21 % of the carbon atoms are substituted either by a hydroxy or a carbonyl moiety (see Fig. 4a). As expected, hydroperoxide is a significant functional group under low NO_x ($R_{-OOH/C} = 7\%$) while nitrate is substantial under high NO_x ($R_{-ONO_2/C} = 5\%$).

Figure 5 shows the distribution of the functional groups for the α -pinene simulations. Molecules are functionalized with a substitution degree ranging from 16 % in the gas phase to 25 % in the aqueous phase. Difunctional C_{10} species dominate both the gas phase and the aqueous phase distribution (60 to 70 % of the carbon atom ratio in each phase). In the gas phase, C_9 and C_8 contribute substantially to the carbon budget (18–23 %). In the aqueous phase, trifunctional C_{10} contribute also substantially to the carbon budget (22–28 %). The gas phase is mainly composed of carbonyl compounds ($R_{>CO/C} = 11\%$ under intermediate NO_x conditions). Nitrates

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($R_{\text{-ONO}_2/\text{C}} = 2.5\%$), hydroxy ($R_{\text{-OH}/\text{C}} = 1.9\%$) and PAN ($R_{\text{-CO(OONO}_2)/\text{C}} = 2.3\%$) moieties contribute to a lesser extent to the gas phase composition. In the aqueous phase, the main contributors to the global functionalization are (hydrated) carbonyls ($R_{>\text{CO}/\text{C}} + R_{\text{-C(OH)(OH)/C}} = 16\%$ under high NO_x conditions). The simulated substitution degree by carboxylic acids and their associated bases ($R_{\text{-CO(OH)/C}} + R_{\text{-CO(O-)/C}}$) is 2.6%. Nitrates are significant under high NO_x ($R_{\text{-ONO}_2/\text{C}} = 4.4\%$) while hydroperoxides have an important contribution under low NO_x conditions ($R_{\text{-OOH}/\text{C}} = 4.5\%$).

3.4 Oxidative trajectories in an oxidation state vs. solubility framework

The gas phase oxidation of the organic species includes competitive processes leading either to the functionalization of the carbon backbone or to its fragmentation. The progressive functionalization of the carbon skeleton may lead to species with low enough volatility to condense. Conversely, fragmentation of the carbon skeleton leads to species with higher volatilities and ultimately to CO_2 . In the context of organic partitioning between gas and aqueous phases, functionalization routes progressively increase the Henry's law coefficient of the species and therefore favor partitioning to the aqueous phase (e.g. Schwarzenbach et al., 2005; Raventos-Duran et al., 2010). The opposite behavior is usually noticed for the fragmentation routes. For example, Fig. 3 shows that for isoprene in all NO_x configurations, functionalized C_5 species are mostly found in water whereas fragmented $\text{C}_{<5}$ species tend to be preferentially found in the gas phase. Figure 4 (Fig. 5) shows that it is also true for octane (α -pinene) where the proportion of functionalized C_8 (C_{10}) species is larger in the aqueous phase and the proportion of fragmented $\text{C}_{<8}$ ($\text{C}_{<10}$) species is larger in the gas phase.

Two dimensional frameworks have been recently proposed to examine the formation and aging of secondary organic aerosols during atmospheric oxidation of hydrocarbons (e.g. Jimenez et al., 2009; Pankow and Barsanti, 2009; Barsanti et al., 2011; Kröll et al., 2011). These frameworks attempt to capture the oxidative trajectories in a space defined by the volatility of the secondary species and their oxidation degree (e.g. Donahue et al., 2011, 2012). A similar two dimensional framework is used here to explore

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the oxidative trajectories in the context of a gas/aqueous multiphase system. We define the first dimension by the Henry's law coefficient H , used as a metric to represent the water solubility of the species. At thermodynamic equilibrium, the distribution of a species i between the gas and the aerosol phase is given by:

$$\xi^i = \frac{N_a^i}{N_a^i + N_g^i} = \left(1 + \frac{1}{H^i RTL}\right)^{-1} \quad (8)$$

where N_a^i and N_g^i (molec cm^{-3} of air) are its number concentrations in the aqueous and gas phase, respectively. With $L = 3 \times 10^{-7}$, a species is equally distributed in the two phases ($\xi = 0.5$) for $H = 1.45 \times 10^5 \text{ Matm}^{-1}$. Species having H less than $1.45 \times 10^3 \text{ Matm}^{-1}$ will therefore almost exclusively be found in the gas phase ($\xi < 0.01$), while species with H greater than $1.45 \times 10^7 \text{ Matm}^{-1}$ will almost exclusively be found in the aqueous phase ($\xi > 0.99$). We use the mean carbon oxidation ($\overline{\text{OS}}_C$) as the second dimension. In this framework, the parent hydrocarbon is placed at the bottom of the graph and the ending point of the oxidative trajectories (CO_2) is placed at the top left ($\overline{\text{OS}}_C = 4$).

Figure 6 shows the distribution of species produced during the gas phase oxidation of isoprene in this solubility/ $\overline{\text{OS}}_C$ space for 4 different times ($N_\tau = 0, 1, 2, 10$). Distributions are shown for the 3 NO_x scenarios. The carbon atom ratio of a given species is proportional to the volume of the bubble. Species contributing for less than 10^{-4} to the total carbon are not shown for clarity. The SAR used to estimate H (Raventos-Duran et al., 2010) provides identical values for distinct position isomers. Position isomers with identical H are lumped to avoid overlap of the bubbles. In Fig. 6, species with a carbon backbone identical to the parent compound (blue bubbles) delineate the functionalization route. Species with a smaller backbone (orange bubbles) delineate trajectories including at least one fragmentation in the oxidation steps.

As expected, the first step of the isoprene oxidation is dominated by fragmentation routes (see Fig. 6). Under high NO_x conditions, oxidation leads mostly to species with

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H in the 10^0 – 10^4 M atm^{-1} range, i.e. low enough to be mostly distributed in the gas phase at thermodynamic equilibrium. At $N_\tau = 10$, 10 species contribute for 90 % of the carbon budget. These species are the expected major isoprene oxidation products, as shown in Table 2. Under low NO_x conditions, the solubility distribution spans more than 10 orders of magnitude. At $N_\tau = 10$, the carbon distribution is shifted to higher values of solubility. Therefore, the carbon atom fraction in the aqueous phase is substantial, reaching 63 % at $N_\tau = 10$ (see Fig. 2i). The major contributors to the aqueous organic composition are an hydroxy-hydroperoxyde ($\text{CH}_3\text{C}(\text{OOH})(\text{CH}_2(\text{OH}))\text{CH}=\text{CH}_2$) and its position isomers.

Figure 7 shows that the octane oxidation is first dominated by the functionalization routes and as oxidation proceeds fragmentation routes become substantial. Species are distributed in a broader range of solubility, at first in the 10^{-3} – 10^8 M atm^{-1} range and then in the 10^1 – 10^{12} M atm^{-1} range after the first oxidation steps. Thus species are at first evenly distributed in both phases and become more prevalent in the aqueous phase after $N_\tau = 2$ (see also Fig. 2). At $N_\tau = 10$, 60 % of the gaseous carbon can be ascribed to 10 species, peroxy acetyl nitrate and peroxy propyl nitrate being the major species, as seen in Table 2. Under low NO_x conditions, the solubility distribution range is approximately the same, but more species are on the high solubility range ($H > 7 \times 10^6$ M atm^{-1}). The fraction of dissolved carbon reaches 77 % at $N_\tau = 10$.

Like isoprene, α -pinene oxidation is dominated by fragmentation (see Fig. 8). H values for most species fall in the 10^5 – 10^{13} M atm^{-1} range, i.e. partition in the aqueous phase at thermodynamic equilibrium. In the gas phase, a difunctional C_{10} PAN-like species is dominant, followed by acetone, formaldehyde and PAN (see Table 2). As expected from the species solubility range, dissolved carbon represents 71 % of the total carbon in low NO_x conditions at $N_\tau = 10$.

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Explicit gaseous oxidation schemes have been generated for three precursors of atmospheric interest (isoprene, octane, α -pinene) using GECKO-A. The partitioning of the secondary organic compounds between gaseous and aqueous phases has been examined for a liquid water content corresponding to clouds and deliquescent aerosols. For $L = 1 \times 10^{-12}$ (i.e. aerosols water), only a small fraction of the secondary organic carbon is influenced by the aqueous phase. For $L = 3 \times 10^{-7}$ (i.e. cloud water), the phase distribution of organic carbon is sensitive to NO_x concentrations. For low NO_x conditions, 50 % (isoprene oxidation) to 70 % (octane oxidation) of the carbon atoms are found in the aqueous phase after the removal of the parent compound ($N_\tau \approx 3$). For high NO_x condition, this ratio is only 5 % in the isoprene oxidation case, but remains large for α -pinene and octane oxidation cases (40 % and 60 %, respectively). This study therefore suggests that most secondary organic species produced during the multigenerational oxidation of anthropogenic and biogenic hydrocarbons should dissolve in the aqueous phase during cloud events.

The simulated oxidative trajectories are examined in a new two dimensional space defined by the mean oxidation state and the water solubility. Isoprene oxidation is dominated by fragmentation routes. The solubility distribution of the isoprene oxidation products appears to be especially sensitive to NO_x , with low NO_x conditions favoring the production of more water soluble species. As a result, the fraction of dissolved carbon decreases from low to high NO_x conditions. Octane oxidation is first dominated by functionalization routes, next by fragmentation routes, producing highly soluble species in both low NO_x and high NO_x conditions. The fragmentation routes dominate the α -pinene oxidation pathways and lead to highly water soluble species whatever the NO_x conditions are.

Once dissolved, organic species follow complex oxidation mechanisms. This study shows that during cloud events, a large fraction of organic matter could be processed in the aqueous phase and modify both the rates of reaction and the identity of their

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products. To the best of our knowledge, this process is currently ignored in current atmospheric chemical models dealing with the oxidation of long chain organics. To explore the contribution of these cloud processes, aqueous oxidation mechanisms are needed for the very large set of species expected to be significantly dissolved in the cloud droplets. Protocols are required to generate consistent and comprehensive aqueous oxidation schemes on a systematic basis. This is the object of ongoing studies.

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Precursor species	Gas phase	Aqueous phase	Total
Isoprene	5.9×10^3	3.2×10^3	9.1×10^3
Octane	1.1×10^5	5.0×10^4	1.6×10^5
α -pinene	3.2×10^5	2.5×10^5	5.6×10^5

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Table 2. Top ten species simulated in gas and aqueous phase for a cloud liquid water content and for intermediate NO_x conditions at $N_t = 10$.

Isoprene		Octane		α -pinene	
Gas phase	Aqueous phase	Gas phase	Aqueous phase	Gas phase	Aqueous phase
HCHO					
				HCHO	

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Table 2. (Continued.)

Isoprene		Octane		α -pinene	
Gas phase	Aqueous phase	Gas phase	Aqueous phase	Gas phase	Aqueous phase

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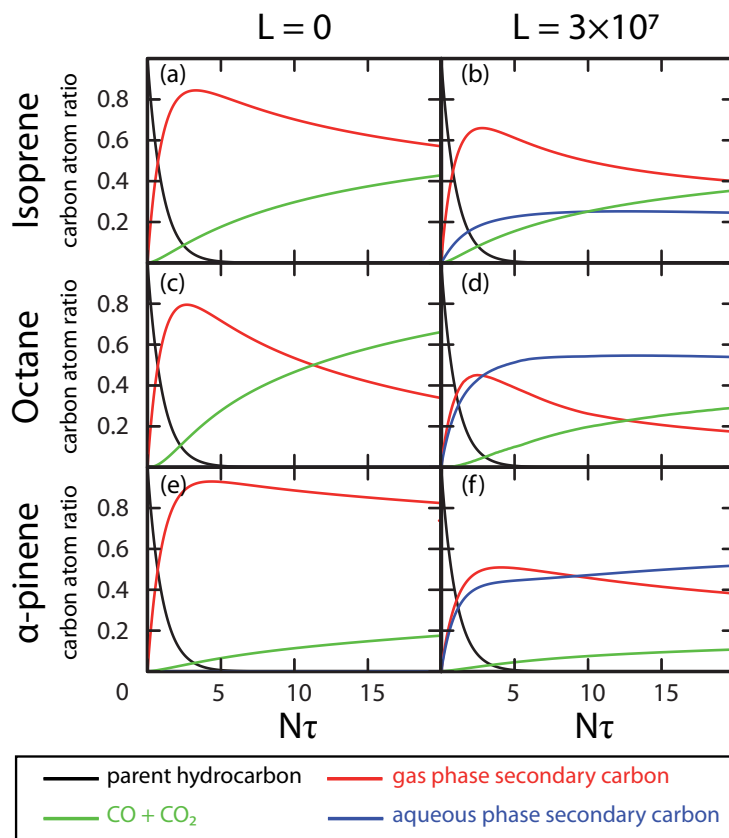


Fig. 1. Carbon budget during the oxidation of isoprene (top row), octane (middle row) and α -pinene (bottom row) for liquid water content of 0 (1st column) and 3×10^{-7} (2nd column), under intermediate NO_x conditions ($\text{NO}_x = 1$ ppb). The time scale is defined as multiples of lifetimes of the initial hydrocarbon, as described in the text.

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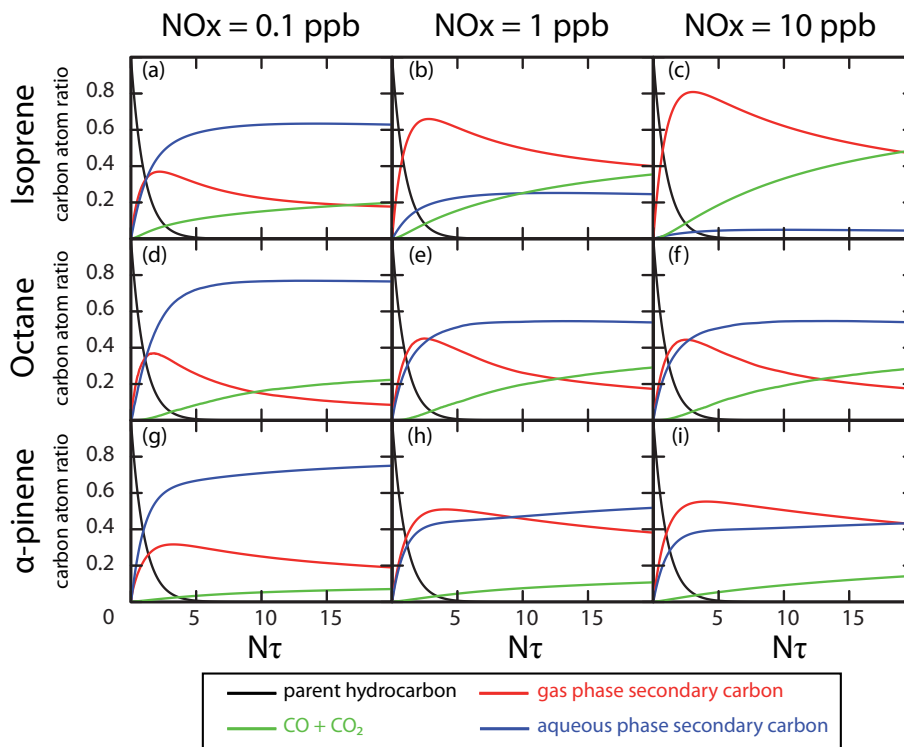


Fig. 2. Carbon budget during the oxidation of isoprene (top line), octane (middle line) and α -pinene (bottom line) for a NO_x concentration of 0.1 ppb (1st column), 1 ppb (2nd column) and 10 ppb (3rd column), with a cloud liquid water content ($L = 3 \times 10^{-7}$). The time scale is described in the text.

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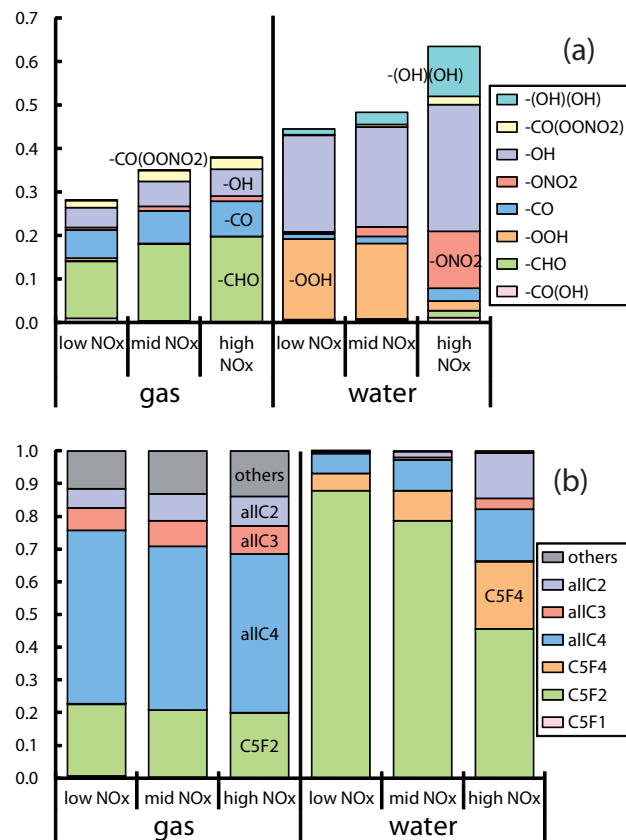


Fig. 3. At $N_t = 2$, simulated distribution in gaseous and aqueous phase of organic moieties ratio ($R_{OF/C}$, **a**) and functionalization (**b**) for a cloud water content during the oxidation of isoprene. C_mF_n category merges species with m carbon atoms bearing n functional groups. The precursor and C1 species are lumped in the *others* category.

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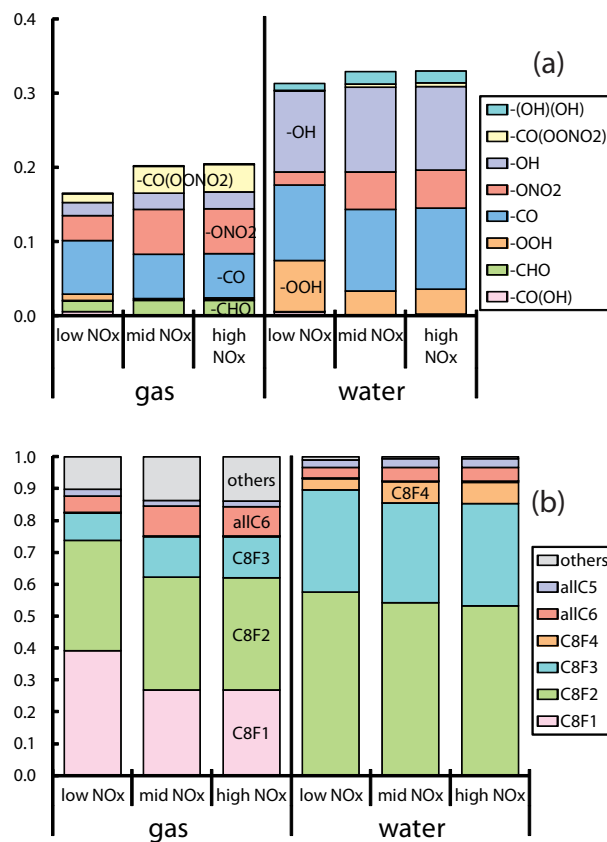


Fig. 4. At $N_t = 2$, simulated distribution in gaseous and aqueous phase of organic moieties ratio ($R_{OF/C}$, **a**) and functionalization (**b**) for a cloud water content during the oxidation of octane. C_mF_n category merges species with m carbon atoms bearing n functional groups. The precursor and C1–C4 species are lumped in the *others* category.

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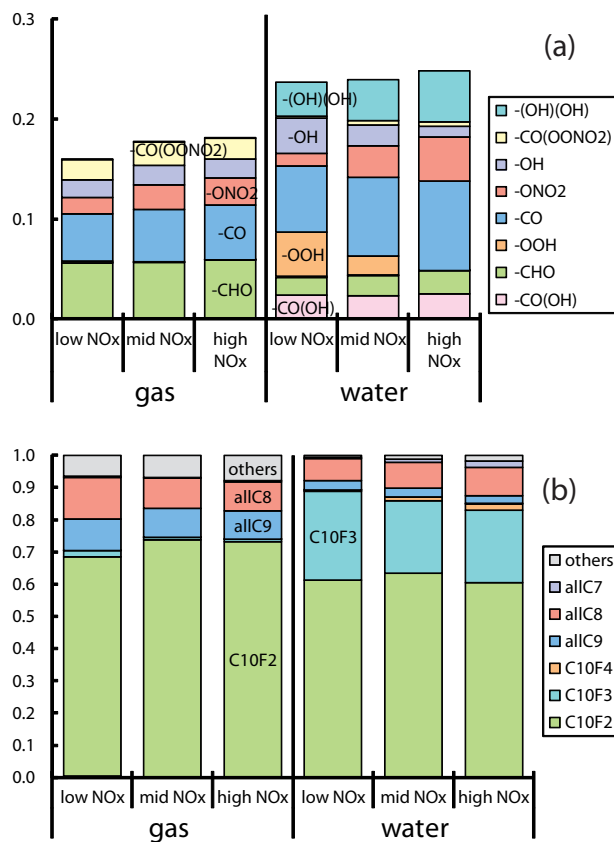


Fig. 5. At $N_t = 2$, simulated distribution in gaseous and aqueous phase of organic moieties ratio ($R_{OF/C}$, **a**) and functionalization (**b**) for a cloud water content during the oxidation of α -pinene. $CmFn$ category merges species with m carbon atoms bearing n functional groups. The precursor and C1–C6 species are lumped in the *others* category.

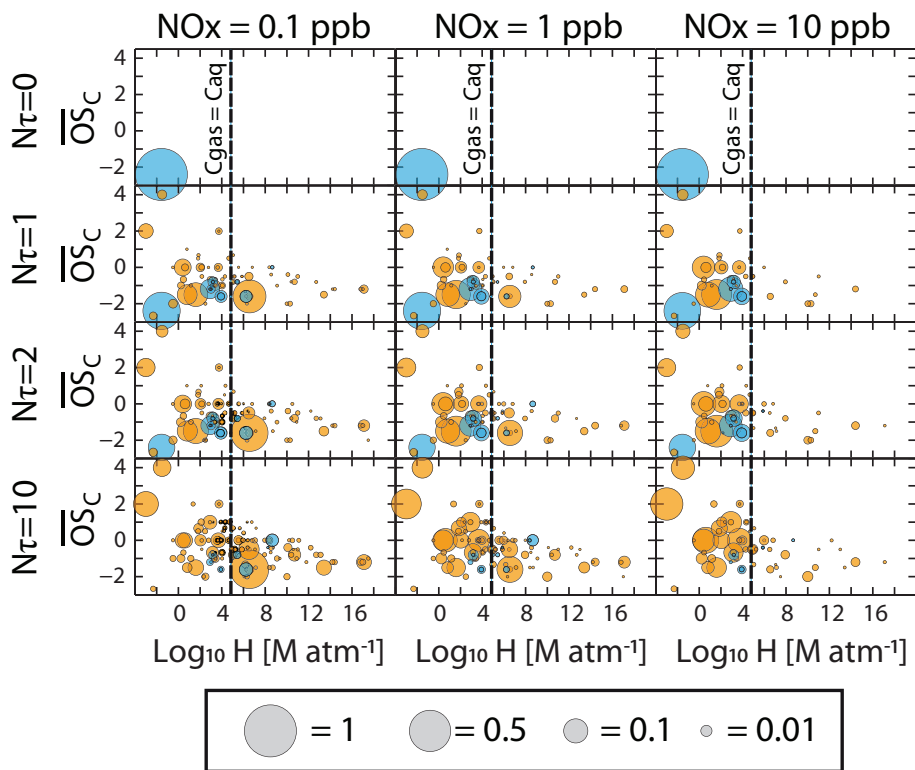


Fig. 6. Solubility and mean oxidation state of the species produced during the oxidation of isoprene under low NO_x (1st column), intermediate NO_x (2nd column) and high NO_x (3rd column) conditions as a function of the number of precursor lifetime. Contribution of a species to the global carbon budget is proportional to the volume of the bubble. Position isomers having identical volatility and oxidation state are lumped in the same bubble. Blue bubbles denote species having the carbon skeleton of the parent hydrocarbon. Orange bubbles denote species with less carbon atoms than the parent compound. The black dashed lines denote the solubility for which a compound is equally distributed in the aqueous and gaseous phases.

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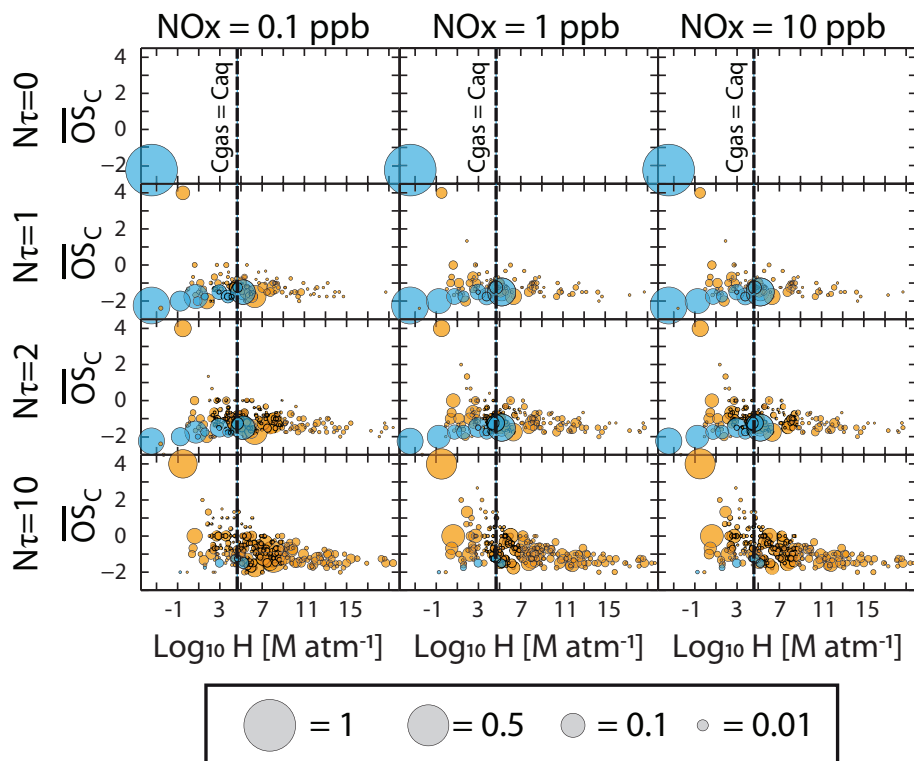


Fig. 7. Solubility and mean oxidation state of the species produced during the oxidation of octane under low NO_x (1st column), intermediate NO_x (2nd column) and high NO_x (3rd column) conditions as a function of the number of precursor lifetime. See Fig. 6 caption for the color code of the bubbles.

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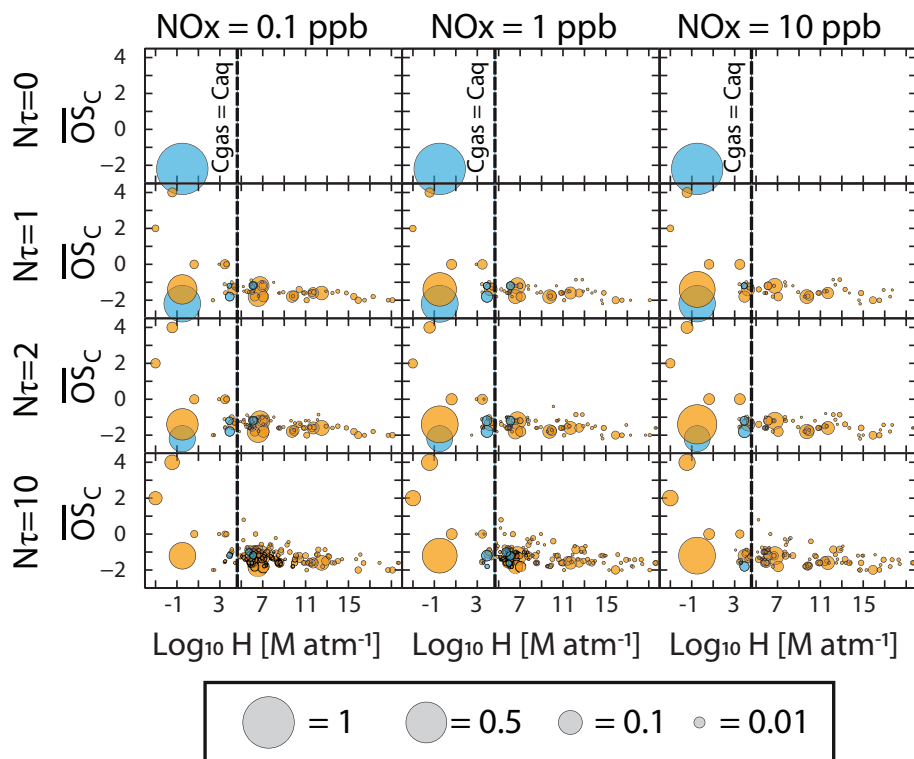


Fig. 8. Solubility and mean oxidation state of the species produced during the oxidation of α -pinene under low NO_x (1st column), intermediate NO_x (2nd column) and high NO_x (3rd column) conditions as a function of the number of precursor lifetime. See Fig. 6 caption for the color code of the bubbles.

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