



# The SOA/VOC/NO<sub>x</sub> system: an explicit model of secondary organic aerosol formation

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# The SOA/VOC/NO<sub>x</sub> system: an explicit model of secondary organic aerosol formation

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## Abstract

Our current understanding of secondary organic aerosol (SOA) formation is limited by our knowledge of gaseous secondary organics involved in gas/particle partitioning. The objective of this study is to explore (i) the potential for products of multiple oxidation steps contributing to SOA, and (ii) the evolution of the SOA/VOC/NO<sub>x</sub> system. We developed an explicit model based on the coupling of detailed gas-phase oxidation schemes with a thermodynamic condensation module. Such a model allows prediction of SOA mass and speciation on the basis of first principles. The SOA/VOC/NO<sub>x</sub> system is studied for the oxidation of 1-octene under atmospherically relevant concentrations. In this study, gaseous oxidation of octene is simulated to lead to SOA formation. Contributors to SOA formation are shown to be formed via multiple oxidation steps of the parent hydrocarbon. The behaviour of the SOA/VOC/NO<sub>x</sub> system simulated using the explicit model agrees with general tendencies observed during laboratory chamber experiments. This explicit modelling of SOA formation appears as a useful exploratory tool to (i) support interpretations of SOA formation observed in laboratory chamber experiments, (ii) give some insights on SOA formation under atmospherically relevant conditions and (iii) investigate implications for the regional/global lifetimes of the SOA.

## 1 Introduction

Progressive gas-phase oxidation of volatile organic compounds (VOC) leads to the formation of a multitude of intermediate species (e.g., [Aumont et al., 2005](#)). These secondary organics are more functionalised than their precursor compounds, and the number of functions typically increases as oxidation proceeds. Highly functionalised species typically have lower saturation vapour pressures and/or higher polarities, allowing substantial gas/particle partitioning, thus leading to secondary organic aerosol (SOA) formation. Once in the aerosol phase, those compounds react further by photochemical reactions that alter particulate composition (e.g., [Molina et al.,](#)

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2004; Stephanou, 2005). Recent measurements indicate that SOA products can react via heterogeneous or particle-phase reactions, forming oligomeric and/or polymeric species, responsible for an important fraction of SOA growth (e.g., Jang et al., 2002; Gao et al., 2004; Kalberer et al., 2004; Tolocka et al., 2004).

5 Despite the substantial impacts of SOA on the environment, SOA modelling is not satisfactorily constrained. A large underestimation of SOA production in current models has been highlighted by recent observations in the boundary layer (e.g., de Gouw et al., 2005; Johnson et al., 2006; Volkamer et al., 2006) as well as in the free troposphere (Heald et al., 2005). Our current understanding of SOA formation is limited by the  
10 lack of knowledge of gaseous secondary organics involved in gas/particle partitioning. SOA formation involves a multitude of semi-volatile organic compounds (SVOC) having complex molecular structures. Their low atmospheric concentrations cause analytical difficulties (e.g., Jacobson et al., 2000; Turpin et al., 2000; Kanakidou et al., 2005). During in situ measurement campaigns, less than 20% of the total particulate organic  
15 mass is typically identified (Rogge et al., 1993; Puxbaum et al., 2000). Moreover major difficulties hinder the simulation of SOA formation on the basis of first principles. Most three-dimensional transport models were developed to represent the chemical evolution of the O<sub>3</sub>/VOC/NO<sub>x</sub> system. These models typically represent organic chemistry with highly simplified mechanisms using lumped or surrogate species (e.g., Gery et al.,  
20 1989; Stockwell et al., 1997; Bey et al., 2001; Brasseur et al., 1998; Carter, 2000; Poisson et al., 2000). The formation of long chain functionalised secondary organics acting as SOA precursors is ignored in those gas-phase oxidation schemes.

Parameterized SOA representations are therefore implemented in 3-D chemistry-transport models in terms of total particle growth. The aerosol creation potential measured in laboratory chamber experiments from a particular hydrocarbon, HC, is currently expressed in terms of aerosol yield  $Y$  defined as:

$$Y = \frac{M_o}{\Delta HC} \quad (1)$$

where  $M_o$  is the organic aerosol mass concentration produced for a given amount of

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HC reacted ( $\Delta HC$ ). The aerosol yield strongly depends on the organic particulate mass which acts as the medium into which oxidation products can be absorbed (e.g., [Odum et al., 1996, 1997](#)). [Odum et al. \(1996\)](#) demonstrated that the evolution of aerosol yield with  $M_o$  can be expressed as:

$$Y = M_o \sum \left( \frac{\alpha_i K_{om,i}}{1 + K_{om,i} M_o} \right) \quad (2)$$

where  $\alpha_i$  is the mass stoichiometric factor of the aerosol-forming species  $i$  and  $K_{om,i}$  is the equilibrium partitioning coefficient for species  $i$ . [Odum et al. \(1996, 1997\)](#) showed that the use of two lumped aerosol-forming products for Eq. (2) fits laboratory yield data with sufficient accuracy. Equation (2) is considered valid only for the final aerosol yield.

This semi-empirical two-product model has been extensively used in 3-D chemistry-transport models (e.g., [Hoffman et al., 1997](#); [Kanakidou et al., 2000](#); [Schell et al., 2001](#); [Chung and Seinfeld, 2002](#); [Tsigaridis and Kanakidou, 2003](#)) where constants  $\alpha_i$  and  $K_{om,i}$  are chosen as the best fit of laboratory chamber data for a given HC.

However, the two-product representation assumes that aerosol-forming species  $i$  is produced from a single oxidation step of the parent hydrocarbon. SVOC formation is suspected to be more complex than arising from first generation oxidation products of a given precursor, with the possibility of multiple oxidation steps ([Kroll and Seinfeld, 2005](#); [Ng et al., 2006, 2007](#)). The relative importance as contributors to SOA formation of those products formed from multiple oxidation steps with regard to direct oxidation products of the parent hydrocarbon remains unknown (e.g., [Kroll and Seinfeld, 2005](#)).

Furthermore, this empirical representation for SOA formation implies a large extrapolation of experimental chamber results carried out at levels of NO<sub>x</sub> and HC that are significantly higher than typical tropospheric conditions (e.g., [Cocker et al., 2001](#); [Vesterinen et al., 2007](#); [Kroll et al., 2007](#)). The potential of an air mass to attain supersaturation during its ageing depends on local chemical factors, especially (i) the emitted HC source amounts influencing the concentration of secondary organic carbon in the plume and (ii) NO<sub>x</sub> chemical regimes that drive the chemical identity of

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SVOC produced during air mass oxidation (i.e. carbon atom number, nature and distribution of functional groups borne by the molecule...), and consequently their volatility. The evolution of the SOA/VOC/NO<sub>x</sub> system still remains difficult to ascertain.

The objective of this work is to explore (i) the role of products of multiple oxidation steps in the production of SOA contributors and (ii) the evolution of the SOA/VOC/NO<sub>x</sub> system. For this purpose, we developed an explicit model describing SOA formation based on thermodynamic and chemical principles that predicts the gas/particle partitioning of individual organics produced during gas-phase oxidation. Such a model allows therefore prediction of SOA mass and speciation on the basis of first-principles. The model is based on the coupling of detailed gas-phase oxidation schemes with a thermodynamic module for condensation (see Fig. 1). Gas-phase oxidation schemes up to CO<sub>2</sub> production are developed using the explicit self-generating approach described by Aumont et al. (2005). Gas/particle partitioning of low-volatility species is represented assuming (i) a basic thermodynamic absorption process (e.g., Pankow, 1994a) and (ii) that the aerosol phase behaves as a pure ideal organic phase. In this exploratory study, no reactions are implemented in the particulate phase. SOA formation is studied here for the complete oxidation of 1-octene. This work has been carried out with a particular focus on the gas/aerosol carbon budget. Section 2 describes the explicit model for SOA formation. The scenarios selected to explore the SOA/VOC/NO<sub>x</sub> system are presented in Sect. 3. SOA formation from multiple oxidation steps of the parent HC is reported in part 4. The simulated evolution of the SOA/VOC/NO<sub>x</sub> system is discussed in Sect. 5.

## 2 SOA formation model

SVOC production might require many successive oxidation steps. Most reaction pathways involved during gas-phase oxidation make minor individual contributions to the organic budget. These minor reaction channels are therefore ignored in current mechanisms, even in the most detailed mechanisms available to date such as the NCAR

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Master Mechanism (Madronich and Calvert, 1990; Aumont et al., 2000) or the University of Leeds' Master Chemical Mechanism (MCM-v3) (Jenkin et al., 2003; Saunders et al., 2003). However, these minor pathways could have a cumulative importance for the formation of those low-volatility species. Highly detailed oxidation schemes are therefore required to simulate the behaviour of organic species during gas-phase oxidation and their interaction with the organic aerosol phase. Such explicit schemes involve a very large number of chemical reactions and intermediate species, far in excess of the number that can be reasonably written manually (Aumont et al., 2005).

## 2.1 Gas-phase oxidation schemes

Explicit gas-phase oxidation schemes are written using the self-generating approach developed by Aumont et al. (2005). This expert system is based on two main elements:

1. A protocol defining a set of rules that lay out the choice of reaction pathways and provide the rate coefficients needed in the mechanism. When available, kinetic data taken from laboratory measurements are assigned to the chemical scheme. Otherwise, an estimation of the rate constant, stoichiometric coefficients and reaction products is performed using structure/activity relationships.
2. A generator which is a computer program that automatically creates the fully-explicit degradation scheme, up to CO and CO<sub>2</sub>, for a set of parent species provided as input on the basis of the predefined protocol.

The protocol and the main running stages of the generator are described in detail by Aumont et al. (2005). Only salient points are summarized here. The development of self-generated chemical schemes requires the identification of all the reactions for each emitted organic compound and for their reaction products. These reactions generally include: (i) initiation of atmospheric degradation by attack with OH, NO<sub>3</sub>, O<sub>3</sub> or photolysis, leading to the formation of peroxy radicals, (ii) reactions of peroxy radicals with NO, NO<sub>2</sub>, NO<sub>3</sub>, HO<sub>2</sub> and with other RO<sub>2</sub> radicals leading to the formation of stable

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reaction intermediates or alkoxy radicals RO and (iii) alkoxy radical reactions with O<sub>2</sub>, unimolecular decomposition or isomerisation leading to the formation of stable reaction intermediates or new peroxy radicals. The possible functional groups produced during the oxidation of parent compounds are ketones, aldehydes, alcohols, hydroperoxides, nitrates, peroxy radicals, alkoxy radicals, carboxylic acids, peracids, peroxyacylnitrates and peroxyacyl radicals. The total number of species generated to fully describe the oxidation grows exponentially with increasing carbon number of precursor (Aumont et al., 2005).

## 2.2 Gas/particle partitioning of semi-volatile organic compounds

The dominant process controlling the gas/particle partitioning of SVOC is expected to be an absorption mechanism (Pankow, 1994a,b; Odum et al., 1996; Hoffman et al., 1997; Griffin et al., 1999; Kalberer et al., 2000). The gas/particle partitioning of organics produced during the gas-phase degradation is based on the absorptive model described by Pankow (1994a,b), which assumes a thermodynamic equilibrium of gaseous oxidation products between gas and particulate phases. Gas/particle partitioning of each organic species can then be described on the basis of Raoult's law:

$$P_i = x_i \gamma_i P_i^{\text{vap}} \quad (3)$$

where  $P_i$  is the equilibrium partial pressure of a species  $i$ ,  $x_i$  its mole fraction in the aerosol phase,  $P_i^{\text{vap}}$  its vapour pressure as pure liquid at the temperature of interest and  $\gamma_i$  its activity coefficient in the aerosol phase. Only equilibria for non-radical intermediate species are considered here.

For aerosol particles expected to be composed of a mixture of similar-type molecules,  $\gamma_i$  is set to unity (e.g., Seinfeld and Pankow, 2003). The liquid vapour pressure (subcooled if necessary) of organic species is estimated using the Myrdal and Yalkowsky method (Myrdal and Yalkowsky, 1997), owing to its reliability for SVOC generated during tropospheric gas-phase oxidation (Camredon and Aumont, 2006). The

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Myrdal and Yalkowsky method is coupled with the Joback structure/property relationship for boiling point estimates (e.g., Reid et al., 1986). Additional group contributions are included to evaluate the vapour pressure of the wide range of compounds involved in SOA formation (see Camredon and Aumont, 2006).

In this exploratory study, no reactions are implemented in the particulate phase. Heterogeneous reactions would shift condensation equilibria towards the aerosol phase. As long as the products of any heterogeneous reactions were less volatile than their reactants, such processes would lead to additional mass in the condensed phase. The aerosol mass simulated here can therefore be seen as a lower limit (e.g., Kroll and Seinfeld, 2005).

### 2.3 System resolution

Time integration for chemical schemes is performed using the two-step solver (Verwer, 1994; Verwer et al., 1996). The gas-phase lifetimes of SVOC are typically greater than half an hour. The characteristic time associated with the gas/particle mass transfer is assumed to be short compared to the timescale required for other production/removal processes of gaseous SVOC. Hence, thermodynamic equilibrium was imposed at each time step (20 min). Gas/particle equilibrium is solved using the iterative method described by Pankow (1994b). For the case of 1-octene presented below, the number of species considered to describe gas-phase oxidation is about  $1.4 \times 10^6$ . Thermodynamic equilibrium is considered for about  $4.0 \times 10^5$  of these oxidation products. To our knowledge, this is the first attempt to describe SOA formation on the basis of a fully explicit model.

### 3 Scenarios

The SOA/VOC/NO<sub>x</sub> system is studied here for the complete oxidation of 1-octene. This species was selected as a representative parent compound because (i) the aerosol

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creation potential of 1-octene has been reported experimentally (Wang et al., 1992; Forstner et al., 1997), (ii) the first steps in gaseous oxidation of alkenes are relatively well established (e.g., Calvert et al., 2000) and (iii) SOA formation is expected from multiple oxidation steps of this volatile precursor.

5 The aerosol creation potential of 1-octene is simulated in a box model. Physical conditions and chemical regimes are held constant throughout the simulation in order to isolate the influence of the initial hydrocarbon concentration or NO<sub>x</sub> regimes on SOA formation. Relative humidity is set to 50%. Temperature is fixed at 298 K. Photolysis frequencies are computed for a zenith angle of 30 degrees for mid-latitude conditions using the TUV model (Madronich and Flocke, 1998). Simulations are performed under various fixed NO<sub>x</sub> mixing ratios, between 50 ppt and 100 ppb. NO<sub>x</sub> levels are adjusted at each time step to sustain the prescribed NO<sub>x</sub> mixing ratio. Finally, simulations are carried out for various initial mixing ratios of the parent hydrocarbon, [HC]<sub>0</sub>, ranging from 1 to 100 ppb.

#### 15 4 Typical temporal evolution of SOA mass and speciation

Results are presented here with a particular focus on the gradual change of organic compounds in the particulate phase during gas-phase oxidation. The various simulations present similar characteristics. Typical profiles are illustrated here with results obtained for the simulation carried out under 1 ppb of NO<sub>x</sub> and starting with an initial loading of 10 ppb of octene. Under those conditions, octene removal is dominated by OH radical chemistry (with a reactivity yield toward OH higher than 90%).

20 The temporal evolutions of octene, secondary organics and inorganic carbon (i.e. CO+CO<sub>2</sub>) during the simulation are shown in Fig. 2a. For the conditions simulated here, the precursor is essentially consumed after 20 h of irradiation. At this time, secondary organics represent the major fraction of the carbon. This fraction is then progressively oxidised in the gas-phase into CO and CO<sub>2</sub>.

The distribution of secondary organics between the gaseous and particulate phases

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is shown in Fig. 2b. SOA mass only appears when a significant fraction (50%) of precursor has been oxidised. Aerosol mass reaches a maximum after about 30 h of oxidation and a slight decrease of SOA mass is then observed. As no aerosol phase reactions are implemented in the model, the gas/particle equilibria of the more volatile compounds are progressively shifted from particle to gas, as gas-phase oxidation proceeds. Once in the gaseous phase, those compounds evolve by oxidation until the final formation of CO and CO<sub>2</sub>. A significant fraction of the carbon still remains in the condensed phase (about 15% of the carbon at the end of the simulation).

The distribution of particulate organics is shown as a function of the chain length in Fig. 2c. This fraction is dominated by species holding 8 carbon atoms, i.e. of the same size as the parent compound. As oxidation proceeds and particulate mass increases, the amount of compounds with shorter carbon chain length also increases.

The distribution of particulate organic compounds bearing 8 carbons is shown in Fig. 2d as a function of the number of functional groups borne by the molecules. C8 compounds in the condensed phase mainly bear 4 functional groups. After 30 h of oxidation, those compounds volatilise into the gas phase again. Tri-functionalised C8 compounds are found in the aerosol phase at the beginning of the oxidation but volatilise rapidly back to the gas phase after 24 h. Species bearing 5 functions appear in particulate matter as gas-phase oxidation proceeds and for the conditions simulated here remain in the particle phase.

The distribution of the organic moieties in the particulate phase is shown as a function of time in Fig. 3. Results are expressed as an organic functional group ( $OF_k$ ) per particulate carbon ratio as:

$$R_{OF_k/C} = \frac{\sum_i n_i^{OF_k} C_i}{\sum_i n_i^C C_i} \quad (4)$$

where  $C_i$  is the concentration of molecule  $i$  in the aerosol phase and  $n_i^{OF_k}$  or  $n_i^C$  are the number of organic functions  $k$  or carbon atoms in the molecule  $i$ , respectively.

The substitution degree of the carbon (i.e.  $\sum_k R_{OFk/C}$ ) is found to be slightly sensitive to oxidation time. As expected, the degree of substitution is rather high with values of about 50%. The dominant moieties in the particulate phase are found to be the alcohol ( $R_{-OH/C}=18\%$ ), nitrate ( $R_{-ONO_2/C}=18\%$ ) and ketone ( $R_{-CO-}/C=13\%$ ) moieties. Hydroperoxides and PANs are found in the 3% range.

In this exploratory study, gaseous oxidation of a relatively high-volatility hydrocarbon, 1-octene, is simulated to lead to SOA formation for representative concentrations of tropospheric levels. Contributors to SOA formation are shown to be highly functionalised products, bearing at least 3 functional groups. These compounds are formed via multiple oxidation steps of the parent HC. Time scales of a few days are indeed required to form those low vapour pressure products. This delay may explain why negligible or small SOA formation is observed in laboratory chamber experiments from the oxidation of relatively high-volatility precursors. Furthermore, some SOA contributors (especially the 4- and 5-functional C8 species) have very low vapour pressure. These compounds remain preferentially in the aerosol phase and SOA evaporation is a slow process. Therefore lifetime of SOA appears likely driven by aerosol reactivity and/or microphysical processes.

## 5 The SOA/VOC/NOx system

The formation of SOA has been illustrated in the previous section with a simulation carried out under 1 ppb of NOx and starting with an initial loading of 10 ppb of octene. SOA formation is quite sensitive to external parameters such as the initial mixing ratio of the parent hydrocarbon,  $[HC]_0$ , and NOx-levels. The sensitivity of the SOA/VOC/NOx system is explored here with a particular focus on (i) the maximum aerosol yield, (ii) the temporal evolution of SOA formation and (iii) SOA speciation. The objective of this section is to assess whether the behaviour simulated using the explicit modelling agrees with general tendencies observed during laboratory chamber experiments.

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## 5.1 Maximum aerosol yields

### 5.1.1 Influence of $[HC]_0$

The dependence of SOA formation on the initial mixing ratio of the parent hydrocarbon has been widely studied in laboratory chamber experiments (e.g., Hurley et al., 2001; Song et al., 2005; Ng et al., 2006; Kroll et al., 2006). An increase of  $[HC]_0$  leads directly to an increase of the aerosol organic mass,  $M_o$ , by increasing the concentrations of the SVOC in the system. An additional effect arises from the increase of the organic mass which acts as the medium into which oxidation product can be absorbed. The dependence of SOA formation on  $M_o$  is generally discussed by observing the evolution of the maximum aerosol yield,  $Y$ , versus  $M_o$  (e.g., Odum et al., 1996, 1997; Song et al., 2005; Presto et al., 2005; Ng et al., 2007; Kroll et al., 2007).  $Y$  increases with  $M_o$ . Notable limit behaviours are that:

- At low particulate organic mass,  $Y$  strongly depends on  $M_o$ . For  $M_o$  equal to zero, a compound will partition into the particulate phase only if its concentration exceeds its saturation vapour pressure. When increasing  $M_o$ , products might be absorbed into the particle phase even though they are present at concentrations below their saturation point. The two-product model (see Eq. 2) predicts an aerosol yield that is directly proportional to  $M_o$  ( $Y \rightarrow M_o \sum \alpha_i K_{om,i}$ ) when  $M_o$  tends to zero.
- At high particulate organic mass,  $Y$  is weakly dependent on  $M_o$ . The two-product model (see Eq. 2) predicts an aerosol yield that is independent of  $M_o$  ( $Y \rightarrow \sum \alpha_i$ ) when  $M_o$  tends to infinity.

Figure 4 shows simulated evolutions of SOA formation as classical plots reported from laboratory chamber experiments: (a) the maximum aerosol mass (denoted  $M_o^{\max}$  hereafter) as a function of  $\Delta[HC]$  (the final growth plot as defined by Ng et al., 2006) and (b) the maximum aerosol yield (denoted  $Y^{\max}$  hereafter) as a function of organic

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aerosol mass concentration (the final yield plot as defined by Ng et al., 2006). These plots are reported for simulations carried out under 10 ppb of NO<sub>x</sub>. The set includes five [HC]<sub>0</sub> values: 1, 5, 10, 50 and 100 ppb. The final growth and yield curves for the two-product model are also reported. The final growth curve is of similar shape to those reported from laboratory chamber experiments (e.g., Hurley et al., 2001; Song et al., 2005; Ng et al., 2006; Kroll et al., 2006).  $M_o^{\max}$  varies from about 3 to 250  $\mu\text{g m}^{-3}$  for 1 and 100 ppb of [HC]<sub>0</sub>, respectively. The final yield curve also has the same shape as those observed in laboratory chamber experiments (e.g., Odum et al., 1996, 1997; Song et al., 2005; Presto et al., 2005; Ng et al., 2007; Kroll et al., 2007).  $Y^{\max}$  ranges from about 0.1 to an asymptotic value of about 0.57. As expected, the effect on  $Y^{\max}$  of changes in  $M_o$  is clearly more pronounced at low  $M_o$  than at higher values.

The explicit approach captures the general qualitative behaviours observed during laboratory chamber experiments of the dependence of SOA formation with [HC]<sub>0</sub>, tendencies that are also reported by the two-product (e.g., Odum et al., 1996) or the one-product approach (Kroll and Seinfeld, 2005).

### 5.1.2 Influence of NO<sub>x</sub>

NO<sub>x</sub>-levels have been shown to largely influence SOA formation during laboratory chamber experiments. Conclusions of those experimental studies are that (i) a higher  $M_o$  is observed under low-NO<sub>x</sub> experiments than under high-NO<sub>x</sub> (e.g., Hatakeyama et al., 1991; Hurley et al., 2001; Johnson et al., 2004; Martin-Riviejo and Wirtz, 2005; Song et al., 2005; Presto et al., 2005; Ng et al., 2007; Kroll et al., 2007), (ii) at high NO<sub>x</sub>,  $M_o$  is found to decrease with increasing NO<sub>x</sub> (e.g., Pandis et al., 1991; Zhang et al., 1992; Kroll et al., 2006) and (iii) at low NO<sub>x</sub>,  $M_o$  is found to increase with increasing NO<sub>x</sub> (e.g., Pandis et al., 1991; Zhang et al., 1992; Kroll et al., 2006).

Figure 5 shows  $M_o^{\max}$  as a function of NO<sub>x</sub> level for simulations carried out with an initial loading of 10 ppb of [HC]<sub>0</sub>. The set includes nine NO<sub>x</sub> levels: 0.05, 0.1, 0.5, 1, 2.5, 5, 10, 50 and 100 ppb. Two regimes of SOA formation dependence on NO<sub>x</sub> level are identified: a first regime, where  $M_o^{\max}$  increases with NO<sub>x</sub> and a second one, where

$M_o^{\max}$  decreases when NOx increases. Transition between those two regimes occurs at a NOx mixing ratio of about 1 ppb. The simulated profile of  $M_o^{\max}$  versus NOx shows a similar shape to those reported from laboratory chamber experiments browsing NOx levels from low to high NOx (e.g., Kroll et al., 2006; Pandis et al., 1991; Zhang et al., 1992).

The explicit approach therefore captures the general features reported from laboratory chamber experiments of the influence of NOx level on SOA formation. This explicit model can as a result be used as an exploratory tool to (i) facilitate interpretations of SOA formation observed in laboratory chamber experiments and (ii) give some insight into SOA formation under atmospherically relevant concentrations.

### 5.1.3 The SOA/VOC/NOx system

The sensitivity of the SOA/VOC/NOx system is explored here on the basis of 45 simulations, conducted with five different initial concentrations of octene (1, 5, 10, 50 and 100 ppb) under nine fixed NOx concentrations (0.05, 0.1, 0.5, 1, 2.5, 5, 10, 50 and 100 ppb). Figure 6 shows  $Y^{\max}$  as a function of NOx level and initial loading of octene, as usually done for ozone isopleths.

At a fixed NOx level,  $Y^{\max}$  increases globally with increasing  $[HC]_0$ . As expected and discussed before,  $Y^{\max}$  is found to be largely dependent on  $[HC]_0$  at low  $[HC]_0$ .  $Y^{\max}$  is expected to tend to an asymptotic value when  $[HC]_0$  tends to infinity. This behaviour is observed at low NOx levels but not at high NOx. The simulated zone focuses on low  $[HC]_0$ , representative of atmospheric levels. The asymptotic value of  $Y^{\max}$  is not reached under those conditions. At a fixed  $[HC]_0$  value, two NOx regimes are highlighted as specified before.  $Y^{\max}$  increases with NOx at low NOx and shows an opposite behaviour at high NOx. Note that  $Y^{\max}$  is highly sensitive to NOx at high  $[HC]_0$ , but remains weakly sensitive to NOx at low  $[HC]_0$ . Maximum  $Y^{\max}$  values are reached for an HC(ppb)/NOx(ppb) ratio of about 10. This constant ratio is also reported in Fig. 6. An increase or decrease of this ratio results in a decrease of simulated  $Y^{\max}$ .

The limitation of SOA formation under high NOx levels has been suggested to be the

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result of the change in (i) the relative level of oxidants, i.e. OH, O<sub>3</sub> and NO<sub>3</sub> (Hurley et al., 2001), and/or (ii) the branching ratio for the recombination of organo-peroxy radicals, RO<sub>2</sub> (e.g., Hatakeyama et al., 1991; Johnson et al., 2004; Presto et al., 2005; Kroll et al., 2006; Ng et al., 2007; Kroll et al., 2007). The increase of aerosol yields with increasing NO<sub>x</sub> at low NO<sub>x</sub> levels remains not understood (e.g., Kroll et al., 2006).

Gas/particle partitioning of a given SVOC occurs when its gas-phase concentration exceeds its equilibrium vapour pressure above a particle surface. Gas/particle partitioning of a given SVOC strongly depends on (i) its chemical identity defining its vapour pressure and (ii) its supersaturation state which is directly linked to its gas-phase concentration. According to the speciation of particulate organic matter given in Fig. 2d, SOA contributors are mainly C<sub>8</sub> organic compounds bearing at least 4 functional groups. Figure 7 shows the time evolution of these secondary organics summed across both phases for simulations starting with an initial amount of 10 ppb of octene. Three cases are reported in Fig. 7 for various NO<sub>x</sub> levels (50 ppt, 1 ppb and 100 ppb). For the low-NO<sub>x</sub> case, the formation of secondary organic species is slow. A maximum concentration of about 8.5 ppbC is reached after 110 h. For the intermediate-NO<sub>x</sub> case, the formation of secondary organics is fast and a maximum value of about 12 ppbC is reached after 30 h. Under high-NO<sub>x</sub> conditions, the formation of secondary organic is slow and lower than for the low and intermediate NO<sub>x</sub> levels. A maximum concentration of 3 ppbC is reached after 170 h. Formation and accumulation of multifunctional compounds bearing at least 4 functional groups is optimal for a NO<sub>x</sub> level of a few ppb. This optimal condition of NO<sub>x</sub> coincides with the maximum  $Y^{\max}$  reached for an initial loading of 10 ppb of octene.

Various processes explain the evolution with NO<sub>x</sub> level of secondary organics acting as SOA contributors. Figure 8 shows the relative contribution of oxidants to the removal of 1-octene as a function of NO<sub>x</sub> level and initial loading of 1-octene. Under the simulated conditions, octene is mainly removed by OH radicals. NO<sub>3</sub> is responsible for less than 1% of octene oxidation. However reactivity toward O<sub>3</sub> can be significant, with an O<sub>3</sub> reaction yield reaching 50%. Reactions of 1-octene with O<sub>3</sub> break the >C=C<

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bond and lead to the formation of smaller (and more volatile) compounds. Figure 6 and Fig. 8 show that for a given  $[\text{HC}]_0$ , the maximum  $Y^{\text{max}}$  is reached when the relative contribution of OH to the removal of the precursor is maximum. The dependence of SOA formation on NO<sub>x</sub> can therefore be interpreted as being partially controlled by the differences in relative oxidant levels. In addition, under low and high NO<sub>x</sub>, the oxidation rate is slow because of low oxidant concentrations. With a slow oxidation rate, the gas-phase concentration of secondary products increases slowly and the SVOC are consequently oxidised before they accumulate in particles (see Fig. 7). Furthermore under high NO<sub>x</sub> levels, reactions with NO produce mostly alkoxy radicals, which can decompose to smaller (and more volatile) compounds. Simulated results lead to the conclusions that the dependence of  $Y^{\text{max}}$  with NO<sub>x</sub> is here the result of (i) the relative contribution of gaseous oxidants, (ii) the gaseous oxidation rate and (iii) the gaseous radical chemistry.

## 5.2 Temporal behaviour

Ng et al. (2006) suggested that the shape of the time-dependent growth curve can give some insight into the processes involved in SOA formation. Especially, this shape reveals the importance and the relative contribution of second generation products to SOA growth.

Figure 9 reports the time-dependent growth curve for simulations carried out under 10 ppb of NO<sub>x</sub>. The set includes the five  $[\text{HC}]_0$  values of 1, 5, 10, 50 and 100 ppb. The final growth curve is also reported (as also shown Fig. 4a). The time-dependent growth does not overlap the final growth curve. This behaviour is interpreted by Ng et al. (2006) as the result of SOA formation occurring after multiple oxidation steps. We showed in the previous section that SOA formation from octene oxidation is the result of species bearing at least 3 functional groups, formed by multiple oxidation steps. The behaviour observed in Fig. 9 therefore confirms the interpretation provided by Ng et al. (2006) to explain the shape of the curve.

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### 5.3 SOA speciation sensitivity

The identities of secondary gaseous organics produced during gas-phase oxidation are a function of NO<sub>x</sub> levels (e.g., [Atkinson, 2000](#)). NO<sub>x</sub> level controls the fate of peroxy radical intermediates by changing the branching ratios in the radical photochemistry.

Organic nitrate formation versus organic peroxide formation is thus directly affected by NO<sub>x</sub>. NO<sub>x</sub> is consequently suspected to influence SOA speciation, and therefore organic particulate matter ageing. At low NO<sub>x</sub>, gaseous reactions with HO<sub>2</sub> may form peroxides (e.g., [Atkinson, 2000](#)). Gas/particle partitioning of hydroperoxides at low NO<sub>x</sub> has been shown in both laboratory chamber experiments ([Docherty et al., 2005](#); [Tobias and Ziemann, 2001](#)) and modelling studies ([Bonn et al., 2004](#); [Johnson et al., 2004, 2005](#)) to represent a dominant fraction of SOA. Under high NO<sub>x</sub>, gaseous reaction of RO<sub>2</sub> with NO produces organic nitrates among other products. Partitioning into nitrate moieties at high NO<sub>x</sub> has been detected in experiments (e.g., [Presto et al., 2005](#)).

The distribution of the organic moieties ( $R_{OFk/C}$ ) in the particulate phase at the maximum aerosol yield is shown in Fig. 10. Those values are plotted as a function of NO<sub>x</sub> for the simulation carried out with 10 ppb of [HC]<sub>0</sub>. The substitution degree of the carbon (i.e.  $\sum_k R_{OFk/C}$ ) is found to be slightly sensitive to NO<sub>x</sub> level and [HC]<sub>0</sub>, with values ranging around 40 to 50 %. At all NO<sub>x</sub> levels, the dominant moieties are found to be the alcohol ( $15\% < R_{OH/C} < 25\%$ ) and the ketone ( $R_{CO-/C} < 13\%$ ). As expected at low NO<sub>x</sub>, hydroperoxide moieties are a large fraction of SOA ( $R_{OOH/C} = 12\%$ ), while at high NO<sub>x</sub>, nitrate moieties prevail ( $R_{ONO2/C} = 18\%$ ).

## 6 Conclusions

An explicit model has been developed to explore (i) the potential of the products of multiple oxidation steps to play a role as SOA contributors and (ii) the evolution of the

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SOA/VOC/NO<sub>x</sub> system. The sensitivity of the SOA/VOC/NO<sub>x</sub> system has been studied for the oxidation of 1-octene under tropospheric relevant concentrations.

In this exploratory study, gaseous oxidation of octene is simulated to lead to SOA formation. Contributors to SOA formation are shown to be formed via multiple oxidation steps of the parent hydrocarbon. Time scales of a few days are indeed required to form those low vapour pressure products. This delay may explain why negligible or small SOA formation is observed in laboratory chamber experiments from the oxidation of relatively high volatile precursors.

The explicit approach captures the qualitative features observed during laboratory chamber experiments of the SOA/VOC/NO<sub>x</sub> system:

- $Y^{\max}$  is found to be largely dependent on  $[\text{HC}]_0$  at low  $[\text{HC}]_0$  and tends to an asymptotic value when  $[\text{HC}]_0$  tends to infinity.
- $Y^{\max}$  increases with NO<sub>x</sub> at low NO<sub>x</sub> and shows an opposite behaviour at high NO<sub>x</sub>.

Maximum  $Y^{\max}$  values are reached for a VOC(ppb)/NO<sub>x</sub>(ppb) ratio of about 10. Simulated results lead to the conclusions that the dependence of  $Y^{\max}$  with NO<sub>x</sub> is here the result of (i) the relative contribution of oxidants, (ii) the gaseous oxidation rate and (iii) the gaseous radical chemistry. Furthermore the simulated temporal behaviour of SOA formation corroborates the interpretation provided by Ng et al. (2006) for SOA formation from multiple oxidation steps of the parent compound. The simulated speciation shows a large contribution of hydroperoxide moieties at low NO<sub>x</sub> while at high NO<sub>x</sub>, nitrate moieties prevail as expected.

As a result, such an explicit model can be used as a useful exploratory tool to (i) facilitate interpretations of SOA formation observed in laboratory chamber experiments, (ii) give some insights of SOA formation under relevant atmospheric conditions and (iii) examine the implications for the regional/global lifetimes of the SOA.

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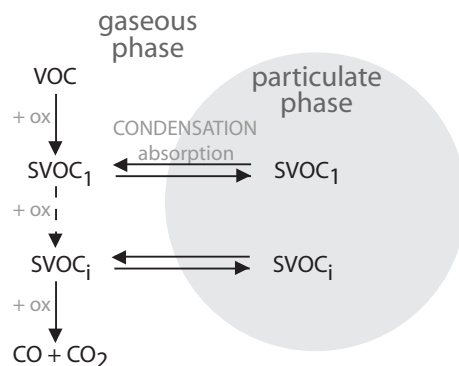
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**Fig. 1.** Schematic diagram of the explicit model of SOA formation.

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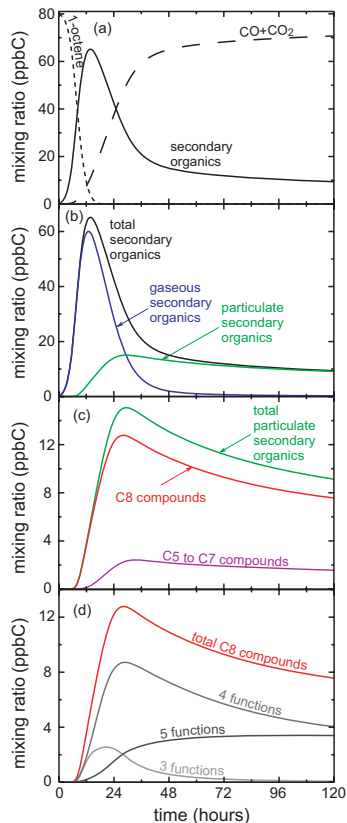
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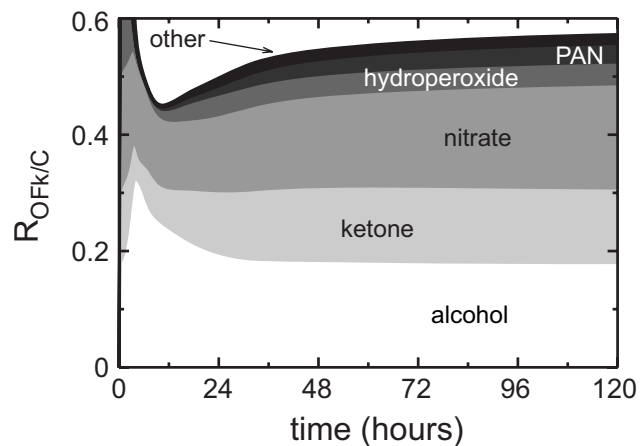


**Fig. 2.** Time evolution of carbonaceous species in the particulate phase during the simulation carried out under 1 ppb of NO<sub>x</sub> and starting with an initial loading of 10 ppb of 1-octene. Panel **(a)**: distribution of the carbon. Panel **(b)**: distribution of secondary organics. Panel **(c)**: distribution of particulate organics as a function of carbon chain length. Panel **(d)**: distribution of particulate C8 organics as a function of the number of functional groups borne by the molecules.

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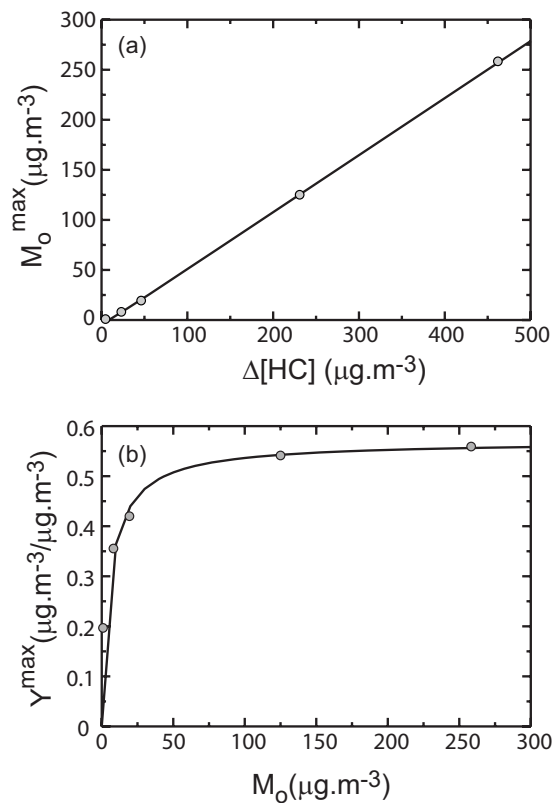


**Fig. 3.** Time evolution of the organic functional group per particulate carbon ratio ( $R_{OFk/C}$ ) during the simulation carried out under 1 ppb of NO<sub>x</sub> and starting with an initial loading of 10 ppb of 1-octene.

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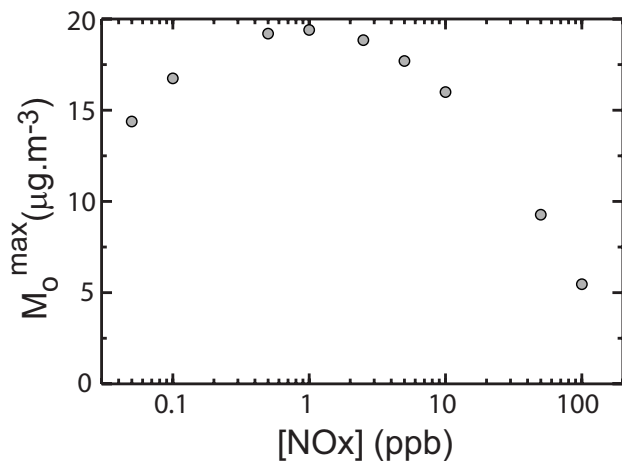


**Fig. 4.** Final growth curve **(a)** and final yield curve **(b)** simulated for the oxidation of 1-octene under 1 ppb of NO<sub>x</sub>. Five simulations were carried out with various initial loads of 1-octene. Each circle represents  $Y^{\max}$  or  $M_o^{\max}$  obtained for a single simulation. The continuous line represents the fit of the data from the two-product model ( $\alpha_1=0.17$ ,  $K_{1,om}=0.08$ ,  $\alpha_2=0.40$ ,  $K_{2,om}=0.26$ ).

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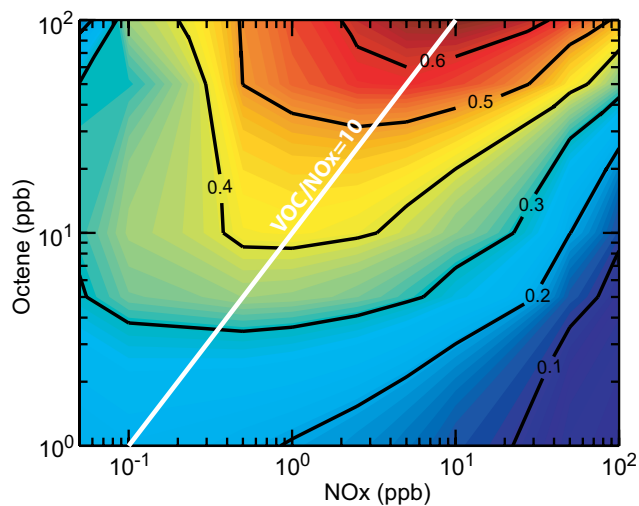


**Fig. 5.**  $M_o^{\max}$  as a function of NO<sub>x</sub> level simulated for the oxidation of an initial loading of 10 ppb of 1-octene. Nine simulations were carried out under various fixed NO<sub>x</sub> levels. Each circle represents  $M_o^{\max}$  obtained for a single simulation.

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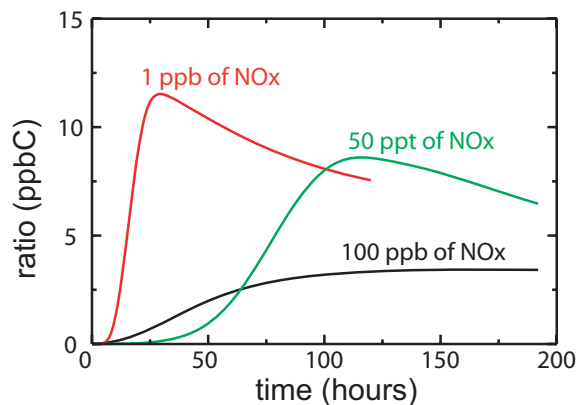


**Fig. 6.**  $\gamma^{\max}$  as a function of NO<sub>x</sub> level and initial loading of 1-octene.

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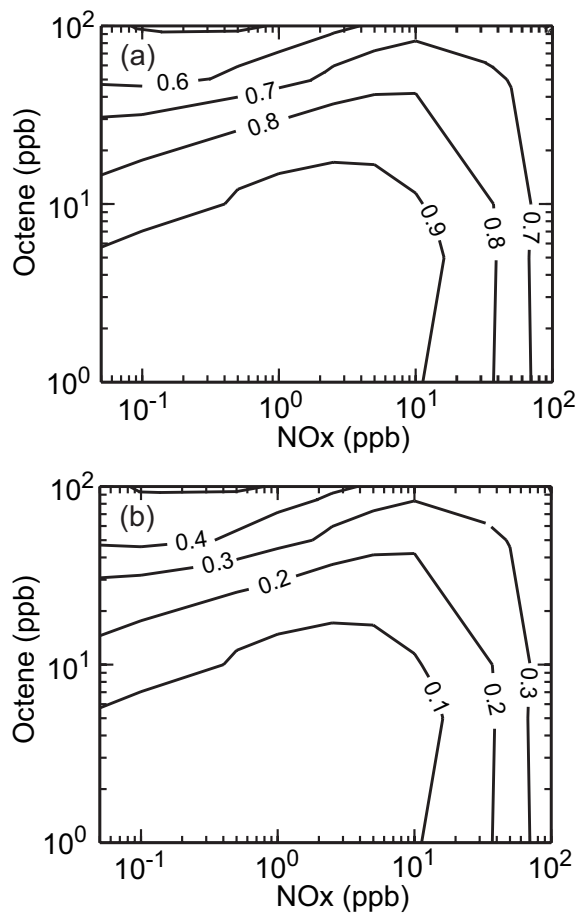
**Fig. 7.** Time evolution of secondary organics suspected to act as SOA contributors (i.e. C8 organics bearing at least 4 functional groups) summed across both phases for simulations starting with an initial loading of 10 ppb of 1-octene and carried out under 50 ppt, 1 ppb and 100 ppb of NO<sub>x</sub>.

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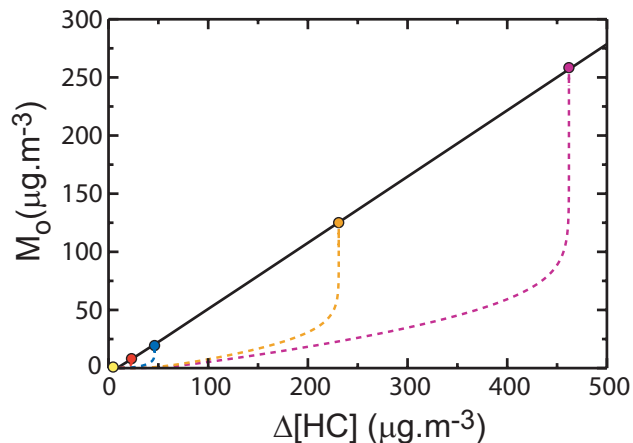


**Fig. 8.** Relative contribution of oxidants (OH **a** and O<sub>3</sub> **b**) to the removal of 1-octene as a function of NO<sub>x</sub> level and initial loading of 1-octene.

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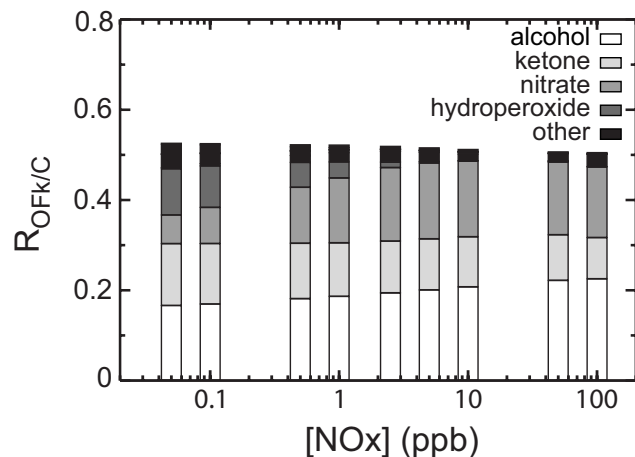


**Fig. 9.** Time-dependent and final growth curves simulated for the oxidation of 1-octene under 1 ppb of NO<sub>x</sub>. Five simulations were carried out with various initial loadings of 1-octene. Each dashed line represents the evolution of  $M_o$  during a single simulation. Each circle represents  $M_o^{\max}$  obtained for this simulation. The continuous line represents the final growth curve.

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**Fig. 10.** Distribution of the ratio of organic functional group per particulate carbon ( $R_{OFk/C}$ ) as a function of  $NO_x$  level for simulations carried out with an initial loading of 10 ppb of 1-octene. The distribution of ( $R_{OFk/C}$ ) is plotted at the maximum aerosol yield.

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